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Note

NIS/H_2SO_4–Silica: a mild and efficient reagent system for the hydrolysis of thioglycosides☆

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Dedicated to Professor David A. Russell, University of East Anglia, Norwich, UK

Abstract—Chemoselective hydrolysis of a variety of thioglycosides in the presence of a wide range of protecting groups has been achieved by using *N*-iodosuccinimide and H_2SO_4 immobilized on silica in good to excellent yields.

Keywords: Thioglycoside; Hydrolysis; H_2SO_4–Silica

Thioglycosides are perhaps the most widely used building blocks in synthetic carbohydrate chemistry owing to their stability under various reaction conditions and the ease of preparation.[1–3] Compatibility of thioglycosides with many protecting groups allows the protecting group manipulations that are required during oligosaccharide synthesis.[3,4] Hence they are often used as glycosyl donors for the synthesis of oligosaccharides and glycoconjugates.[5] Furthermore, they can be used in chemoselective glycosylation strategies due to their inertness towards activating agents other than those targeting anomeric thio functionality.[6]

Apart from the obvious requirement of stability towards the reaction conditions employed, it is desirable that the anomeric protecting group be removed to afford the respective hemiacetal or that it can be transformed into other glycosyl donors for further glycosylation. Suitably protected hemiacetals are also useful substrates for Wittig or Horner–Emmons reactions in the synthesis of enantiomerically pure natural products. Therefore, hydrolysis of thioglycosides to the corresponding hemiacetals has become an important requirement in synthetic carbohydrate chemistry.

Considering the excellent glycosylation properties of thioglycosides under mild conditions, one would anticipate that thioglycosides should be easily hydrolysable by using standard thioglycoside activation procedure in the presence of H_2O as acceptor. Unfortunately this conversion is not so trivial. Numerous procedures have been reported in the literature for the hydrolysis of thioglycosides including thiophilic heavy metal salts, NBS or NIS in wet acetone,[7–9] $AgNO_3$ in wet acetone,[10,11] NBS in combination with aqueous $NaHCO_3$ or aqueous $CaCO_3$ in THF,[5] Bu_4NIO_4 and triflic acid,[12] Bu_4NIO_4 with $TrB(C_6H_5)_4$,[12] $Bu_4NIO_4/HClO_4$,[12] NBS/HCl,[13] $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$–$H_2O_2$ with $HClO_4/NH_4Br$,[14] V_2O_5–H_2O_2/NH_4Br,[15] NIS/TfOH,[16] Chloramin-T[17] and, very recently, NIS/TFA.[18] Despite their potential use under specific reaction conditions, many of these methods suffer from use of toxic materials, harsh reaction conditions, low yields and incompatibility with various protecting groups. Therefore, a mild procedure for the hydrolysis of thioglycosides, compatible with a range of protecting groups, would be useful. Noting the recent reports on the use of H_2SO_4–silica in various organic reactions,[19] we felt that sulfuric acid immobilized on silica (H_2SO_4–silica) could act as a good protic acid source under mild and safer conditions than other silica-supported reagents such as $HClO_4$–silica.[20] This communication describes the successful use of H_2SO_4–silica

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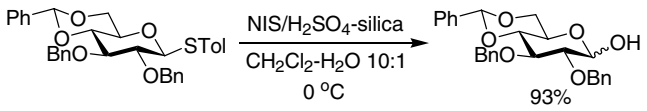


Scheme 1. NIS/H_2SO_4-promoted hydrolysis of thioglycosides.

in conjunction with NIS for the hydrolysis of thioglycosides in good to excellent yields (75–95%) without affecting a diverse range of protecting groups (Scheme 1).

Our initial experiment with *p*-tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**1**) using 1.1 equiv of NIS and H_2SO_4–silica in wet CH_2Cl_2 at 0 °C afforded the corresponding hemiacetal (**2**) in 93% yield after chromatographic purification (Table 1, entry 1). No deprotection of the acid labile benzylidene protecting group was observed on TLC, thus affirming the mildness of the reaction condition. Successful execution of this reaction prompted us to evaluate its utility on a diverse range of carbohydrate derivatives.

