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A Cyclic Sulfate Approach to the Synthesis of 1,4-Dideoxy-1,4-imino Derivatives of L-Xylitol, L-Arabinitol and D-Xylitol

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A CYCLIC SULFATE APPROACH TO THE SYNTHESIS OF 1,4-DIDEOXY-1,4-IMINO DERIVATIVES OF L-XYLITOL, L-ARABINITOL AND D-XYLITOL

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ABSTRACT: Polyhydroxylated pyrrolidines are readily accessible by ring opening of a 1,4-cyclic sulfate function in pentitol derivatives by nitrogen nucleophiles and further processing of the *in situ* generated charged sulfate group.

It is well documented that competitive inhibitors of glycosidases are valuable tools to study in detail the mechanisms associated with glycoprotein processing[1,2]. Moreover, this type of inhibitors show great promise as therapeutics[3-6]. Among these inhibitors are polyhydroxylated piperidines and pyrrolidines, which are analogues of carbohydrates of which the ring oxygen and the anomeric hydroxyl group have been replaced by a nitrogen and hydrogen, respectively.

As part of an ongoing programme[7-10] directed toward the design of effective glycosidase inhibitors we report here the synthesis of the pyrrolidines 1,4-dideoxy-1,4-imino-L-xylitol (**1**), 1,4-dideoxy-1,4-imino-L-arabinitol (**2**) and 1,4-dideoxy-1,4-imino-D-xylitol (**3**).

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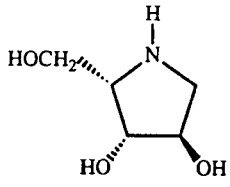
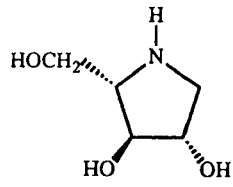


1



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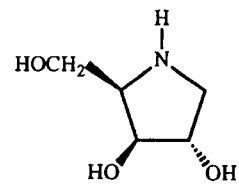
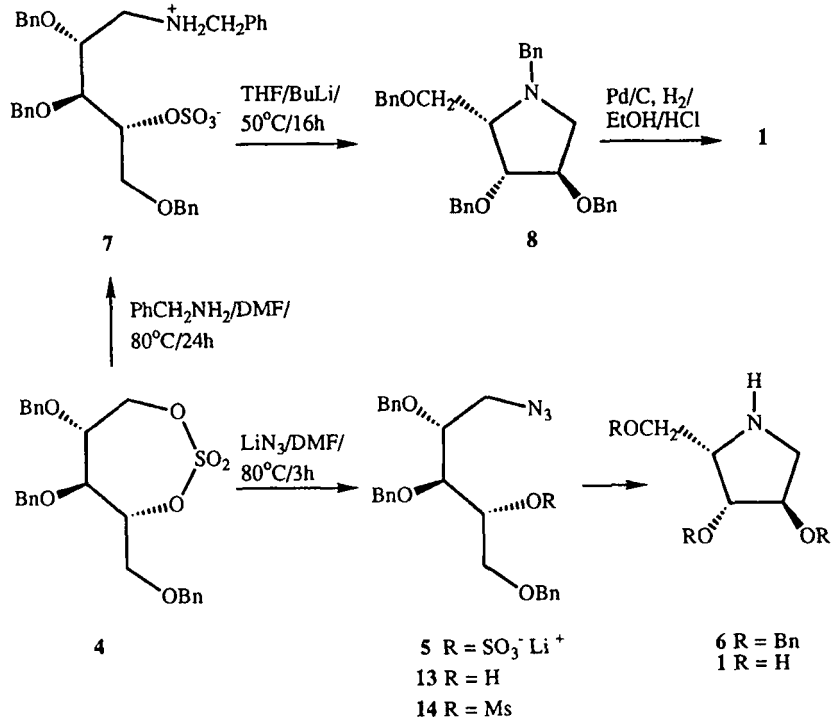


3

Up to now, several routes to 1,4-dideoxy-1,4-iminopentitol derivatives have been described. Thus apart from enzymatic[11,12] and *de novo*[13] approaches to 1,4-dideoxy-1,4-iminopentitols, much effort has been directed to achieve the same goal using carbohydrates[14-24].

