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Note

An efficient route to thioglycosides with the 2,3-anhydro-D-ribo stereochemistry

Jayant N. Tilekar and Todd L. Lowary*

Department of Chemistry and Alberta Ingenuity Centre for Carbohydrate Science, Gunning–Lemieux Chemistry Centre, University of Alberta, Edmonton, AB, Canada T6G 2G2

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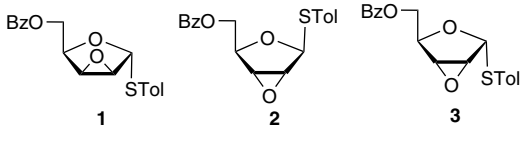
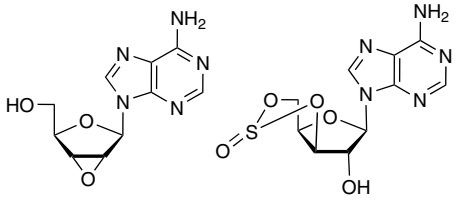
Abstract—An improved route for the synthesis of *p*-tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio-β-D-ribofuranoside and its α anomer, which are important intermediates in the synthesis of α- and β-D-arabinofuranosides, has been developed. The products are obtained in six steps from D-xylose in 39% overall yield.

Keywords: 2,3-Anhydro sugars; Thioglycosides; Thiofuranosides; Synthesis

We have previously demonstrated the utility of 2,3-anhydrosugar thioglycosides **1** and **2** and the corresponding glycosyl sulfoxides in the synthesis of α- and β-arabinofuranosides[1,2] and 2′,3′-anhydronucleosides.[3] The routine use of this methodology is dependent upon convenient methods for the synthesis of these glycosyl donors, and in our earlier studies,[1,2] we had developed an efficient route for the preparation of **1**. In contrast, the method we used previously for the preparation of **2** was rather long and cumbersome. When considering alternate approaches for the synthesis of **2**, the other published routes[4–7] to this ring system were unattractive given the large number of steps required and/or the incompatibility of the chemistry with a thioglycoside moiety.





Mindful of the need to develop a better route for the preparation of **2**, we were attracted to a recent paper by Takatsuki et al.[8] that described the preparation of 2′,3′-anhydro-D-ribofuranosyl-adenine (**4**) from 3′,5′-*O*-sulfinyl-D-xylofuranosyl-adenine (**5**). In this Note, we report the use of the Takatsuki methodology for the preparation of **2** and the corresponding α-anomer **3**, which is also a substrate for our glycosylation methodology.[2]

The route (Scheme 1) began with the tetraacetate **6**, which was synthesized in 91% yield from D-xylose using the boric acid-mediated process developed by Furneaux et al.[9] The thioglycoside was then installed upon reaction of **6** with *p*-thiocresol and boron trifluoride etherate, which afforded a 5:1 β:α mixture of *p*-thiocresyl thioglycosides **7** and **8** in 89% combined yield. The anomers could be separated at this stage, and each was carried forward separately. Thus, treatment of **7** with sodium methoxide yielded **9** in 92% yield. Reaction of this triol with thionyl chloride in acetonitrile and pyridine gave an 83% yield of the 3,5-*O*-sulfinyl-β-D-xylofuranosyl thioglycoside **11**, which was then converted to the epoxide **13** upon treatment with sodium bicarbonate

* Corresponding author. Tel.: +1 760 492 1861; fax: +1 760 492 7705; e-mail: tlowary@ualberta.ca

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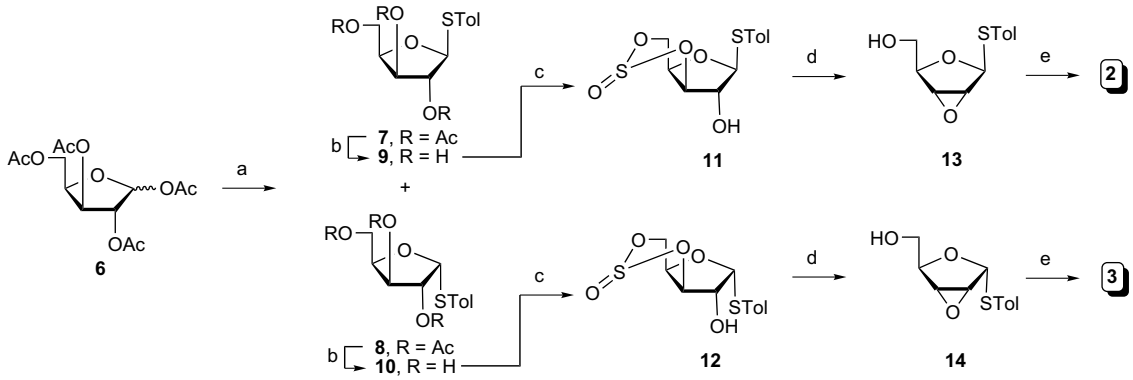

