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First synthesis of 4,5-*O*-isopropylidene-6-thio-D-galactono-1,6-lactone as a precursor of D-galactothioseptanose

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Abstract—Displacement of the bromide group in methyl 6-bromo-6-deoxy-2,3:4,5-di-*O*-isopropylidene-D-galactonate **7**, with potassium thioacetate gave methyl 6-(*S*)-acetyl-2,3:4,5-di-*O*-isopropylidene-6-thio-D-galactonate **8** in quantitative yield. Regioselective removal of the 2,3-ketal protecting group afforded methyl 6-(*S*)-acetyl-4,5-*O*-isopropylidene-6-thio-D-galactonate **11** in 70% yield. Saponification of compound **11** gave the 6-(*S*)-4,5-*O*-isopropylidene-6-thio-D-galactonic acid **12** in quantitative yield. Treatment of **12** with DIC/HOBt as coupling reagents gave, after cyclisation; the target compound: 4,5-*O*-isopropylidene 6-thio-D-galactono-1,6-lactone **13** in 49% yield.

1. Introduction

Thiosugars with a sulfur atom in the ring[1] were first prepared by Schwarz et al.[2] and Adley et al.[3] in 1961. In particular the synthesis of 5-thio-α-D-xylopyranose, the first example of a thioaldose has been described. Since then, it has been developed by Whistler et al.,[4] Al-Masoudi and Hughes,[5] Hashimoto and Yuasa[6] and others.[7] Thioaldoses exhibit remarkable biological activities, such as inhibition of glycosidase,[8] for example, 5-thio-D-glucose inhibits D-glucose transport across membranes and also the release of insulin.[1] 5-Thio-L-fucose was found to be a potent inhibitor of bovine α-L-fucosidase.[9] Glycosides of 1,5-dithio-D-xylopyranose, in particular, have proved to be orally active antithrombotic agents.[10]

The only natural thiosugar isolated from the marine sponge *Clathia pyramida* is 5-thio-D-mannose.[11] Other thiosugars have so far been obtained by transformation of natural sugars (Fig. 1). The synthesis and biological activity as glycosidase inhibitors has been reported for only a limited number of seven-membered sulfurated cyclic compounds so far.[12]

The synthesis of 1,6-anhydro-1-thiohexitols (thiepanes) was first developed by Jarman and Griggs,[13] Kuszmann and Sohàr[14] and more recently by Depezay et al.[12,15] and Benazza et al.[16] The first example of glycothioseptanose was described by Cox and Owen.[17]

Since then it has been prepared, by Kuszmann et al.[18] from hexitols in nine steps, via the corresponding 1,6-anhydro-1-thiohexitols, by using a Pummerer rearrangement as a key step: 1,6-anhydro-3,4- *O*-isopropylidene-1-thiohexitols were converted into sulfoxides, which after hydrolysis, acetylation and subsequent Pummerer

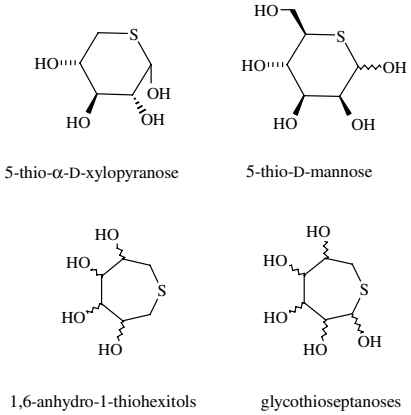

Figure 1. Examples of thiosugars.

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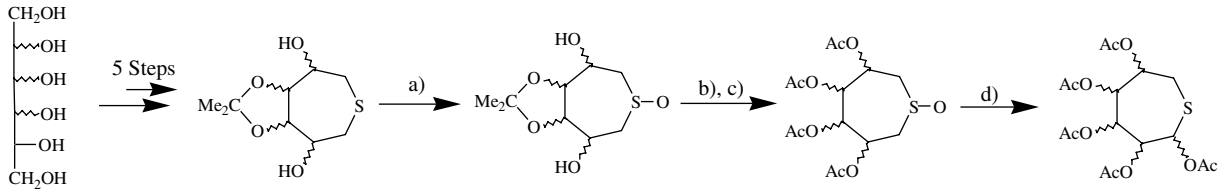


Scheme 1. Reagents and conditions: (a) $NaIO_4$; (b) TFA/H_2O; (c) Ac_2O/Pyridine; (d) Ac_2O.

rearrangement gave the penta-*O*-acetyl-thioseptanose anomers[18] (Scheme 1).