Table 1 represents the experimental results of the NIS/H_2SO_4–silica-mediated hydrolysis of a diverse set of thioglycosides. These results clearly show that the reaction is effective irrespective of the substitution pattern and the nature of the protecting groups in the starting thioglycoside. Most of the reactions went to completion within 30 min at 0 °C as monitored by TLC. It is worth noting that both alkyl and aryl thioglycosides are equally reactive under these conditions and the reaction is compatible with acid labile benzylidene, isopropylidene, *p*-methoxybenzyl (PMB), chloroacetyl (CA) and silyl ether groups as well as the phthaloyl protecting group. Moreover, the nature of the parent glycoside (gluco-, galacto-, manno- or rhamnopyranosyl or arabinofuranosyl or di- and trisaccharide) appears to have no influence on the outcome of the hydrolysis. A scale-up reaction using 20 mmol of compound **1** showed no considerable change in the yield, proving the applicability of the reagent system in large-scale preparations.

To justify the utility of the current protocol, the hemiacetal **4** obtained from the per-O-acetylated *p*-tolyl thioglucoside (**3**) was converted to the trichloroacetimidate derivative using trichloroacetonitrile and DBU. The per-O-acetylated glucosyltrichloroacetimidate thus obtained was glycosylated with ethyl 2,3-*O*-isopropylidene-1-thio-L-rhamnopyranoside in the presence of H_2SO_4–silica to obtain a novel disaccharide thioglycoside that can act as a glycosyl donor for further glycosylation (Scheme 2).

In conclusion, we have introduced a new reagent system for the hydrolysis of thioglycosides. A wide range of commonly used protecting groups remain unaffected under these conditions. Furthermore, we have demonstrated the synthetic utility of the hydrolyzed product in oligosaccharide synthesis. Further studies on the application of H_2SO_4–silica as a promoter for various trichloroacetimidate donors are underway in our laboratory and the results will be reported in due course.

1. Experimental

1.1. General methods

Commercial reagents were used without further purification unless otherwise stated. Analytical TLC was performed on silica gel 60-F_{254} (Merck) with detection by fluorescence and/or by charring following immersion in a 10% ethanolic solution of sulfuric acid. Flash chromatography was performed with Silica Gel 60 (Fluka). ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Unity plus spectrometer at 300 and 75 MHz, respectively, using $(CH_3)_4Si$ as internal standards.

1.2. Preparation of H_2SO_4 immobilized on silica

To a slurry of silica gel (5 g, mesh 60–120, Spectrochem, India) in diethyl ether (20 mL) was added commercially available concd H_2SO_4 (250 μL) and the solvent was evaporated under vacuum. The free flowing silica thus obtained was heated at 110 °C for 2 h and kept in a desiccator over P_2O_5 for further use.

1.3. General procedure for the hydrolysis of thioglycosides

To a stirred mixture of the thioglycoside (1 mmol) in CH_2Cl_2–H_2O (10:1, 5 mL) was added NIS (1.2 mmol) followed by H_2SO_4–silica (100 mg) at 0 °C. The mixture was allowed to stir at that temperature until TLC showed complete conversion of the starting material (Table 1). The mixture was diluted with CH_2Cl_2 and was washed successively with aq $Na_2S_2O_3$, aq $NaHCO_3$ and brine. The organic layer was collected, dried (Na_2SO_4) and evaporated. The crude residue was purified by column chromatography using an appropriate mixture of *n*-hexane and EtOAc to afford a pure hydrolyzed product.

