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Regioselective sulfamoylation at low temperature enables concise syntheses of putative small molecule inhibitors of sulfatases

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Regioselective sulfamoylation of primary hydroxyl groups enabled a 5-step synthesis (overall yield 17%) of the first reported small molecule inhibitor of sulfatase-1 and 2, (2S,3R,4R,5S,6R)-4,5-dihydroxy-2-methoxy-6-((sulfamoyl-oxy)methyl)tetrahydro-2H-pyran-3-yl)sulfamate (methyl 2-deoxy-2-sulfamino-6-O-sulfamoyl-α-D-glucopyranoside, 1), which obviated the use of hydroxyl protecting groups and is a marked improvement on the reported 9-step synthesis (overall yield 9%) employing hazardous trifluoromethylsulfonyl azide. The sulfamoylation methodology was used to prepare a range of derivatives of 1, and inhibition data was generated for Sulf-2, ARSA and ARSB.

Introduction

The human sulfatase enzymes, sulfatase-1 (Sulf-1) and sulfatase-2 (Sulf-2), were first cloned in 2002 and have been implicated in both the FGF and wnt signalling pathways. The FGF signalling pathway is known to affect cell proliferation, invasion, migration and angiogenesis, while the wnt signalling pathway has been implicated in cell growth and proliferation. Sulf-1 and Sulf-2 have selectivity for removing sulfates from the 6-position of glucosamine residues in heparan sulfate proteoglycans (HSPGs), which consist of a protein core conjugated to multiple heparan sulfate polysaccharide chains. The HSPG chains are composed to a large extent of repeating disaccharide units of hexuronic acid (glucuronic acid or iduronic acid) and glucosamine. Weakly active small molecule dual inhibitors of Sulf-1 and Sulf-2 have been reported. The most active inhibitor was (2S,3R,4R,5S,6R)-4,5-dihydroxy-2-methoxy-6-((sulfamoyl-oxy)methyl)tetrahydro-2H-pyran-3-yl)sulfamate (methyl 2-deoxy-2-sulfamino-6-O-sulfamoyl-α-D-glucopyranoside, 1), a derivative of glucosamine sulfate, which bears an O-sulfamate at the 6-position and a N-sulfate on the amino function. The reported IC₅₀ values for 1 are 95 μM and 130 μM against Sulf-1 and Sulf-2, respectively.

The published synthesis from (D)-(+-)glucosamine 2 provided compound 1 by a 9-step route in 9% overall yield. The amino group of 2 was converted into azido through a diazo transfer reaction with triflic azide, a reagent with a well-documented explosion hazard. The use of this reagent in the presence of dichloromethane further exacerbates the risk, as this combination can form diazidomethane, another high energy compound with an inherent explosion hazard. The anomic methoxy group was installed, followed by a sequence of 3 steps requiring benzyl protection of the 3- and 4-hydroxy groups. After sulfamate formation on the unprotected 6-hydroxy group, the azido group was reduced to an amino function, which was converted to an N-sulfate. Finally, deprotection of the 3- and 4-benzyl ethers provided 1.

Improved Synthesis of 1

In order to prepare inhibitor 1 as a tool for further study of the biological implications of inhibition of Sulf-1 and Sulf-2, we investigated an alternative route that avoids triflic azide and minimises the use of protecting groups, thus reducing the number of steps and improving the efficiency of the synthesis. We sought a strategy to compound 1 that dispensed with protection/deprotection at the 3- and 4-positions of glucosamine.

Selective sulfamoylation of the primary hydroxyl groups in di- and tri-hydroxylated compounds using (N-(tert-butoxycarbonyl)-N-[(triethylenedi-ammonium) sulfonyl]azaide) gave only moderate yields and regioselectivity on simple alkanediols, required the synthesis of the reagent and a subsequent acidic deprotection step to liberate the primary sulfamate. We therefore investigated an alternative approach using sulfamoyl
chloride as the sulfamoylating reagent, exploiting the differential reactivity of primary versus secondary alcohols to achieve direct regioselective sulfamoylation of the O\(^2\)-position (Scheme 1).