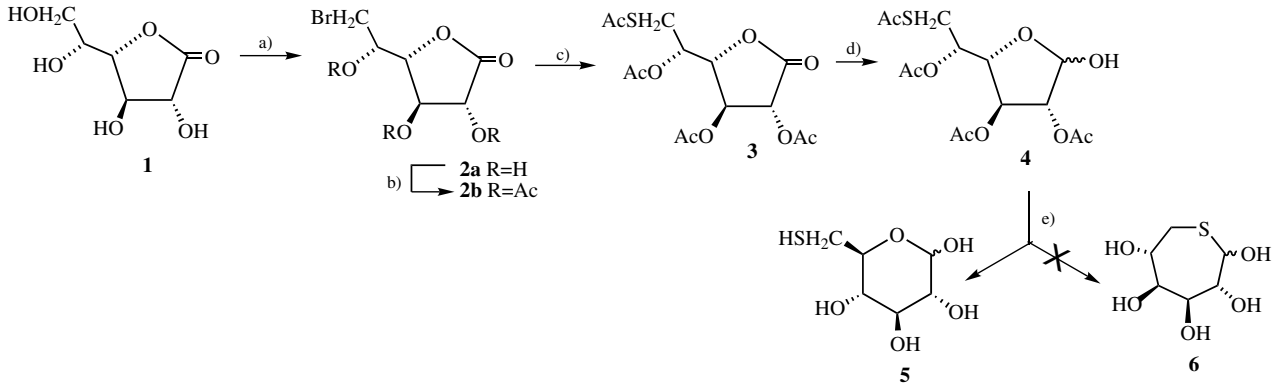
2. Results and discussion

Previously, we have reported the synthesis of 5-thio-D-pentopyranoses.[19,20] In continuation of our interest in the synthesis of thiosugars, we decided to synthesise D-glycothioseptanose derivatives. Initially, for the synthesis of D-galactothioseptanose, we tried to apply our strategy, which was previously developed for D-pentono-1,4-lactones. We used D-galactono-1,4-lactone **1** as starting materials via the C-6 brominated derivative **2** as a key intermediate (Scheme 2). Treatment of D-galactono-1,4-lactone with PPh_3–CBr_4 in pyridine[21] followed by reaction of the resultant bromide lactone **2a** (82%) with acetic anhydride, in the presence of perchloric acid, gave 2,3,5-tri-*O*-acetyl-6-bromo-deoxy-D-galactono-1,4-lactone **2b** in good yield (96%). Displacement of the bromine group in **2b** with potassium thioacetate gave the 2,3,5-tri-*O*-acetyl-6-(*S*)-acetyl-6-thio-D-galactono-1,4-lactone **3** in 94% yield. the reduction of the lactone functionality in compound **3** was achieved with disiamylborane in tetrahydrofuran to give 2,3,5-tri-*O*-acetyl-6-(*S*)-acetyl-6-thio-D-galactofuranose **4** in 70% yield. Unfortunately, Zemplén deacetylation of lactol **4**, with sodium methoxide, gave a mixture containing, according to NMR spectroscopy, the two anomers of the 6-deoxy-6-thio-D-galactopyranose **5** as the only product, in 91% yield and trace amounts of the expected D-galactothioseptanose **6** (Scheme 2).