1.4. 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (2)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **2** (417 mg, 93%) as colourless oil. ^1H NMR ($CDCl_3$) δ: 7.55–7.28 (m, 15H, aromatic protons), 5.60 (s, 1H, PhC*H*), 5.21 (d, 1H, $J_{1,2} = 3.0$ Hz, H-1), 5.00–4.73 (4d, 4H, $J = 11.4$ Hz, $2 \times CH_2Ph$), 4.06 (t, 1H, $J_{2,3} = J_{3,4} = 8.7$ Hz, H-3), 3.78 (t, 1H, $J_{3,4} = J_{4,5} = 8.7$ Hz, H-4), 3.73–3.61 (m, 3H, H-2, H-6a, H-6b),

Table 1. Results of the hydrolysis of thioglycosides using NIS–H_2SO_4–silica[a]

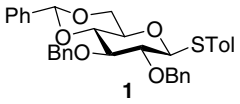
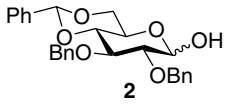
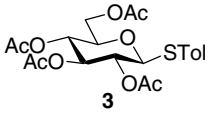
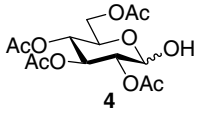
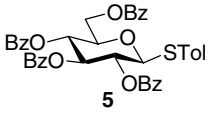
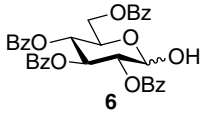
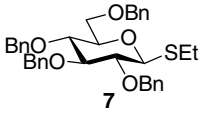
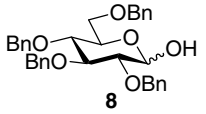
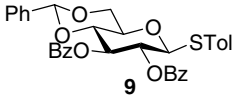
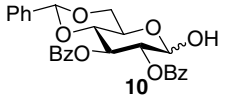
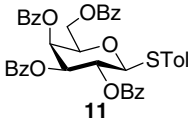
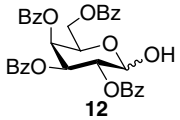
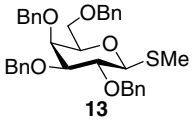
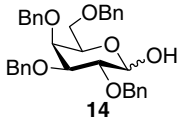
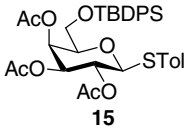
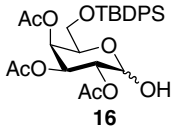
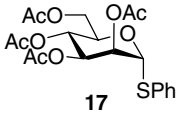
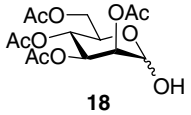
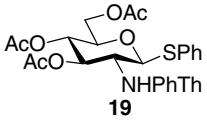
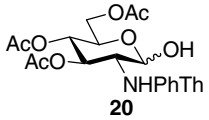
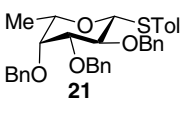
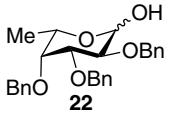
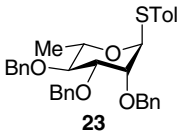
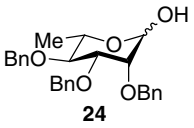
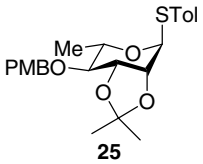
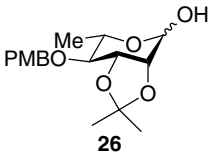
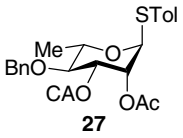
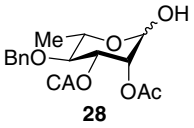
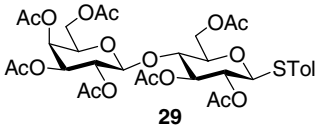
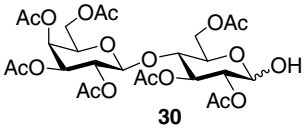
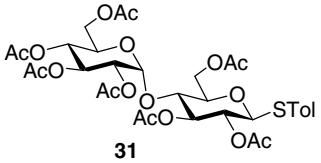
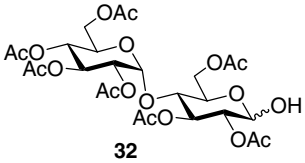
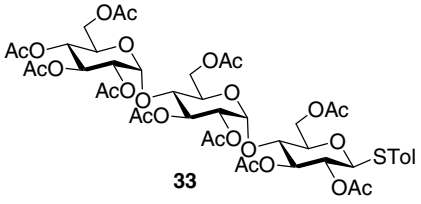
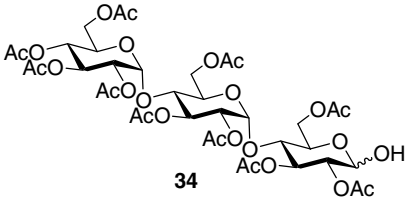
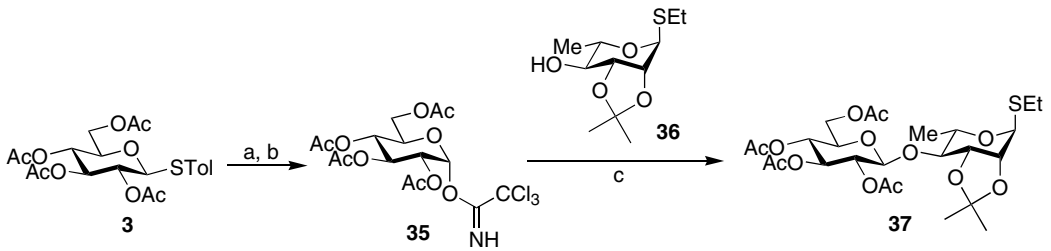
Entry	Starting material	Product	Time (min)	Yield (%)[b]	Ref. (if known)
1	 **1**	 **2**	30	93	
2	 **3**	 **4**	30	90	21
3	 **5**	 **6**	30	87	14
4	 **7**	 **8**	30	91	8
5	 **9**	 **10**	30	78	
6	 **11**	 **12**	30	89	22
7	 **13**	 **14**	30	86	15
8	 **15**	 **16**	30	75	
9	 **17**	 **18**	30	90	17
10	 **19**	 **20**	45	88	
11	 **21**	 **22**	30	95	17