Protection of glucosamine 2 with a benzylcarbamate (Cbz) group under standard conditions,\(^9\) gave intermediate 3 in 92% yield. Heating 3 in methanolic hydrogen chloride gave a 5 to 1 ratio of \(\alpha\) to \(\beta\) anomers under thermodynamic control. The desired \(\alpha\) anomer 4 was easily separated in 73% yield.

Regioselective sulfamoylation was initially attempted using sulfamoyl chloride (H\(2\)NSO\(2\)Cl) prepared by reaction of sulfamoyl isocyanate with formic acid.\(^10\) Suitable solvent systems for sulfamate formation were identified using 4-nitrophenethyl alcohol 7 as a model substrate. For optimisation studies it was preferable to generate H\(2\)NSO\(2\)Cl in solution in acetonitrile, prior to addition to substrate in DMA, to allow control of gas evolution on scale-up. Reaction of the acetonitrile solution of H\(2\)NSO\(2\)Cl with 7 in DMA (Method 1) resulted in efficient conversion to 8 within 5 minutes at room temperature. Further studies showed that DMF (Method 2) and 10% DMA in acetonitrile (Method 3) were also suitable for the sulfamoylation of 7 to 8, and allowed the reaction to be performed at -40 °C, giving high conversions after 24 hours and similar reaction profiles.

Scheme 1: Synthesis of 1a, 1b, 10, 11 and 16 from D-glucosamine. Reagents and conditions: a) CbzCl, NaHCO\(_3\), H\(_2\)O, 92%; b) HCl/MeOH, 80 °C, 18 h, 73%; c) Method 1 H\(_2\)NSO\(2\)Cl, DMA/toluene, -15 °C, 43%; Method 2 H\(_2\)NSO\(2\)Cl, DMF/CH\(_2\)CN, -40 °C, 55%; Method 3 H\(_2\)NSO\(2\)Cl, 10% DMA/MeCN, -40 °C, 19%; d) H\(_2\)/Pd/C, MeOH, 40 °C, 2 h, 99%; e) R\(^1\) = SO\(_3\)Na; i) Py,SO\(_4\), H\(_2\)O, pH 9-10, ii) EtOAc/MeOH/NH\(_2\)OH, 43%; f) R\(^1\) = MeSO\(_3\); MeSO\(_3\)Cl, Et\(_2\)NH, CH\(_2\)Cl\(_2\), 0 °C-rt., 1 h, 28%; R\(^1\) = CF\(_3\)SO\(_3\); CF\(_3\)SO\(_3\)Cl, Et\(_3\)NH, CH\(_2\)Cl\(_2\)/dioxane, 0 °C, 1 h, 33%, R\(^1\) = CO(CH\(_2\))\(_2\)CO\(_2\)H; succinimide derivative, H\(_2\)O/dioxane, r.t., 18 h, 18%; f) 1,1,1-trichloroethylylsulfonyl imidazolium tetrafluoroborate (1 eq.), THF, 60 °C, 18 h, 61%; g) R\(^1\) = SO\(_3\)Na i) Zn (15 eq.), MeOH, H\(_2\)O, 60 °C, 1 h; ii) Ion exchange chromatography on Dowex 50Wx8/200 Na form, H\(_2\)O, 93%.

The developed conditions were applied for sulfamoylation of 4. After 18 hours at -40 °C, a further 0.15 equivalent of H\(_2\)NSO\(2\)Cl was added to each reaction and stirring was continued for a further 3 hours. Chromatographic purification led to isolation of 55% product 5 using Method 2, but only 19% with Method 3. Full details of sulfamoylation methods 1-3 are given in the general procedures in the Supplementary Information.