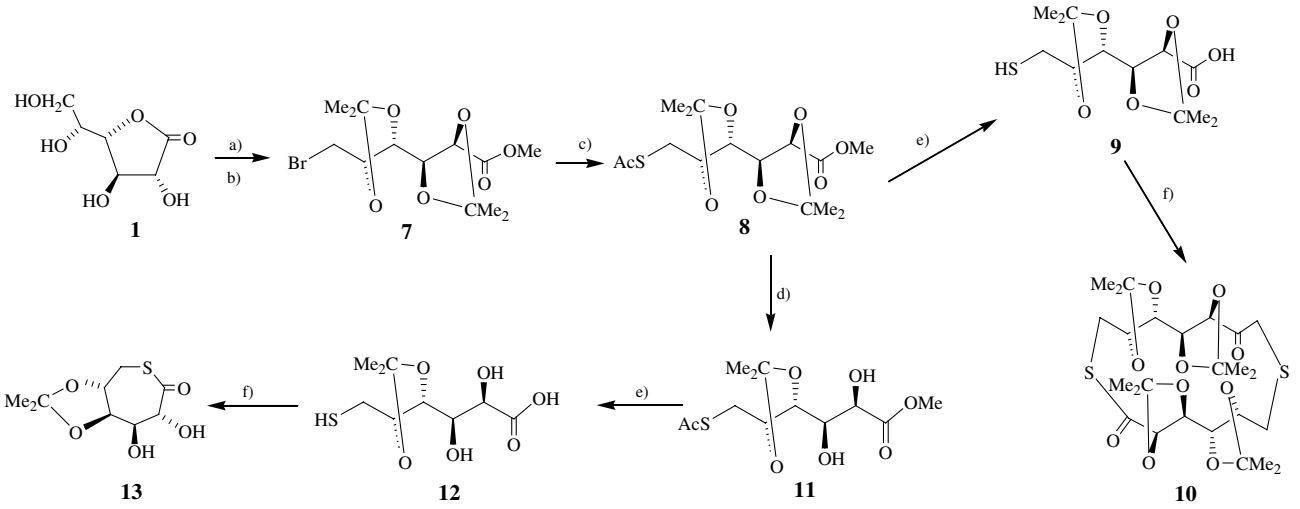
Due to the difficulties in the preparation of D-galactothioseptanose, we attempted an alternative strategy for the synthesis of 6-thio-D-galactono-1,6-lactone **13** starting from **1** (Scheme 3).

Treatment of **1** with HBr in acetic acid afforded the corresponding 6-bromo-6-deoxy derivative. The crude product was treated by 2,2-dimethoxypropane to give the methyl 6-bromo-6-deoxy-2,3:4,5-di-*O*-isopropylidene-D-galactonate **7**,[22] as described by Varela and Romero Zaliz, in 90% yield. Displacement of the bromide group in **7**, with potassium thioacetate in DMF gave methyl 6-(*S*)-acetyl-2,3:4,5-di-*O*-isopropylidene-6-thio-D-galactonate **8** in 95% yield. Hydrolysis of the thioester and ester functions of **8** under alkaline conditions led to 6-deoxy-2,3:4,5-di-*O*-isopropylidene-6-thio-D-galactonic acid **9** in quantitative yield. Thioester formation between the acid-segment and the thiol-segment using coupling method *N*,*N*′-diisopropylcarbodiimide/1-hydroxybenzotriazole (DIC/HOBt), in DMF, afforded (3*R*,4*S*,5*S*,6*R*,10*R*,11*S*,12*S*,13*R*)-2,9-dione-1,8-dithiacyclotetradecane-3,4:5,6; 10,11:12,13-tetra-*O*-isopropylideneoctaoxy **10** in 45% yield. The mass spectrum of **10** showed a diagnostic peak at *m*/*z* 571 $(M + Na)^+$. The title compound was identified by elemental analysis and NMR spectra which showed, in particular, a signal of carbonyl at 205 ppm. This result could be explained by the rigidity of the seven-membered ring carrying two isopropylidene groups.

To make the ring less rigid we carried out a regioselective removal of the ketal protecting group, in 2,3 in **8**, by acid hydrolysis and obtained methyl 6-(*S*)-acetyl-4,5-*O*-isopropylidene-6-thio-D-galactonate **11** in 70% yield. Saponification of compound **11** gave the 6-deoxy-4,5-*O*-isopropylidene-6-thio-D-galactonic acid **12** in quantitative yield. The last step of the sequence, the



Scheme 2. Reagents and conditions: (a) PPh_3/CBr_4; (b) Ac_2O, $HClO_4$; (c) KSAc/DMF; (d) disiamylborane/THF; (e) MeONa/MeOH.