Table 1 (*continued*)

Entry	Starting material	Product	Time (min)	Yield (%)[b]	Ref. (if known)
12	 **23**	 **24**	30	93	
13	 **25**	 **26**	30	90	
14	 **27**	 **28**	30	86	
15	 **29**	 **30**	45	82	17
16	 **31**	 **32**	45	85	17
17	 **33**	 **34**	45	82	23

[a] All compounds were characterized by NMR spectroscopy and mass spectrometry, data for the known compounds are in agreement with those reported in the literature.
[b] Yields reported are those obtained after chromatographic purification.



Scheme 2. Reagents and conditions: (a) NIS/H_2SO_4–silica, CH_2Cl_2–H_2O (10:1), 0 °C; (b) CCl_3CN, DBU, CH_2Cl_2; (c) H_2SO_4–silica, CH_2Cl_2, 0 °C.

3.45 (m, 1H, H-5); ^{13}C NMR δ: 138.1, 137.3, 128.9, 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 126.0 (aromatic carbons), 101.2 (*C*HPh), 92.1 (C-1), 82.9, 79.3 (*C*H_2Ph), 78.3, 75.7, 73.7, 68.6, 62.4. ESIMS: *m*/*z* calcd for $[C_{27}H_{28}O_6]NH_4^+$: 466.2230. Found: 466.2232.