The Cbz protecting group was removed from 5 in quantitative yield under palladium-catalysed flow hydrogenation conditions in methanol to give 6. Addition of sulfur trioxide-pyridine complex to 6 in an aqueous medium (pH 9-10), resulted in chemoselective sulfation of the amino group to give 1 in 43% yield.\(^11\) Thus, the target monosaccharide 1 was obtained in a 17% overall yield in only five steps (Scheme 1).

An alternative N-sulfation process via a trichloroethyl protected sulfate provided 1 in a superior yield of 56% over two steps from 6 via 9 (Scheme 1). Incorporation of this sulfation protocol into the synthesis of 1 improved the overall yield for the preparation of this key Sulf-2 inhibitor to 21% over six steps.

**Synthesis of Analogues of 1**

From the homology model of F. heparinum sulfatase, it has been proposed that the sulfate on N\(^2\) of the glucosamine residue in heparan sulfate may affect binding solely by enhancing the hydrogen bond donor ability of the N\(^2\)-hydrogen atom.\(^12\) To explore this hypothesis for Sulf-2, sulfonamides 10 and 11 that would affect NH acidity were synthesised as shown in Scheme 1.

Slow evaporation of a dilute methanolic solution of 10 provided a crystal suitable for small molecule X-ray crystallography. The structure (Figure 1) confirmed the assignment of the O\(^2\)- sulfamate regiochemistry and that as expected, the pyranose core adopts a chair conformation. The amino hydrogen atoms of the sulfonamides are amongst the strongest H-bond donors, with N(H)•••O distances ranging between 2.7 Å (270 pm) and 3.2 Å.\(^13\) Molecules of 10 form a 2-dimensional network of double layered sheets comprising hydrogen bonds (O-H•••O and NH•••O) with donor-acceptor distances of 2.85-3.10 Å. The H-bond distances are in the range reported for amido-functionalised monosaccharides.\(^14\)

Succinamide derivative 16 was prepared by reaction of 6 with succinic anhydride (Scheme 1). The importance of the anomeric stereochimistry of the monosaccharide template was investigated by preparing \(\beta\) anomer 20 (see Supplementary Material: Scheme S1). Reaction of 3 with a 1.25 M methanolic HCl solution for 1 hour gave a 3:2 ratio of \(\alpha\) to \(\beta\) anomers, allowing isolation of a 37% yield of 4 and 21% of 17. Sulfamoylation of 17 using Method 1 gave a 19% yield of 18, which was converted into target 20 with no epimerisation at the anomeric centre.

To assess whether the N-sulfate could be replaced by a hydroxyl group, analogues were prepared in a single step from commercially available methyl \(\alpha\)-D-glucopyranoside 12 and methyl
α-D-mannopyranoside 14 using sulfamoylation Method 2. The reaction did not proceed cleanly and isolated yields of only 25% of 13 and 9% of 15 were obtained. Sulfamoylation of the 2-position is a likely confounding factor in this reaction, consistent with the empirically observed order of reactivity of the hydroxyl groups of glucopyranosides (6 > 2 > 3 > 4) in reactions with benzyl chloride.15

For removal of the anomeric subunit of 1 (Scheme 2), treatment of 3 with acetyl chloride16 gave 21. Radical hydrodechlorination with tributyltin hydride and AIBN gave a 47% isolated yield of 22. Tributyltin hydride could be replaced by the less toxic tris(trimethylsilyl)silane,17 resulting in a cleaner reaction profile and a straightforward purification on silica, leading to an improved isolated yield of 90% for 22. Deprotection of the acetyl groups under Zemplén conditions18 proceeded in high yield to triol 23. The use of sulfamoylation Method 1, gave a 34% yield of 24, which was progressed using the conditions described for the previous analogues, to provide 26.

From consideration of the structure of heparan sulfate, it was concluded that the binding site of Sulf-2 accommodates further saccharide units at the reducing end of the monosaccharide template. In an effort to develop SARs for this region, alternative anomeric substituents were investigated. Thus, reaction of 3 with isopropyl alcohol and 4 M HCl/dioxane gave predominantly 25% isolated yield. Sulfamoylation using Method 1 gave a 37% yield of 26, which was progressed through deprotection/sulfation steps (Scheme 3) to provide target 30.