Recently, we demonstrated that cyclic sulfates of carbohydrates proved to be valuable intermediates[25-28] in the synthesis of biologically interesting compounds. In order to enlarge the scope of this methodology we were interested to find out whether cyclic sulfates of carbohydrates could be used in a synthetic route to pyrrolidines **1**, **2** and **3**.

In an earlier report, Sharpless[29] showed that 1,2-cyclic sulfates could be converted into aziridines. For example, nucleophilic opening of a 1,2-cyclic sulfate function with lithium azide gave the corresponding azidosulfate, which after reduction with lithium aluminium hydride, cyclized to an aziridine. Alternatively, treatment of a 1,2-cyclic sulfate with benzylamine and subsequent deprotonation of the aminosulfate compound by *n*-butyllithium afforded the corresponding aziridine. In order to investigate whether the Sharpless aziridine approach could be extended to 1,4-cyclic sulfates we applied this method for the preparation of pyrrolidines. To this end, known[27] 2,3,5-tri-*O*-benzyl-D-arabinitol 1,4-sulfate (**4**) was treated with lithium azide in dimethylformamide for 3 h at 80°C to give, as outlined in Scheme 1, the 1-azido-4-sulfate intermediate **5**. The formation of **5** was indirectly corroborated by its mild hydrolysis with sulfuric acid to afford **13**. However, *in situ* reductive cyclization of **5** with lithium aluminum hydride in tetrahydrofuran was abortive. On the other hand, reaction of cyclic sulfate **4** with benzylamine in dimethylformamide for 24 h at 80°C gave intermediate **7**. Treatment of **7** with *n*-butyllithium in tetrahydrofuran for 16 h at 50°C furnished, after purification by column chromatography, homogeneous **8**. Catalytic hydrogenolysis of the benzyl groups with palladium on charcoal in a mixture of ethanol and



Scheme 1

hydrochloric acid resulted in the isolation of 1,4-dideoxy-1,4-imino-L-xylitol (**1**) in 36% overall yield for the three steps. The ^{1}H- and ^{13}C NMR data of precursor **8** and target molecule **1** were in excellent agreement with the data reported[22,24] for these compounds. In a similar sequence of events, starting from D-xylose and L-arabinose, compounds **2** and **3** could be prepared in 25% and 34% yield, based on 2,3,5-tri-*O*-benzyl-D-xylitol 1,4-sulfate (**9**) and 2,3,5-tri-*O*-benzyl-L-arabinitol 1,4-sulfate (**11**), respectively. Both pyrrolidines were in all aspects (specific optical rotation, ^{1}H- and ^{13}C NMR spectroscopy) identical with those previously synthesized[16-18,22].

The one-pot two-step procedure was, presumably due to the low leaving group capacity of the sulfate group, not completely satisfactory. In order to explore the feasibility to increase the overall yield of **1** from **4**, we followed the synthetic

route outlined in Scheme 1. Treatment of cyclic sulfate **4** with lithium azide and subsequent removal of the sulfate group in intermediate **5** by mild acidic hydrolysis gave, after silica gel chromatography, 1-azido-2,3,5-tri-*O*-benzyl-1-deoxy-D-arabinitol (**13**). Reductive cyclization of **13**, as reported by Duréault[23] starting from a closely related 1,4-azido alcohol derivative, did not afford the expected pyrrolidine **6**. Fortunately, esterification of **13** with mesyl chloride in the presence of pyridine furnished compound **14**. Reduction of the azide function in mesylate **14** with palladium black in ethanol, following the procedure of Fleet[16,17], was accompanied by intramolecular cyclization to yield, as gauged by ^{13}C NMR spectroscopy, pyrrolidine **6** which was further hydrogenolyzed with palladium black in acetic acid. Work up and purification gave 1,4-dideoxy-1,4-imino-L-xylitol (**1**, 65% based on **4**), which was in every aspect identical with the earlier prepared compound **1** (Scheme 1). In this respect it is interesting to note that the efficacy of the alternative cyclic sulfate approach was also recently nicely illustrated by Kibayashi and Machinaga[30,31] in the preparation of *trans*-2,5-dialkylated pyrrolidines.