Scheme 3. Reagents and conditions: (a) HBr/AcOH, rt, 2 h; (b) $Me_2C(OMe_2)$ and Me_2CO, rt, 16 h; (c) KSAc/DMF, rt, 2 h; (d) AcOH/H_2O, 45 °C, 18 h; (e) NaOH, EtOH–H_2O, 50 °C, 1 h; (f) DIC/HOBt, DMF, rt, 18 h.

treatment of **12** with DIC/HOBt as coupling reagents in DMF afforded, after cyclisation, the target compound: 4,5-*O*-isopropylidene-6-thio-D-galactono-1,6-lactone **13** in 49% yield.

3. Conclusion

In summary, we have reported the first synthesis of 4,5-*O*-isopropylidene-6-thio-D-galactono-1,6-lactone in five steps in 31% overall yield. The title compound, after reduction, could give D-galactothioseptanose.

4. Experimental

4.1. General

Melting points were determined on a Buchi 535 apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-370 digital polarimeter, using a sodium lamp ($\lambda = 589$ nm) at 24 °C. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, in MeOD or in DMSO-d_6. Me_4Si was used as an internal standard on a Bruker 300 MHz spectrometer. Thin-layer chromatography (TLC) was performed on E. Merck glass plates silica gel sheets (SilicaGel F254) and visualised under UV light and/or stained with phosphomolybdic acid–aqueous H_2SO_4 solution. Column chromatography was carried out on silica gel (E. Merck 230–400 mesh). Mass spectra were recorded using electron impact (40 eV). All the solvents were distilled before use.

4.1.1. 2,3,5-Tri-*O*-acetyl-6-bromo-6-deoxy-D-galactono-1,4-lactone 2b. The crude material of **2a**[21] (2 g) was treated with Ac_2O (20 mL) in the presence of perchloric acid (2 drops). After 30 min at 0 °C, under an inert atmosphere, the solution was concentrated and the residue added to water and extracted with CH_2Cl_2; the extracts were dried, filtered and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with (7:3, hexanes–EtOAc gave **2b** (2.9 g, 96%) as a white solid: R_f 0.54 (3:2 hexanes–EtOAc); mp 100–102 °C; $[\alpha]_D^{24} = -9$ (*c* 1.0, $CHCl_3$). lit.[23] $[\alpha]_D^{20} = -10.1$ (*c* 2.5, $CHCl_3$); mp 100–101 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 5.58 (d, 1H, $J = 7.0$ Hz), 5.32 (t, 1H, $J = 6.7$ Hz), 5.17 (m, 1H, $J = 2.2$, 7.5 Hz), 4.79 (dd, 1H, $J = 2.3$, 6.7 Hz), 3.48 (d, 2H, $J = 6.6$ Hz), 2.12 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 170.0, 169.6, 169.6, 168.5, 77.7, 72.7, 72.4, 69.8, 27.9, 20.9, 20.8, 20.7. Anal. Calcd for $C_{12}H_{15}BrO_8$: C, 39.26; H, 4.12; Br, 21.76. Found: C, 39.24; H, 4.14; Br, 21.75.

4.1.2. 2,3,5-Tri-*O*-acetyl-6-*S*-acetyl-6-thio-D-galactono-1,4-lactone 3. To a solution of **2b** (1.4 g, 3.8 mmol) in *N*,*N*-dimethylformamide (10 mL) was added potassium thioacetate (0.52 g, 1.2 equiv). The mixture was stirred under an inert atmosphere at room temperature for 10 min. The mixture was filtered and concentrated under reduced pressure to yield a crude product, which was partitioned between CH_2Cl_2 and water. The CH_2Cl_2 extracts were dried, filtered and concentrated. Column chromatography (7:3, hexanes–EtOAc) of the residue afforded **3** (1.3 g, 94%) as a yellow syrup: R_f 0.7 (3:2 hexanes–EtOAc); $[\alpha]_D^{24} = +23$ (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.52 (d, 1H, $J = 6.8$ Hz), 5.28 (t, 1H, $J = 6.7$ Hz), 5.13 (m, 1H), 4.54 (dd, 1H, $J = 2.8$,6, 6.7 Hz), 3.04 (d, 2H, $J = 7.5$ Hz), 2.10 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 170.1, 169.7, 168.6, 78.9, 72.8, 72.5, 69.5, 29.4, 20.8. Anal. Calcd for $C_{14}H_{18}O_9S$: C, 46.40; H, 5.01; S, 8.85. Found: C, 46.35; H, 5.05; S, 8.37.