Scheme 1. Reagents and conditions: (a) *p*-TolSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 → 25 °C, 89% 5:1 β:α; (b) $NaOCH_3$, CH_3OH, rt, 92% for **9**, 89% for **10**; (c) $SOCl_2$, CH_3CN, pyridine, 5 °C, 83% for **11**, 87% for **12**; (d) $NaHCO_3$, Et_3N, DMF, 90 °C, 60% for **13**, 70% for **14**; (e) BzCl, pyridine, 0 °C → rt, 93% for **2**, 88% for **3**.

and triethylamine in DMF at 90 °C for 60 h. The epoxide-forming reaction proceeded in 60% yield, with the byproducts being unreacted starting material and triol **9**. Formation of the epoxide was readily apparent from the ^{13}C NMR spectrum of **13**, which showed two methine carbons at 58.67 and 57.74 ppm, as would be expected for these 2,3-anhydrosugars.[2,10] Once epoxide **13** was in hand, it was converted to **2** in 93% yield using conventional benzoylation conditions. The ^1H and ^{13}C NMR spectra of **2** obtained via the route shown in Scheme 1 were identical to those previously reported for this compound.[2] The overall yield for the conversion of **7** into **2** was 43%. Using identical transformations, the α-thioglycoside **8** was converted to epoxide **3** in 48% overall yield. It was also possible to convert the mixture of **7** and **8** into the epoxy thioglycosides **2** and **3**. When this mixture was carried through the sequence, the two products were obtained in a combined 43% overall yield.

In summary, an improved route for the synthesis of thioglycosides **2** and **3** has been developed. The products are obtained in six steps from D-xylose in 39% overall yield. Our previous route to these glycosylating agents, which also started with D-xylose, provided the two compounds in nine steps and 27% overall yield. Thus, this new route is an improvement both in terms of number of steps and overall yield.

1. Experimental

1.1. General methods

Reactions were carried out in oven-dried glassware. Solvents were distilled from appropriate drying agents before use. Unless stated otherwise, all reactions were carried out under a positive pressure of argon and were monitored by TLC on Silica Gel 60 F_{254} (0.25 mm, E. Merck). Spots were detected under UV light or by charring with 10% H_2SO_4, in EtOH. All solutions were concentrated under vacuum, and all column chromatography was performed on Silica Gel 60 (40–60 μm). The ratio between Silica Gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C and are in units of degrees mL/g dm. ^1H NMR spectra were recorded at 500 MHz, and chemical shifts are referenced to either Me_4Si (δ 0.0, $CDCl_3$), HOD (δ 4.78, D_2O) or CD_3OH (δ 4.78, CD_3OD). ^{13}C NMR spectra were recorded at 100 MHz, and ^{13}C chemical shifts are referenced to internal $CDCl_3$ (δ 77.23, $CDCl_3$), CD_3OD (δ 48.9, CD_3OD), or external dioxane (δ 67.40, D_2O). ^1H NMR chemical shifts were assigned though ^1H–^1H COSY experiments, and ^{13}C NMR chemical shifts were assigned by comparison with values in the literature[11] and/or by inspection. Electrospray-ionization mass spectra (ESIMS) were recorded on samples suspended in mixtures of THF and CH_3OH with added NaCl.

1.2. *p*-Tolyl 2,3,5-tri-*O*-acetyl-1-thio-β-D-xylofuranoside (7) and *p*-tolyl 2,3,5-tri-*O*-acetyl-1-thio-α-D-xylofuranoside (8)