In conclusion, the results described in this paper indicate that precursors of cyclic sulfates of carbohydrates are useful for the preparation of chirally pure 1-azidopentitol compounds (*e.g.* **13**) and the biologically interesting 1,4-dideoxy-1,4-iminopentitols (*i.e.* **1** - **3**).

EXPERIMENTAL

Optical rotations of the Na_D-line were obtained at 20°C using a Perkin-Elmer 141 polarimeter. TLC analysis was performed on silica gel (Schleicher & Schüll, F 1500 LS 254). Compounds were visualized by UV light and by spraying with conc. sulfuric acid in MeOH (2/8, v/v), or a solution of $(NH_4)_2MoO_4$ (25 g) and ammonium cerium(IV) sulfate (10 g) in 10% aq. H_2SO_4, followed by charring at 140°C for a few minutes. Column chromatography was performed on Merck Kieselgel (230-400 mesh, ASTM). Evaporations were carried out below 40°C under reduced pressure (20 mm or 1 mm Hg). ^1H NMR spectra were measured at 300 MHz using a Bruker WM-300 spectrometer, equipped with an ASPECT-2000 computer, operating in the Fourier transform mode. ^{13}C NMR spectra were measured at 50.1 MHz using a Jeol JNM-FX 200 spectrometer on line with a JEC 980 B computer. Chemical shifts were given in ppm (δ) relative to tetramethylsilane (TMS) as internal standard.

2,3,5-Tri-*O*-benzyl-1,4-dideoxy-1,4-imino-*N*-benzyl-L-xylitol (8); Typical Procedure:

Cyclic sulfate **4** (484 mg, 1 mmol) and benzylamine (218 µL, 2 mmol) are dissolved in DMF (4 mL). After stirring for 24 h at 80°C, the mixture is evaporated and concentrated from *p*-xylene (3 x 10mL). Residue **7** is dissolved in THF (10 mL) and *n*-butyllithium (1.25 mL, 1.6 M, 2 mmol) in hexane is added. After stirring for 16 h at 50°C, the mixture is extracted with EtOAc, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4) and concentrated. The resulting oil is chromatographed on silica gel (eluent: CH_2Cl_2/acetone, 97:3) to give **8**; yield: 183 mg (37%); R_f 0.49 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ +30.5 (*c* = 1, $CHCl_3$) {Lit[24] $[\alpha]_D^{20}$ +30.5 (*c* = 0.95, $CHCl_3$)}.

^1H NMR ($CDCl_3$): δ = 2.32 (dd, 1 H, $J_{1,1'}$= 10.2 Hz, $J_{1,2}$ = 5.5 Hz, H-1), 3.14 (m, 1 H, H-4), 3.27 (dd, 1 H, $J_{1',2}$ = 6.0 Hz, H-1'), 3.48 (d, 1 H, J = 13.3, NCH*H*Ph), 3.64 (dd, 1 H, $J_{4,5}$ = 5.2 Hz, $J_{5,5'}$ = 9.7 Hz, H-5), 3.85 (dd, 1 H, $J_{4,5'}$ = 6.0 Hz, H-5'), 3.99 (m, 1 H, H-2), 4.06 (dd, 1 H, H-3), 4.11 (d, 1 H, NC*H*HPh), 4.3 - 4.7 (m, 6 H, CH_2Ph), 7.0 - 7.5 (m, 20 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 56.9 (C-1), 59.1 (N*C*H_2Ph), 64.9 (C-4), 69.1, 71.0, 71.8, 73.1 (C-5, *C*H_2Ph), 81.7, 83.2 (C-2, C-3), 125 - 129 (CH_{arom}), 137.9, 138.2, 138.7 (C_{arom}).