4.1.3. 2,3,5-Tri-*O*-acetyl-6-*S*-acetyl-6-thio-D-galactofuranose 4. To 2,3,5-tri-*O*-acetyl-6-*S*-acetyl-6-thio-D-galactono-1,4-lactone **3** (0.3 g, 0.82 mmol), at 0 °C, was added disiamylborane freshly prepared (10 equiv) in THF. The mixture was stirred, under an inert atmosphere, at room temperature for 18 h. Then MeOH was added and the solution kept for 30 min and concentrated. The crude material was diluted with CH_2Cl_2 and washed with water. The CH_2Cl_2 extracts were dried,

filtered and concentrated. Column chromatography (7:3 and 3:2, hexanes–EtOAc) of the residue afforded **4** (0.213 g, 70%) as a colourless syrup: R_f 0.35 (3:2 hexanes–EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) (α anomer) δ 5.38 (m, 1H), 5.38 (m, 1H), 5.05 (m, 2H), 4.31 (t, 1H, J = 4.9 Hz), 3.3 (dd, 1H, J = 5.1, 14.1 Hz), 3.00 (dd, 1H, J = 8.0, 14.2 Hz), 2.12 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 170.5, 100.8, 82.2, 77.2, 70.8, 30.0, 21.3. ^{1}H NMR (300 MHz, $CDCl_3$) (β anomer) δ 5.44 (d, 1H, J = 4.4 Hz), 5.38 (m, 1H), 5.05 (t, 1H, J = 4.8 Hz), 2.35 (d, 2H, J = 9.7 Hz), 2.12 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 170.2, 96.0, 80.4, 76.9, 75.6, 72.3, 30.8, 21.3. Anal. Calcd % for $C_{14}H_{20}O_9S$: C, 46.15; H, 5.53; S, 8.80. Found % C, 46.42; H, 5.83; S, 8.43.

4.1.4. 6-Deoxy-6-thio-D-galactopyranose 5. To 2,3,5-tri-*O*-acetyl-6-*S*-acetyl-6-thio-D-galactono-1,4-lactone **4** (0.2 g, 0.55 mmol) in MeOH (10 mL) was added NaOMe (1 M, 2.74 mL, 10 equiv). The mixture was stirred for 2 h at room temperature. The solution was passed through an ion exchange resin (Dowex 50 × 8–100 ion) filtered and concentrated. The crude material was diluted with CH_2Cl_2 and washed with water. The CH_2Cl_2 extracts were dried, filtered and concentrated. Column chromatography (9:1, EtOAc–MeOH) of the residue afforded 6-deoxy-6-thio-D-galactopyranose **5** (0.96 g, 91%) as a colourless syrup: R_f 0.22 (9:1, EtOAc–MeOH). ^{1}H NMR (300 MHz, MeOD) (α anomer) δ 4.45 (d, 1H, J = 5.0 Hz), 3.90 (m, 1H), 3.68 (dd, 1H, J = 4.9, 9.6 Hz), 3.4–3.5 (m, 2H), 2.72 (m, 1H); ^{13}C NMR (75 MHz, MeOD) δ 97.7, 77.2, 72.6, 70.3, 69.8, 24.2. ^{1}H NMR (300 MHz, MeOD) (β anomer) δ 5.13 (d, 1H, J = 3.5 Hz), 3.9–4.0 (m, 2H), 3.76 (dd, 1H, J = 3.6, 7.0 Hz), 3.4 (m, 1H), 2.72 (m, 1H); ^{13}C NMR (75 MHz, MeOD) δ 93.2, 74.0, 72.3, 69.8, 24.2. Anal. Calcd % for $C_6H_{12}O_5S$: C, 36.73; H, 6.16; S, 16.34. Found % C, 36.20; H, 6.21; S, 16.80.