Tetraacetate **6**[9] (1.0 g, 3.14 mmol) was dissolved in dry CH_2Cl_2 (20 mL) and cooled to 0 °C before *p*-thiocresol (0.46 g, 3.77 mmol) was added. The mixture was stirred for 20 min under argon, and $BF_3{\cdot}OEt_2$ (1.99 g, 15.7 mmol) was added via syringe. After 1.5 h, the mixture was neutralized with Et_3N (2.2 mL, 15.7 mmol), diluted with CH_2Cl_2, and then washed with water and brine. The organic layer was dried (Na_2SO_4) and evaporated, and the crude product was purified by chromatography (10:1 hexane–EtOAc) to give **7** (0.88 g, 74%) as an oil: R_f 0.38 (3:1 hexane–EtOAc); $[\alpha]_D$ −97.4 (*c* 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.43 (dd, 2H, *J* 7.9, 2.2 Hz, aryl), 7.13 (dd, 2H, *J* 8.0, 0.5 Hz, aryl), 5.29 (dd, 1H, $J_{2,3}$ 2.2 Hz, $J_{3,4}$ 5.0 Hz, H-3), 5.25 (dd, 1H, $J_{1,2}$ 3.3 Hz, $J_{2,3}$ 2.2 Hz, H-2), 5.18 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.44 (ddd, 1H, $J_{3,4}$ 5.0 Hz, $J_{4,5a}$ 10.2 Hz, $J_{4,5b}$ 6.4 Hz, H-4), 4.30 (dd, 1H, $J_{4,5a}$ 5.2 Hz, $J_{5a,5b}$ 11.7 Hz, H-5a),

4.26 (dd, 1H, $J_{4,5b}$ 6.4 Hz, $J_{5a,5b}$ 11.7 Hz, H-5b), 2.33 (s, 3H, aryl-CH_3), 2.09 (s, 3H, C(O)CH_3), 2.07 (s, 3H, C(O)CH_3), 2.04 (s, 3H, C(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.51 (C=O), 169.59 (C=O), 169.17 (C=O), 138.25 (aryl), 133.29 (2, aryl), 129.74 (2, aryl), 129.36 (aryl), 90.19 (C-1), 80.40 (C-4), 78.37 (C-2), 75.26 (C-3), 62.05 (C-5), 21.12 (aryl-CH$_3$), 20.79 (C(O)CH$_3$), 20.73 (C(O)CH$_3$), 20.57 (C(O)CH$_3$); ESIMS: *m/z* calcd for $[C_{18}H_{22}O_7S]Na^+$: 405.0979. Found: *m/z* 405.0980. Further elution with 10:1 hexane–EtOAc gave **8** (0.18 g, 15%) as an oil: R_f 0.39 (3:1, hexane–EtOAc); $[\alpha]_D$ +148 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.39 (dd, 2H, *J* 8.0, 1.7 Hz, aryl), 7.12 (dd, 2H, *J* 8.0, 0.4 Hz, aryl), 5.78 (d, 1H, $J_{1,2}$ 5.4 Hz, H-1), 5.44–5.40 (m, 2H, H-3, H-2), 4.65 (ddd, 1H, $J_{3,4}$ 5.4 Hz, $J_{4,5a}$ 5.4 Hz, $J_{4,5b}$ 5.4 Hz, H-4), 4.25 (dd, 1H, $J_{4,5a}$ 5.4 Hz, $J_{5a,5b}$ 11.8 Hz, H-5a), 4.18 (dd, 1H, $J_{4,5b}$ 5.4 Hz, $J_{5a,5b}$ 11.8 Hz, H-5b), 2.33 (s, 3H, aryl-CH_3), 2.09 (s, 3H, C(O)CH_3), 2.08 (s, 3H, C(O)CH_3), 2.03 (s, 3H, C(O)CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 170.45 (C=O), 169.66 (C=O), 169.50 (C=O), 138.02 (aryl), 132.83 (2, aryl), 129.80 (2, aryl), 129.62 (aryl), 89.77 (C-1), 77.49 (C-4), 75.61 (C-2), 75.01 (C-3), 61.23 (C-5), 21.10 (aryl-CH$_3$), 20.78 (C(O)CH$_3$), 20.62 (C(O)CH$_3$), 20.61 (C(O)CH$_3$); ESIMS: *m/z* calcd for $[C_{18}H_{22}O_7S]Na^+$: 405.0979. Found: *m/z* 405.0981.