1.5. 4,6-*O*-Benzylidene-2,3-di-*O*-benzoyl-D-glucopyranose (10)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **10** (372 mg, 78%) as foam. ^{1}H NMR ($CDCl_3$) δ: 8.12–7.28 (m, 15H, aromatic protons), 6.14 (t, 1H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 5.87 (t, 1H, $J_{2,3} = J_{3,4} = 9.3$ Hz, H-3), 5.70 (br s, 1H, H-1), 5.57 (s, 1H, C*H*Ph), 5.31 (dd, 1H, $J_{1,2} = 4.8$ Hz, $J_{2,3} = 9.3$ Hz, H-2), 4.39 (m, 1H, H-6a), 3.97–3.85 (m, 3H, H-4, H-5, H-6b), 3.45 (br s, 1H, O*H*); ^{13}C NMR δ: 165.7, 165.6 ($2 \times$ *C*OPh), 136.8, 136.6, 133.9, 133.4, 133.0, 128.8, 128.7, 128.6, 128.2, 128.0, 126.1, 126.0 (aromatic carbons), 101.6 (*C*HPh), 91.2 (C-1), 74.8, 72.7, 69.8, 66.8, 63.2. ESIMS: *m*/*z* calcd for $[C_{27}H_{24}O_8]NH_4^+$: 494.1815. Found: 494.1813.

1.6. 2,3,4-Tri-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-D-galactopyranose (16)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **16** (408 mg, 75%) as colourless oil. ^{1}H NMR ($CDCl_3$) δ: 7.68–7.35 (m, 10H, aromatic carbons), 6.30 (d, 1H, $J_{1,2} = 3.0$ Hz, H-1), 5.28 (dd, 1H, $J_{1,2} = 3.0$ Hz, $J_{2,3} = 7.8$ Hz, H-2), 5.25 (m, 1H, H-4), 5.20 (dd, 1H, $J = 2.7$, 7.8 Hz, H-3), 3.91 (m, 1H, H-5), 3.72 (m, 2H, H-6a, H-6b), 3.16 (br s, 1H, O*H*), 2.15, 2.08, 1.93 (3s, 9H, $3 \times$ COCH_3), 1.06 (s, 9H, C(CH_3)$_3$). ^{13}C NMR δ: 171.4, 169.3, 169.2 ($3 \times$ *C*OCH$_3$), 135.5, 133.0, 129.6, 127.6 (aromatic carbons), 91.4 (C-1), 73.5, 72.3, 69.6, 67.8, 62.4, 26.6, 20.7, 20.6, 19.8 ($3 \times$ CO*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{28}H_{36}O_9Si]NH_4^+$: 562.2472. Found: 562.2474.

1.7. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-D-glucopyranose (20)

The reaction was quenched after 45 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **20** (540 mg, 88%) as colourless oil. ^{1}H NMR ($CDCl_3$) δ: 7.87–7.71 (m, 4H, aromatic protons), 5.83 (dd, 1H, $J_{1,2} = 8.4$ Hz, $J_{2,3} = 9.3$ Hz, H-2), 5.63 (d, 1H, $J_{1,2} = 8.4$ Hz, H-1), 5.17 (m, 2H, H-3, H-4), 4.33–4.17 (m, 2H, H-6a, H-6b), 3.93 (m, 1H, H-5), 2.14, 2.05, 1.87 (3s, 9H, $3 \times$ COCH_3); ^{13}C NMR δ: 170.8, 170.1, 169.9 ($3 \times$ *C*OCH$_3$), 169.6, 167.8 (Phth C=O), 134.7, 134.4, 131.3, 131.0, 123.9, 123.6 (aromatic carbons), 92.6 (C-1), 71.9, 70.6, 67.9, 62.1, 55.9 (C-2), 20.9, 20.7, 20.4 ($3 \times$ CO*C*H$_3$). ESIMS: *m*/*z* calcd for $[C_{20}H_{21}O_{10}N]NH_4^+$: 453.1509. Found: 453.1508.