4.1.5. Methyl 6-(*S*)-acetyl-2,3:4,5-di-*O*-isopropylidene-6-thio-D-galactonate 8. To a solution of **7**[22] (0.32 g, 0.9 mmol) in *N*,*N*-dimethylformamide (10 mL) was added potassium thioacetate (0.144 g, 1.4 equiv) as in the case of **2b**, to give, after column chromatography (8:1, hexanes–EtOAc), **8** in quantitative yield, as a yellow oil: R_f 0.8 (3:2 hexanes–EtOAc). $[\alpha]_D^{24} = +4.9$ (c 0.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 (d, 1H, J = 5.6 Hz), 4.28 (dd, 1H, J = 5.8, 6.1 Hz), 4.06 (m, 1H), 3.75 (t, 1H, J = 6.1 Hz), 3.71 (s, 3H), 3.28 (dd, 1H, J = 4.1, 13.9 Hz), 3.02 (dd, 1H, J = 6.3, 13.9 Hz), 1.40 (s, 1H), 1.32 (s, 6H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 171.6, 112.4, 110.4, 80.2, 79.7, 77.8, 77.0, 52.8, 32.0, 30.8, 27.8, 27.4, 27.3, 26.3. Anal. Calcd % for $C_{15}H_{24}O_7S$: C, 51.71; H, 6.94; S, 9.20. Found % C, 51.23; H, 6.48; S, 9.78.

4.1.6. 2,3:4,5-Di-*O*-isopropylidene-6-thio-D-galactonic acid 9. To a solution of the thioacetate derivative **8** (0.36 g, 1.17 mmol) in EtOH–H_2O (3:1, 16 mL) was added NaOH (0.236 g, 5 equiv). The mixture was stirred for 1 h at 50 °C. The solution was passed through Amberlite resin (IR-120H), filtered and concentrated to afford **9** (0.290 g, 98%) as a white solid: R_f 0.34 (3:2 hexanes–EtOAc); mp 56–58 °C; $[\alpha]_D^{24} = +6$ (c 0.3, MeOH); ^{1}H NMR (300 MHz, MeOD) δ 4.48 (d, 1H, J = 5.6 Hz), 4.42 (t, 1H, J = 5.8 Hz), 4.20 (m, 1H), 4.05 (t, 1H, J = 6.1 Hz), 2.88 (dd, 1H, J = 4.1, 13.9 Hz), 2.79 (dd, 1H, J = 5.7, J = 13.8 Hz), 1.46 (s, 12H); ^{13}C NMR (75 MHz, MeOD) δ 174.5, 111.7, 109.9, 80.0, 79.8, 79.7, 77.4, 26.9, 26.8, 26.5, 25.6. Anal. Calcd % for $C_{12}H_{20}O_6S$: C, 49.30; H, 6.90; S, 10.97. Found % C, 49.00; H, 6.69; S, 10.20.

4.1.7. (3*R*,4*S*,5*S*,6*R*,10*R*,11*S*,12*S*,13*R*)-2,9-Dione-1,8-dithiacyclotetradecane-3,4:5,6;10,11:12,13-tetra-*O*-isopropylideneoctaoxy 10. To a stirred solution of **9** (2.4 g, 8.21 mmol) in dry DMF (180 mL) was carefully added DIC (5 equiv) at 0 °C, followed by HOBt (5 equiv) and the mixture stirred at room temperature for 1 day. After evaporation of 100 mL of solvent, the solution was allowed to stand at 4 °C overnight and additional urea was precipitated and removed by filtration. The filtrate was concentrated and the viscous oil obtained, was then eluted on silica-gel column, using hexanes–EtOAc (7:3) to afford **10** (1.01 g, 45%) as a white solid: R_f 0.76 (7:3 hexanes–EtOAc); mp 75–76 °C; $[\alpha]_D^{24} = -26.1$ (c 0.5, MeOH). ^{1}H NMR (300 MHz, MeOD) δ 4.70 (d, 1H, J = 8.2 Hz), 4.26 (dd, 2H, J = 3.5, 9.1 Hz), 4.02 (m, 1H), 3.54 (dd, 1H, J = 4.0, 13.5 Hz), 2.71 (dd, 1H, J = 10.6 Hz), 1.55 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, MeOD) δ 200.8, 11.4, 110.7, 80.5, 80.2, 79.6, 72.5, 30.9, 26.6, 26.4, 26.2, 25.8. Anal. Calcd % for $C_{24}H_{36}O_{10}S_2$: C, 52.55; H, 6.56; S, 11.68. Found % C, 52.58; H, 6.53; S, 11.64.