The anomeric position of glucosamine in HSPGs is linked to an iduronic acid residue. Hence, polar groups at this position may be able to mimic interactions of the polar functionality of the iduronate residue with the Sulf-2 protein. The allyloxy group was introduced into the anomeric position using allyl alcohol and 4 M HCl/dioxane gave predominantly α-anomer 27 in 73% isolated yield. Sulfamoylation using Method 1 gave a 37% yield of 28, which was progressed through deprotection/sulfation steps (Scheme 3) to provide target 30.

Scheme 3: Reagents and conditions:

- R1 = R2 = CH3. a) AcCl, r.t., 48 h, 55%; b) Bu3SnH/AIBN, 110 °C, 1.5 h, 47%, or ii) (TMS)2SiH/AIBN, 110 °C, 1.5 h, 92%; c) NaOMe (cat.), MeOH, r.t., 2 h, 85%; d) CISO3NH2, Tol/DMA, -15 °C, 2 h, 34%; e) H2/5% Pd/C, MeOH/CH2Cl2, 40 °C, 2 h, 98%; f) SO3-Py, H2O, pH 9-10, r.t., 2 h, 24%.

- R1 = OCH2CH=CH2, R2 = nPr. a) Allyl alcohol, HCl/dioxane, 60 °C, 2 h, 37%; b) ClSO2NH2, Tol/DMA, -15 °C, 2.5 h, 40%; c) H2/10% Pd/C, MeOH/CH2Cl2, 40 °C, 2 h, 100%; d) SO3-Py, H2O, pH 9-10, r.t., 90 min, 27%.

- R1 = OCH2CH=CH2, R2 = CH2CH2OH: a) Allyl alcohol, HCl/dioxane, 60 °C, 4 h, 52%; b) ClSO2NH2, Tol/DMA, -15 °C, 2.5 h, 40%; c) H2/10% Pd/C, MeOH/CH2Cl2, 40 °C, 3 h, 78%; d) SO3-Py, H2O, pH 9-10, r.t., 1 h, 30%.

R1 = O(CHO2)2OBn: a) 3-(Benzoxyl)propan-1-ol, HCl/dioxane, 75 °C, 5 h, 31%; b) CISO3NH2, DMF, -40 °C, 18 h, 57%; c) H2/5% Pd/C, EtOH, 20 °C, 1 h, 75%; d) SO3-Py, H2O, pH 9-10, r.t., 18 h, 62%.

- R1 = O(CHO2)2OBn: a) 3-(Benzyloxy)propan-1-ol, HCl/dioxane, 75 °C, 5 h, 31%; b) CISO3NH2, DMF, -40 °C, 18 h, 57%; c) H2/5% Pd/C, EtOH, 20 °C, 1 h, 75%; d) SO3-Py, H2O, pH 9-10, r.t., 18 h, 62%.

Incorporation of 3-benzylxyopropanol at the C1'-position of 3 gave a 31% yield of a anomer 46 (Scheme 3). Sulfamoylation using Method 2 gave 47 in 57% yield. Palladium catalysed hydrogenation allowed deprotection of both O-benzyl and N-Cbz groups to give 48, which was sulfated on nitrogen to yield target 49. Chemoselective removal of the carbamate from 47 was achieved by...
flow hydrogenation, providing 50, which was sulfated using the pH-controlled sulfation conditions to give benzoxymethyl derivative 51 in 62% yield (Scheme 3).

Oxidative cleavage of the allyl group of 38 using NaIO4 with catalytic RuCl3 afforded 39 (Scheme 4). Alkylation of the carboxylic acid 39 gave ester 40. Deprotection of the acetate groups using Zemplén conditions proceeded in high yield to 41, which was sulfamoylated to 42 in 67% yield using Method 2. Hydrolysis of ester 42 to the corresponding carboxylic acid 43 prior to deprotection of the amino functionality afforded 44. The latter was sulfamoylated to acid 45.