1,4-dideoxy-1,4-imino-L-xylitol hydrochloride (1); Typical procedure:

Pyrrolidine **8** (100 mg, 0.2 mmol) is dissolved in a mixture of ethanol (3 mL) and aq. HCl (1 mL, 2 M). Palladium (10%) on charcoal (60 mg) is added, and the mixture is shaken under a hydrogen atmosphere (0.2 MPa) for 24 h at 20°C. The mixture is filtered and evaporated to give **1**; yield: 34 mg (98%); $[\alpha]_D^{20}$ -5.1 (*c* = 1, H_2O); {Lit[22] $[\alpha]_D^{20}$ -9.9 (*c* = 0.71, H_2O)}.

^1H NMR (D_2O): δ = 3.32 (d, 1 H, $J_{1,1'}$ = 13.0 Hz, H-1), 3.68 (dd, 1 H, $J_{1',2}$ = 4.3 Hz, H-1'), 3.8-4.0 (m, 2 H, H-4, H-5), 4.04 (dd, 1 H, $J_{4,5'}$ = 8.6 Hz, $J_{5,5'}$ = 15.5 Hz, H-5'), 4.34 (m, 1 H, H-3), 4.41 (m, 1 H, H-2).

^{13}C NMR (CD_3OD): δ = 52.0 (C-1), 59.0 (C-5), 65.1 (C-4), 75.9, 76.1 (C-2,C-3).

Compound **1** is prepared as described for 1-azido-2,3,5-tri-*O*-benzyl-1-deoxy-4-*O*-methylsulfonyl-D-xylitol (see ref. 16 and 17) starting from **14** (83%). The spectroscopic data were identical to those obtained by following the typical procedure from **8**.

2,3,5-Tri-*O*-benzyl-D-xylitol 1,4-sulfate (9):

Compound **9** is prepared as described for 2,3,5-tri-*O*-benzyl-D-arabinitol 1,4-sulfate (see ref. 27) starting from D-xylose.

Yield: 55% (based on D-xylose); R_f 0.84 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ +19.1 (*c* = 1, $CHCl_3$).

$C_{26}H_{28}O_7S$ calc. C 64.45 H 5.82
(484.6) found 64.49 5.75

^{13}C NMR ($CDCl_3$): δ = 66.8, 67.5 (C-1, C-5), 71.1, 73.0, 73.1 (CH_2Ph), 72.6, 73.8, 78.3 (C-2, C-3, C-4), 127-129 (CH_{arom}), 136.6, 136.7, 137.1 (C_{arom}).

2,3,5-Tri-*O*-benzyl-1,4-dideoxy-1,4-imino-*N*-benzyl-L-arabinitol (10):

Compound **10** is prepared as described for **8** starting from cyclic sulfate **9**.

Yield: 25%; R_f 0.66 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ +21.9 (*c* = 1, $CHCl_3$).

$C_{33}H_{35}NO_3$ calc. C 80.29 H 7.15
(493.6) found 80.33 7.20

^1H NMR ($CDCl_3$): δ = 2.56 (dd, 1 H, $J_{1,1'}$ = 10.7 Hz, $J_{1,2}$ = 5.1 Hz, H-1), 2.87 (m, 1 H, H-4), 3.04 (d, 1 H, H-1'), 3.49 (d, 1 H, J = 13.2 Hz, NC*H*HPh), 3.60 (m, 2 H, H-5, H-5'), 3.8 - 4.0 (m, 2 H, H-2, H-3), 4.13 (d, 1 H, NCH*H*Ph), 4.3 - 4.7 (m, 6 H, C*H*$_2$Ph), 7.0 - 7.5 (m, 20 H, H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 56.8 (C-1), 59.0 (N*C*H_2Ph), 68.3 (C-4), 70.2, 71.1, 71.3, 73.1 (C-5, *C*H_2Ph), 81.4, 85.7 (C-2, C-3), 126 - 129 (CH_{arom}), 137.8, 138.1, 138.6 (C_{arom}).