4.1.8. Methyl 6-(*S*)-acetyl-4,5-*O*-isopropylidene-6-thio-D-galactonate 11. To a mixture AcOH/H_2O (8:2, 20 mL) was added the galactonate derivative **8** (1 g, 2.87 mmol). The solution was stirred for 18 h at 45 °C and washed with saturated $NaHCO_3$. CH_2Cl_2 and water were added, the CH_2Cl_2 extracts dried, filtered and concentrated under reduced pressure to afford a residue, which was chromatographed on silica gel (3:2, hexanes–EtOAc) to give **11** (0.615 g, 70%) as a colourless syrup: R_f 0.3 (3:2 hexanes–EtOAc). $[\alpha]_D^{24} = -10.3$ (c 0.66, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 (d, 1H, J = 1.8 Hz), 4.19 (m, 1H), 3.95 (dd, 1H, J = 1.9, 8.8 Hz), 3.74 (s, 3H), 3.72 (dd, 1H, J = 2.0, 8.9 Hz), 3.31 (dd, 1H, J = 3.3, 14.3 Hz), 3.22 (dd, 1H, J = 5.5, 14.4 Hz), 2.45 (s, 3H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 175.0, 110.1, 79.2, 77.9, 74.4, 71.3, 53.2, 32.7, 30.7, 27.4. Anal. Calcd % for $C_{12}H_{20}O_7S$: C, 46.74; H, 6.54; S, 10.40. Found % C, 46.54; H, 6.12; S, 10.00.

4.1.9. 6-Deoxy-4,5-*O*-isopropylidene-6-thio-D-galactonic acid 12. To a solution of the thioacetate derivative **11** (0.36 g, 1.17 mmol) in EtOH–H_2O (3:1, 16 mL) was added NaOH (0.236 g, 5 equiv) as in case of **8** to give **12**, in quantitative yield, as a colourless syrup: $[\alpha]_D^{24} = +17.2$ (c 0.46, MeOH); ^{1}H NMR (300 MHz, MeOD) δ 4.36 (d, 1H, J = 1.1 Hz), 4.18 (m, 1H), 3.95 (m, 2H), 2.92 (dd, 1H, J = 3.0, 13.8 Hz), 2.78 (dd, 1H, J = 6.6, 14.0 Hz); ^{13}C NMR (75 MHz, MeOD) δ 175.8, 109.8, 81.8, 77.9, 74.3, 71.2, 27.8, 26.8, 26.7. Anal. Calcd

% for $C_9H_{16}O_6S$: C, 42.85; H, 6.39; S, 12.71. Found % C, 42.55; H, 6.09; S, 12.40.

4.1.10. 4,5-*O*-Isopropylidene-6-thio-D-galactono-1,6-lactone 13. To a solution of the D-galactonic acid derivative **12** (0.143 g, 0.57 mmol) in dry DMF (10 mL) was carefully added DIC (5 equiv) at 0 °C followed by HOBt (5 equiv), as in case of **9** to give, after column chromatography (3:2, hexanes–EtOAc), **13** (0.136 g, 49%) as a white solid: R_f 0.6 (EtOAc); mp 46–48 °C; $[\alpha]_D^{24} = +0.6$ (*c* 0.54, MeOH). ^{1}H NMR (300 MHz, MeOD) δ 5.20 (d, 1H, $J = 8.8$ Hz), 4.42 (dd, 1H, $J = 1.46$, 8.8 Hz), 4.23 (dd, 1H, $J = 1.4$, 4.4 Hz), 4.18 (m, 1H), 3.90 (d, 1H, $J = 15.5$ Hz), 2.95 (dd, 1H), 1.41 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, MeOD) δ 202.4, 110.9, 78.9, 76.6, 69.8, 68.6, 31.3, 25.9, 24.5. Anal. Calcd % for $C_9H_{14}O_5S$: C, 46.14; H, 6.02; S, 13.69. Found % C, 46.38; H, 6.30; S, 13.28.

Acknowledgements

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