1.3. *p*-Tolyl 1-thio-β-D-xylofuranoside (9)

A solution of **7** (100 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (10 mL) at rt was treated with 1 M $NaOCH_3$ in CH_3OH (2 mL). After stirring for 3 h, the reaction mixture was neutralized by the addition of dry ice and then concentrated. The crude product was purified by chromatography (1:1 hexanes–EtOAc) to yield **9** (62 mg, 92%) as a white solid: R_f 0.11 (1:1, hexane–EtOAc); $[\alpha]_D$ −196 (*c* 0.5, CH_3OH); mp 108–109 °C; ^{1}H NMR (500 MHz, CD_3OD): δ_H 7.47 (dd, 2H, *J* 6.5, 1.7 Hz, aryl), 7.26 (d, 2H, *J* 8.0 Hz, aryl), 5.15 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1), 4.27 (ddd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5a}$ 4.3 Hz, $J_{4,5b}$ 6.6 Hz, H-4), 4.23–4.20 (m, 1H, H-3), 4.12 (dd, 1H, $J_{1,2}$ 4.2 Hz, $J_{2,3}$ 3.6 Hz, H-2), 3.80 (dd, 1H, $J_{4,5a}$ 4.3 Hz, $J_{5a,5b}$ 12.1 Hz, H-5a), 3.68 (dd, 1H, $J_{4,5b}$ 6.6 Hz, $J_{5a,5b}$ 12.1 Hz, H-5b), 2.33 (s, 3H, aryl-CH_3); ^{13}C NMR (100 MHz, D_2O): δ_C 139.90 (aryl), 133.50 (2 aryl), 130.89 (2 aryl), 129.67 (aryl), 91.34 (C-1), 82.74 (C-4), 81.28 (C-2), 76.36 (C-3), 61.32 (C-5), 21.05 (aryl-CH$_3$). Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.28; H, 6.13; ESIMS: *m/z* calcd for $[C_{12}H_{16}O_4S]$ Na^+: 279.0662. Found: *m/z* 279.0661.

1.4. *p*-Tolyl 1-thio-α-D-xylofuranoside (10)

A solution of **8** (1.5 g, 3.9 mmol) in CH_2Cl_2 (25 mL) and CH_3OH (25 mL) at rt was treated with 1 M $NaOCH_3$ in CH_3OH (8 mL). After stirring for 3 h, the reaction mixture was neutralized by the addition of dry ice and then concentrated. The crude product was purified by chromatography (1:1, hexanes–EtOAc) to yield **10** (0.89 g, 89%) as a white solid: R_f 0.11 (1:1, hexane–EtOAc); $[\alpha]_D$ +247 (*c* 0.5, CH_3OH); mp 144–146 °C; ^{1}H NMR (500 MHz, CD_3OD): δ_H 7.39 (dd, 2H, *J* 6.5, 1.7 Hz, aryl), 7.08 (dd, 2H, *J* 8.0, 0.5 Hz, aryl), 5.63 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1), 4.30–4.27 (m, 1H, H-4) 4.26 (dd, 1H, $J_{1,2}$ 4.3 Hz, $J_{2,3}$ 2.1 Hz, H-2), 4.15 (dd, 1H, $J_{2,3}$ 2.1 Hz, $J_{3,4}$ 3.8 Hz, H-3), 3.79 (dd, 1H, $J_{4,5a}$ 5.1 Hz, $J_{5a,5b}$ 11.7 Hz, H-5a), 3.68 (dd, 1H, $J_{4,5b}$ 6.0 Hz, $J_{5a,5b}$ 11.7 Hz, H-5b), 2.28 (s, 3H, aryl-CH_3); ^{13}C NMR (100 MHz, CD_3OD): δ_C 137.87 (aryl), 133.71 (aryl), 132.41 (2, aryl), 130.57 (2 aryl), 93.19 (C-1), 81.77 (C-4), 80.31 (C-2), 78.07 (C-3), 61.61 (C-5), 21.10 (aryl-CH$_3$). Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.13; H, 6.49; ESIMS: *m/z* calcd for $[C_{12}H_{16}O_4S]Na^+$: 279.0662. Found: *m/z* 279.0664.

1.5. *p*-Tolyl 3,5-*O*-sulfinyl-1-thio-β-D-xylofuranoside (11)