1,4-dideoxy-1,4-imino-L-arabinitol hydrochloride (2):

Compound **2** is prepared as described for **1** starting from the fully protected **10**.

Yield: 100%; $[\alpha]_D^{20}$ -30.6 (*c* = 1, H_2O); {Lit[16,17]. $[\alpha]_D^{20}$ -34.6 (*c* = 0.37, H_2O); Lit[18]. $[\alpha]_D^{20}$ -27.8 (H_2O)}.

^1H NMR (D_2O): δ = 3.34 (dd, 1 H, $J_{1,1'}$ = 12.6 Hz, $J_{1,2}$ = 2.8 Hz, H-1), 3.58 (dd, 1 H, $J_{1',2}$ = 4.8 Hz, H-1'), 3.60 (m, 1 H, $J_{4,5}$ = 8.1 Hz, $J_{4,5'}$ = 4.8 Hz, H-4), 3.84 (dd, 1 H, $J_{5,5'}$ = 12.1 Hz, H-5), 3.96 (dd, 1 H, H-5'), 4.09 (m, 1 H, H-3), 4.33 (dt, 1 H, H-2).

^{13}C NMR (D_2O): δ = 50.6 (C-1), 59.5 (C-5), 67.2 (C-4), 74.9, 76.3 (C-2, C-3).

2,3,5-Tri-*O*-benzyl-L-arabinitol 1,4-sulfate (11):

Compound **11** is prepared as described for 2,3,5-tri-*O*-benzyl-D-arabinitol 1,4-sulfate (see ref. 27) starting from L-arabinose.

Yield: 64% (based on L-arabinose); R_f 0.71 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ -26.9 (*c* = 1, $CHCl_3$).

$C_{26}H_{28}O_7S$ calc. C 64.45 H 5.82
(484.6) found 64.47 5.79
^{13}C NMR ($CDCl_3$): δ = 67.8, 68.0 (C-1, C-5), 73.6, 73.8, 75.6 (*C*H_2Ph), 78.1, 79.7, 81.3 (C-2, C-3, C-4), 127-129 (CH_{arom}), 137.3, 137.5, 137.7 (C_{arom}).

2,3,5-Tri-*O*-benzyl-1,4-dideoxy-1,4-imino-*N*-benzyl-D-xylitol (12):

Compound **12** is prepared as described for **8** starting from cyclic sulfate **11**.
Yield: 35%; R_f 0.49 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ -31.0 (*c* = 1, $CHCl_3$).
$C_{33}H_{35}NO_3$ calc. C 80.29 H 7.15
(493.6) found 80.35 7.23
^1H- and ^{13}C-NMR spectral data are identical to those of compound **8**.

1,4-dideoxy-1,4-imino-D-xylitol hydrochloride (3):

Compound **3** is prepared as described for **1** starting from the fully protected **12**.
Yield: 97%; $[\alpha]_D^{20}$ +6.0 (*c* = 1, H_2O); {Lit[22]. $[\alpha]_D^{20}$ +7.4 (*c* = 0.68, H_2O)}.
^1H- and ^{13}C-NMR spectral data are identical to those of compound **1**.