An approach employing Barton-McCombie radical deoxygenation to allow preparation of C- and C'-methylene targets 57 and 63 was inspired by a similar strategy described for the synthesis of a series of activators of the glmS-riboswitch of Staphylococcus aureus.\textsuperscript{20}

![Scheme 5: Reagents and conditions:](image)

**Scheme 5:** Reagents and conditions: a) PhCH(OMe)2, p-TsOH, DMF, 75 °C, 3 h, 79%; b) i) CS(Im)2, toluene, 110 °C, 3 h; ii) TMS,SiH, AIBN, 110 °C, 1 h, 83%; c) i) p-TSA (cat), MeOH/CH2Cl2, µW, 80 °C, 20 min; ii) 10% K2CO3 (aq), 72%; d) ClSO2NH2, DMF, -40 °C, 24 h, 36%; e) H2/10% Pd/C, AcOH, 40 °C, 2 h, 97%; f) SO3.Py, H2O, pH 9-10, r.t., 2 h, 21%.

The 4- and 6-positions of 4 were selectively protected as benzylidene acetal 52 (Scheme 5)\textsuperscript{2} which gave an isolated yield of 79%. Radical deoxygenation of 52 under modified Barton-McCombie conditions\textsuperscript{22,23} using tris(trimethylsilyl)amine\textsuperscript{24} gave 53 in 83% isolated yield.\textsuperscript{24} Complete removal of the benzylidene acetal from 53 afforded diol 54. Regioselective sulfamate formation using Method 2 gave a 36% yield of 55. Hydrogenation followed by N-sulfation, gave 57. The synthesis of C'-methylene derivative 63 required selective protection of the 3- and 6-hydroxy groups. The order of reactivity of the hydroxy groups of methyl-D-glucopyranoside\textsuperscript{25} is conserved in D-glucosamine systems, enabling selective protection at the 3- and 6-positions.\textsuperscript{20} Using the literature conditions at room temperature resulted in no selectivity, with only 7% of 58 being obtained along with 69% of tris(benzyl) product. Reducing the reaction temperature to -40 °C allowed 58 to be isolated in a 72% yield (Scheme 6). Radical deoxygenation of 58 provided 59, which was deprotected to give a 68% yield of diol 60. Sulfamoylation gave 61 in 51% yield, with subsequent N-deprotection and sulfate formation providing target 63.

Introduction of alkoxyl substituents at the 4-position of 1 was investigated starting from 3,6-dibenzoyl protected intermediate 58. Benzylation using bundle’s reagent (benzy1-2,2,2-trichloroacetimidate) with catalytic triflic acid\textsuperscript{26,27} provided 62 benzyl ether 64 in 78% yield (Scheme 6). Reaction of 64 with lithium aluminium hydride allowed isolation of 65 in 69% yield. Sulfamoylation using Method 2 gave 66 in 52% yield, which was deprotected selectively in the presence of the benzyl ether under mild palladium-catalysed flow hydrogenation conditions, to give 67 which was sulfated to 68.

**Biological Data**

Inhibition of Sulf-2, and counter-screening against aryl sulfatases A (ARSA) and B (ARSB) was assessed. Compounds were assayed for their ability to inhibit the desulfation of 4-methylumbelliferyl sulfate (4-MUS) to the fluorescent phenol, 4-methylumbelliferone (4-MU), at a single concentration of 1 mM. In this assay format, lead monosaccharide sulfamate 1 exhibited less than 10% inhibition of Sulf-2 activity, and also demonstrated no inhibition of ARSA or ARSB. The measured Sulf-2 inhibition of 1 was in contrast to the reported literature value (IC₅₀ = 130 µM), which may reflect differences in the assay procedures. Specifically, the assay employed by Schelwies and colleagues\textsuperscript{3} involved pre-incubation of the inhibitor and Sulf-2 followed by a 10-fold dilution into the assay mixture prior to determination of the residual enzyme activity; however, the IC₅₀ cited relates to the inhibitor concentration in the undiluted sample and not in the final enzymatic reaction. In the data presented here, all values relate to inhibitor concentrations in the final enzymatic assay and as indicated at the concentration of 1 tested, 1 mM, there was no significant Sulf-2 inhibition. All analogues prepared also displayed poor inhibition of Sulf-2.