1.8. 2,3,4-Tri-*O*-benzyl-L-rhamnopyranose (24)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **24** (404 mg, 93%) as colourless oil. ^{1}H NMR ($CDCl_3$) δ: 7.44–7.28 (m, 15H, aromatic protons), 5.20 (s, 1H, H-1), 5.03 (d, 1H, $J = 11.4$ Hz, CH_2Ph), 4.85–4.69 (m, 5H, CH_2Ph), 4.00 (br d, 1H, $J_{3,4} = 7.8$ Hz, H-3), 3.87 (m, 1H, H-2), 3.72 (t, 1H, $J_{3,4} = J_{4,5} = 7.8$ Hz, H-4), 3.44 (m, 1H, H-5), 1.40 (d, 3H, $J_{5,6} = 6.3$ Hz, H-6). ^{13}C NMR δ: 138.5, 138.3, 138.2, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.4 (aromatic carbons), 92.7 (C-1), 82.9, 80.4, 75.3, 75.2, 72.7, 72.1, 68.0, 17.8 (C-6). ESIMS: *m*/*z* calcd for $[C_{27}H_{30}O_5]NH_4^+$: 452.2437. Found: 452.2436.

1.9. 2,3-*O*-Isopropylidene-4-*O*-*p*-methoxylbenzyl-L-rhamnopyranose (26)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **26** (292 mg, 90%) as foam. ^{1}H NMR ($CDCl_3$) δ: 7.29–7.27 (2d, 4H, aromatic protons), 5.33 (s, 1H, H-1), 4.82, 4.56 (2d, $J = 11.4$ Hz, CH_2–C$_6$H$_4$–OCH$_3$), 4.30 (t, 1H, $J_{3,4} = J_{4,5} = 7.8$ Hz, H-4), 4.16 (d, $J_{2,3} = 3.6$ Hz, H-2), 3.94 (dd, 1H, $J_{2,3} = 3.6$ Hz, $J_{3,4} = 7.8$ Hz, H-3), 3.80 (s, 3H, C$_6$H$_4$–OCH_3), 3.26 (dq, 1H, $J_{4,5} = 7.8$ Hz, $J_{5,6} = 6.3$ Hz, H-5), 1.52, 1.38 (2s, 6H, isopropylidene–CH_3), 1.25 (d, 1H, $J_{5,6} = 6.3$ Hz, H-6). ^{13}C NMR δ: 159.1, 130.2, 129.5, 113.6 (aromatic carbons), 109.0, 91.7 (C-1), 80.2, 78.4, 76.5, 72.5, 64.8, 55.1 (C$_6$H$_4$–O*C*H$_3$), 29.6, 27.8 (isopropylidene–*C*H$_3$), 17.9 (C-6). ESIMS: *m*/*z* calcd for $[C_{17}H_{24}O_6]NH_4^+$: 342.1917. Found: 342.1915.

1.10. 2-*O*-Acetyl-4-*O*-benzyl-3-*O*-chloroacetyl-L-rhamnopyranose (28)

The reaction was quenched after 30 min. Column chromatography using *n*-hexane–EtOAc (3:1) yielded compound **28** (320 mg, 86%) as foam. ^{1}H NMR ($CDCl_3$) δ: 7.35–7.27 (m, 5H, aromatic protons), 5.38 (dd, 1H, $J_{2,3} = 3.3$ Hz, $J_{3,4} = 8.1$ Hz, H-3), 5.24 (br d, 1H, $J_{2,3} = 3.3$ Hz, H-2), 5.10 (s, 1H, H-1), 4.66 (s, 2H, CH_2Ph), 4.08 (m, 1H, H-5), 3.87 (d, 2H, OCOCH_2Cl), 3.52 (t, 1H, $J = 8.1$ Hz, H-4), 2.10 (s, 3H, COCH_3), 1.28 (d, 3H, $J_{5,6} = 6.3$ Hz, H-6); ^{13}C NMR δ: 170.9 (*C*OCH$_3$), 166.3 (*C*OCH$_2$Cl), 137.8, 128.3, 127.7 (aromatic carbons), 91.7 (C-1), 78.6, 74.9, 73.5, 70.6, 67.4, 40.5 (CO*C*H$_2$Cl),

20.8 ($CO\underline{C}H_3$), 17.8 (C-6). ESIMS: *m/z* calcd for $[C_{17}H_{21}O_7Cl]NH_4^+$: 390.1320. Found: 390.1315.