1-Azido-2,3,5-tri-*O*-benzyl-1-deoxy-D-arabinitol (13):

To a solution of cyclic sulfate **4**[27] (484 mg, 1 mmol) in DMF (5 mL) is added LiN_3 (100 mg, 2 mmol). The mixture is stirred at 80°C until (3 h) TLC analysis showed complete conversion of the cyclic sulfate into **5**, having low mobility. The mixture is concentrated and dissolved in THF (5 mL). Conc. H_2SO_4 (50 μL) and water (18 μL) are injected and stirring is continued for 0.5 h at ambient temperature. The mixture is diluted with EtOAc (20 mL) and washed twice with sat. aq. $NaHCO_3$ (5 mL). The organic layer is dried (Na_2SO_4), concentrated and purified by silica gel column chromatography [eluent: CH_2Cl_2/acetone, 95:5] to give **13**; yield: 382 mg (85%); R_f 0.68 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ -12.3° (*c* = 1, $CHCl_3$).
$C_{26}H_{29}N_3O_4$calc. C 69.78 H 6.53
(447.5) found 69.95 6.61
I.R. (neat): 2100 cm^{-1} (N_3).
^1H NMR ($CDCl_3$): δ = 2.74 (d, 1 H, $J_{4,OH}$ = 5.4 Hz, 4-OH), 3.39 (dd, 1 H, $J_{1,1'}$ = 12.6 Hz, $J_{1,2}$ = 5.0 Hz, H-1), 3.50 (dd, 1 H, $J_{1',2}$ = 6.9 Hz, H-1'), 3.5 - 3.7 (m, 3 H, H-3, H-5, H-5'), 3.82 (ddd, 1 H, $J_{2,3}$ = 3.7 Hz, H-2), 3.94 (m, 1 H, H-4), 4.4 - 4.7 (m, 6 H, CH_2Ph), 7.1 - 7.4 (m, 15 H_{arom}).
^{13}C NMR ($CDCl_3$): δ = 51.6 (C-1), 70.4, 77.9, 78.5 (C-2, C-3, C-4), 71.0 (C-5), 73.4, 73.6, 74.0 (*C*H_2Ph), 127-129 (CH_{arom}), 137.7, 137.9 (C_{arom}).

1-Azido-2,3,5-tri-*O*-benzyl-1-deoxy-4-*O*-methylsulphonyl-D-arabinitol (14): To a solution of **13** (200 mg, 0.45 mmol) and pyridine (0.5 mL) in CH_2Cl_2 (3 mL) is added MsCl (0.18 mL, 2.3 mmol) at 0°C. After stirring for 1 h, the solution is diluted with CH_2Cl_2 (15 mL), washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4) and concentrated. The residue is chromatographed on silica gel (eluent: CH_2Cl_2/acetone, 99:1) to afford **14**; yield: 217 mg (92%); R_f 0.89 (CH_2Cl_2/acetone, 97:3); $[\alpha]_D^{20}$ -11.2 (*c* = 1, $CHCl_3$).

$C_{27}H_{31}N_3O_6S$ calc. C 61.70 H 5.94
(525.6) found 61.85 5.98

I.R. (neat): 2100 cm^{-1} (N_3).

^1H NMR ($CDCl_3$): δ = 2.96 (3 H, s, CH_3SO_2), 3.33 (1 H, dd, H-1, $J_{1,1'}$ = 12.8 Hz, $J_{1,2}$ = 5.4 Hz, H-1), 3.42 (dd, 1 H, $J_{1',2}$ = 6.4 Hz, H-1'), 3.6 - 4.0 (m, 4 H, H-2, H-3, H-5, H-5'), 4.4 - 4.8 (m, 6 H, CH_2Ph), 4.96 (m, 1 H, H-4), 7.1 - 7.4 (m, 15 H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 38.3 (CH_3S), 51.0 (C-1), 68.6 (C-5), 73.2, 73.2, 74.1 (CH_2Ph), 77.8, 78.0 (C-2, C-3), 81.7 (C-4), 127-129 (CH_{arom}), 137.0, 137.2 (C_{arom}).

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