Only two compounds exhibited significant inhibition of ARSA. The β-anomer of 1 inhibited 70% of ARSA activity at 1 mM, and also inhibited ARSB to a similar extent (67% inh @ 1 mM). The unsubstituted 2-amino derivative of 1 was selective for ARSA (86% inh @ 1 mM) over ARSB (3% inh @ 1 mM). The N-Cbz derivative of 1 exhibited some degree of selectivity for inhibition of ARSB (44% inh @ 1 mM) with no inhibition of ARSA at this concentration.

**Conclusions**

A short synthesis of the purported inhibitor 1 of Sulf-1 and Sulf-2 has been developed. Optimised low temperature conditions
were developed with a model substrate and applied to a monosaccharide template, resulting in the first regioselective sulfamoylation of a carbohydrate. The developed route allows access to 1 in five steps and 17% overall yield compared to 9 steps and 9% yield for the previously published procedure. A range of analogues has been prepared using the regioselective sulfamate formation methodology, exploring diversification at the 1, 2, 3, and 4-positions of the glucosamine template. Compound 1, and all derivatives prepared were found to have minimal inhibition of Sulf-2, in contrast to claims in ref. 5.

Table 1: Sulfatase inhibition data

| Cmpd | Sulf-2 | ARSA | ARSB | R1 | R2 | R3 | R4 |
|-------|--------|------|------|----|----|----|----|
| 1     | 0      | 0    | 0    | α-OMe | NH2SO4Na | OH | OH |
| 26    | 0      | 0    | 32   | NH2SO4H4 | OH | OH |
| 20    | 70     | 67   | β-OMe | NH2SO4Na | OH | OH |
| 37    | 0      | 0    | 0    | α-(OCH2)2OH | NH2SO4Na | OH | OH |
| 49    | 0      | 0    | 0    | α-(OCH2)OH | NH2SO4H4 | OH | OH |
| 45    | 0      | 0    | 0    | α-CH2CO2H | NH2SO4Na | OH | OH |
| 51 n.t. | 40  | 77   | 0    | α-(OCH2)2OBn | NH2SO4H4 | OH | OH |
| 30    | 0      | 0    | 19   | α-OPr | NH2SO4H4 | OH | OH |
| 34    | 0      | 0    | 0    | α-OPr | NH2SO4H4 | OH | OH |
| 10    | 0      | 0    | 12   | α-OMe | NH2SO4Me | OH | OH |
| 11 n.t. | 25  | 55   | 0    | α-OMe | NH2SO4CF3 | OH | OH |
| 16    | 0      | 0    | 33   | α-OMe | NH2CO(CH2)2CO2H | OH | OH |
| 6     | 0      | 0    | 44   | α-OMe | NH2CO2H | OH | OH |
| 5     | 0      | 86   | 3    | α-OMe | NH2 | OH | OH |
| 13    | 7      | 0    | 11   | α-OMe | OH | OH | OH |
| 15    | 0      | 0    | 14   | α-OMe | OH | OH | OH |
| 57    | 0      | 0    | 12   | α-OMe | NH2SO4Na | H | H |
| 63    | 0      | 0    | 21   | α-OMe | NH2SO4Na | OH | H |
| 68    | 0      | 0    | 0    | α-OMe | NH2SO4Na | OH | OBn |

*% inhibition at 1 mM; n.t. = not tested

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