To an ice-cooled solution (5 °C) of **9** (1.3 g, 5 mmol) in CH_3CN (25 mL) was added pyridine (2.05 mL, 25 mmol) and thionyl chloride (1.85 mL, 25 mmol), and the mixture was stirred at 5 °C. After 3 h water (5 mL) was added, and the mixture was stirred for 10 min. The solution was extracted with EtOAc (3 × 25 mL), and the organic layer was washed with water and brine, before being dried (Na_2SO_4), filtered, and concentrated. The crude product was purified by chromatography (1:6 hexanes–EtOAc) to yield **11** (1.27 g, 83%) as a white solid: R_f 0.41 (1:1 hexane–EtOAc); $[\alpha]_D$ −106.1 (*c* 0.5, $CHCl_3$); mp 127–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.45 (dd, 2H, *J* 6.4, 1.8 Hz, aryl), 7.14 (dd, 2H, *J* 8.0, 0.4 Hz, aryl), 5.19 (d, 1H, $J_{1,2}$ 2.1 Hz, H-1), 4.89 (dd, 1H, $J_{4,5a}$ 2.2 Hz, $J_{5a,5b}$ 12.8 Hz, H-5a), 4.77 (d, 1H, $J_{3,4}$ 2.7 Hz, H-3), 4.40 (dd, 1H, $J_{2,OH}$ 4.2 Hz, $J_{1,2}$ 2.1 Hz, H-2), 4.18–4.12 (m, 2H, H-4, H-5b), 2.57 (d, 1H, $J_{OH,2}$ 4.2 Hz, exchanges with D_2O), 2.34 (s, 3H, aryl-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.04 (aryl), 132.58 (2, aryl), 130.12 (aryl), 129.78 (2, aryl), 93.14 (C-1), 81.35 (C-4), 73.20 (C-2), 71.46 (C-3), 55.79 (C-5), 21.12 (aryl-CH$_3$). Anal. Calcd for $C_{12}H_{14}O_5S_2$: C, 47.67; H, 4.67. Found: C, 47.61; H, 4.39; ESIMS: *m/z* calcd for $[C_{12}H_{14}O_5S_2]Na^+$: 325.0175. Found: *m/z* 325.0174.

1.6. *p*-Tolyl 3,5-*O*-sulfinyl-1-thio-α-D-xylofuranoside (12)

To an ice-cooled solution (5 °C) of **10** (0.28 g, 10.9 mmol) in CH_3CN (15 mL) was added pyridine (0.45 mL, 54.6 mmol), and thionyl chloride (0.40 mL, 54.6 mmol) and reaction mixture was stirred at 5 °C. After 3 h water (3 mL) was added, and the mixture was stirred for

10 min. Workup of the reaction as described for the preparation of **11** provided a crude product that was purified by chromatography (1:8 hexanes–EtOAc) to yield **12** (0.287 g, 87%) as a white solid: R_f 0.43 (1:1 hexane–EtOAc); $[\alpha]_D$ +194 (*c* 0.5, $CHCl_3$); mp 149–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.43 (d, 2H, *J* 8.1 Hz, aryl), 7.15 (d, 2H, *J* 7.9 Hz, aryl), 5.75 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 4.96 (d, 1H, $J_{3,4}$ 1.6 Hz, H-3), 4.92 (dd, 1H, $J_{4,5a}$ 2.1 Hz, $J_{5a,5b}$ 13.0 Hz, H-5a), 4.44 (dd, 1H, $J_{1,2}$ 3.9 Hz, $J_{2,OH}$ 3.7 Hz, H-2), 4.33 (m, 1H, H-4), 4.14 (d, 1H, $J_{5a,5b}$ 13.0 Hz, H-5b), 2.94 (d, 1H, $J_{OH,2}$ 3.6 Hz, exchanges with D_2O), 2.34 (s, 3H, aryl-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.20 (aryl), 132.41 (2, aryl), 130.06 (2, aryl), 129.24 (aryl), 93.59 (C-1), 76.60 (C-4), 71.87 (C-2), 71.21 (C-3), 55.97 (C-5), 21.11 (aryl-*C*H_3). Anal. Calcd for $C_{12}H_{14}O_5S_2$: C, 47.67; H, 4.67. Found: C, 47.49; H, 4.48; ESIMS: *m*/*z* calcd for $[C_{12}H_{14}O_5S_2]Na^+$: 325.0175. Found: *m*/*z* 325.0177.