1.11. Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (37)

p-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**1**) (1.0 g, 2.2 mmol) was converted to the corresponding hemiacetal **2** using the general procedure. To a solution of compound **2** (700 mg, 2 mmol) in CH_2Cl_2 (10 mL) was added CCl_3CN (600 μL, 6 mmol) followed by DBU (catalytic amount). After 30 min when the starting material was completely converted to a faster moving spot (TLC), the solution was diluted with CH_2Cl_2 (10 mL), and washed with cold water (2×20 mL). The organic layer was collected, dried (Na_2SO_4) and evaporated. The crude residue was purified by column chromatography using *n*-hexane–EtOAc (2:1) to afford pure per-*O*-acetylated glucopyranosyl trichloroacetimidate (**35**, 800 mg). To a mixture of the trichloroacetimidate (**35**, 800 mg, 1.6 mmol) and ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (**36**, 323 mg, 1.3 mmol) and MS 4 Å (500 mg) in dry CH_2Cl_2 (15 mL) was added H_2SO_4–silica (50 mg) at 0 °C under argon. The mixture was stirred at 0 °C for 1 h when the consumption of the starting material was found to be complete (TLC). The mixture was then filtered through Celite, the organic layer was washed with aq $NaHCO_3$ and brine, dried (Na_2SO_4) and evaporated. The crude mixture was purified by column chromatography using *n*-hexane–EtOAc (3:1) to afford the desired disaccharide (**37**, 640 mg, 85%); $[\alpha]_D^{25}$ +35; ^{1}H NMR ($CDCl_3$) δ: 5.24 (t, 1H, $J_{3',4'} = J_{4',5'} = 9.3$ Hz, H-4′), 5.05 (t, 1H, $J_{2',3'} = J_{3',4'} = 9.3$ Hz, H-3′), 4.98 (s, 1H, H-1), 4.94 (dd, 1H, $J_{1',2'} = 7.8$ Hz, $J_{2',3'} = 9.3$ Hz, H-2), 4.23–4.07 (m, 4H, H-1′, H-6′$_a$, H-6′$_b$, H-2), 4.03 (t, 1H, $J_{3,4} = J_{4,5} = 6.3$ Hz, H-4), 3.95 (dd, 1H, $J_{2,3} = 3.9$ Hz, $J_{3,4} = 6.3$ Hz, H-3), 3.70 (m, 1H, H-5′), 3.60 (dd, 1H, $J_{4,5} = 6.3$ Hz, $J_{5,6} = 6.0$ Hz, H-5), 2.55 (m, 2H, S–C$\underline{H}_2$–CH$_3$), 2.08, 2.07, 2.03, 2.01 (4s, 12H, $4 \times COC\underline{H}_3$), 1.53, 1.34 (2s, 6H, isopropylidene C$\underline{H}_3$), 1.25 (d, $J_{5,6} = 6.0$ Hz, H-6); ^{13}C NMR ($CDCl_3$) δ: 171.0, 170.6, 169.8, 169.4 ($4 \times \underline{C}OCH_3$), 109.6 ($\underline{C}(CH_3)_2$), 100.0 (C-1′), 87.9 (C-1), 79.9, 76.9, 73.7, 70.3, 69.2, 68.7, 67.4, 64.9, 63.4, 28.4, 26.8 (isopropylidene $\underline{C}H_3$), 21.1 (4 $CO\underline{C}H_3$), 18.4 (C-6), 15.0 (S–CH$_2$–$\underline{C}H_3$); HRMS: *m/z* calcd. for $[C_{25}H_{38}O_{13}S{+}NH_4]^+$: 596.2377. Found: 596.2378.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.09.005.

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