1.7. *p*-Tolyl 2,3-anhydro-1-thio-β-D-ribofuranoside (13)

To a solution of thioglycoside **11** (80 mg, 0.26 mmol) in DMF (5 mL) was added Et_3N (0.19 mL, 1.3 mmol) and $NaHCO_3$ (111 mg, 1.3 mmol), and the reaction mixture was heated at 90 °C. After 60 h the solution was concentrated and the crude product thus obtained was purified by chromatography (1:6 hexanes–EtOAc) to yield **13** (35 mg, 60%) as an oil: R_f 0.41 (1:1 hexane–EtOAc); $[\alpha]_D$ −276 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.40 (d, 2H, *J* 8.1 Hz, aryl), 7.14 (d, 2H, *J* 7.9 Hz, aryl), 5.54 (s, 1H, H-1), 4.31 (dd, 1H, $J_{4,5a}$ 4.0 Hz, $J_{4,5b}$ 4.0 Hz, H-4), 3.96 (d, 1H, $J_{2,3}$ 2.7 Hz, H-3), 3.89 (d, 1H, $J_{2,3}$ 2.7 Hz, H-2), 3.85–3.75 (m, 2H, H-5a, H-5b), 2.62 (d, 1H, $J_{OH,5}$ 4.2 Hz, exchanges with D_2O), 2.34 (s, 3H, aryl-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 138.36 (aryl), 132.43 (2, aryl), 130.09 (2, aryl), 128.81 (aryl), 87.62 (C-1), 81.11 (C-4), 62.61 (C-5), 58.67 (C-2), 57.74 (C-3), 21.11 (aryl-*C*H_3); ESIMS: *m*/*z* calcd for $[C_{12}H_{14}O_3S]Na^+$: 261.0478. Found: 261.0552.

1.8. *p*-Tolyl 2,3-anhydro-1-thio-α-D-ribofuranoside (14)

To a solution of thioglycoside **12** (65 mg, 0.20 mmol) in DMF (5 mL) was added Et_3N (0.15 mL, 1.0 mmol) and $NaHCO_3$ (90 mg, 1.0 mmol), and the reaction mixture was heated at 90 °C. After 48 h the reaction mixture was concentrated, and the crude product thus obtained was purified by chromatography (1:4 hexanes–EtOAc) to yield **14** (35 mg, 70%) as a oil: R_f 0.37 (1:1 hexane–EtOAc); $[\alpha]_D$ +50.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.45 (d, 2H, *J* 8.2 Hz, aryl), 7.14 (d, 2H, *J* 7.9 Hz, aryl), 5.42 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.42 (dd, 1H, $J_{4,5a}$ 4.2 Hz, $J_{4,5b}$ 4.2 Hz, H-4), 4.02 (dd, 1H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 2.8 Hz, H-2), 3.81–3.67 (m, 3H, H-3, H-5a, H-5b), 2.34 (s, 3H aryl-CH_3), 1.68 (dd, 1H, $J_{OH,5a}$ 5.9 Hz, $J_{OH,5b}$ 5.9 Hz, exchanges with D_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 137.81 (aryl), 132.50 (2, aryl), 130.33 (2, aryl), 129.79 (aryl), 87.65 (C-1), 80.44 (C-4), 62.89 (C-5), 59.45 (C-2), 57.95 (C-3), 21.10 (aryl-*C*H_3); ESIMS: *m*/*z* calcd for $[C_{12}H_{14}O_3S]Na^+$: 261.0478. Found *m*/*z* 261.0550.

1.9. *p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio-β-D-ribofuranoside (2)

Compound **13** (0.12 g 0.50 mmol) was dissolved in dry pyridine (8 mL) and cooled to 0 °C. After 10 min benzoyl chloride (0.087 mL, 0.75 mmol) was added dropwise over 10 min. The reaction mixture was allowed to stir for 2 h while warming to rt, and then it was diluted with CH_2Cl_2. The organic layer was washed with 1 N HCl (5 mL), satd aq $NaHCO_3$ (5 mL) and then water. The organic layer was dried with Na_2SO_4, filtered, and concentrated. The product was purified by chromatography (12:1 hexanes–EtOAc) to yield **2** (0.16 g, 93%). The NMR data obtained for the product were identical to those previously reported.[2]

1.10. *p*-Tolyl 2,3-anhydro-5-*O*-benzoyl-1-thio-α-D-ribofuranoside (3)

Compound **14** (0.14 g 0.58 mmol) was dissolved in dry pyridine (10 mL) and cooled to 0 °C. After 10 min benzoyl chloride (0.11 mL, 0.88 mmol) was added dropwise over 10 min. The reaction mixture was allowed to stir for 2 h while warming to rt and then diluted with CH_2Cl_2. Workup as described for the preparation of **2**, gave a crude product that was purified by chromatography (10:1 hexanes–EtOAc) to yield **3** (0.176 g, 88%). The NMR data obtained for the product were identical to those previously reported.[2]

Acknowledgements

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