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Note

Synthesis of the tetrasaccharide α-D-Glc*p*-(1→3)-α-D-Man*p*-(1→2)-α-D-Man*p*-(1→2)-α-D-Man*p* recognized by Calreticulin/Calnexin

Emiliano Gemma,[a] Martina Lahmann[a] and Stefan Oscarson[b,*]

[a]*Department of Chemistry, Göteborg University, S-412 96 Gothenburg, Sweden*
[b]*Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden*

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Abstract—The title compound as its methyl glycoside was efficiently synthesized using a block synthesis approach. Halide-assisted glycosidations between 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl iodide and ethyl 2-*O*-acetyl-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside using triphenylphosphine oxide as promoter yielded, with complete α-selectivity, a disaccharide building block in high yield. The perbenzylated derivative of this proved to be an excellent donor affording 88% of the protected target tetrasaccharide in an NIS/AgOTf-promoted coupling to a known methyl dimannoside acceptor. Deprotection through catalytic hydrogenolysis then gave the target compound in 47% overall yield.

Keywords: Calreticulin substrates; Iodide glycosyl donors; Triphenylphosphine oxide promotion; Thioglycoside block donor

The title tetrasaccharide is the important part of an N-glycan structure recognized by the lectins Calreticulin/Calnexin. This recognition is a major event of the folding procedure of all proteins glycosylated with N-glycan chains.[1–4] Thus, interaction studies between this carbohydrate structure and the chaperone proteins are of immense biological interest. We have earlier synthesized the title tetrasaccharide as well as the glucose-containing di- and trisaccharide parts.[5] These compounds have been used in ITC-studies with Calreticulin and various mutants thereof.[5,6] Other syntheses of the tetrasaccharide have also been reported.[7,8] Furthermore, the syntheses of monodeoxy analogues of the trisaccharide, to pinpoint the importance of each hydroxyl group in the interaction, have been performed.[9] New mutants of the proteins are continuously prepared to investigate in further detail the binding and the binding site and consequently more oligosaccharides are constantly needed for various interaction experiments. Here, we present an improved synthesis of the title tetrasaccharide using a block synthesis approach, which also facilitates the synthesis of the glucose-containing trisaccharide part.

Although efficient, there were some drawbacks in our earlier published syntheses,[5] mainly the need for HPLC-purification after introduction of the glucose moiety due to incomplete stereoselectivity in these couplings. Also, the preparation of the third mannose residue was cumbersome. Since we considered the stereospecific coupling of the glucose residue to be the most problematic glycosylation in the synthesis, a new approach was designed where this linkage is formed early in the synthesis to produce a disaccharide thioglycoside donor block, which can then be used for the synthesis of both the tri- and tetrasaccharide.

Orthoesterification of unprotected α-D-mannopyranosides yields the 2,3;4,6-di-*O*-orthoester derivatives.[10,11] However, simple regioselective acetylation of the primary hydroxyl group[12] (→**2**) prior to orthoesterification allowed efficient formation of the 2,3-*O*-monoorthoester

* Corresponding author. Tel.: +46 8 16 24 80; fax: +46 8 15 49 08; e-mail: s.oscarson@organ.su.se

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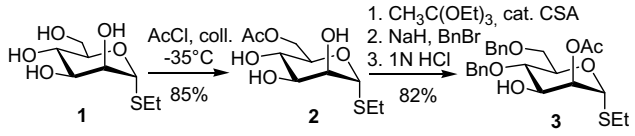
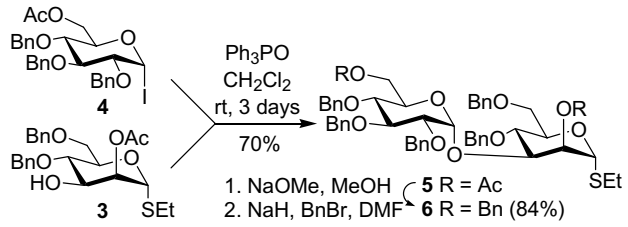


Scheme 1. Synthesis of thioglycoside acceptor.

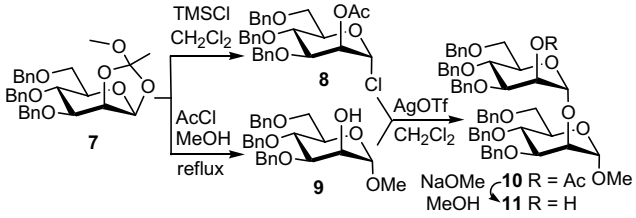
(Scheme 1). This derivative was then directly 4,6-di-*O*-benzylated and the orthoester subsequently opened to give the desired 3-OH acceptor **3**.

To obtain complete α-selectivity in the introduction of the glucose residue, a rather elaborately protected glucose donor, methyl 4,6-*O*-benzylidene-3-*O*-pivaloyl-2-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside, can be utilized as has been shown by Ito and co-workers.[13] We reasoned that halide-assisted conditions[14] should allow the use of simpler donors and also be compatible with thioglycoside acceptors. However, the standard donor (benzylated glucosyl bromide) used earlier for O-glycoside acceptors[15] did not work with the thioglycoside acceptor **3**, wherefore alternatives were tested. Iodo-sugars, easily obtained, for example, from the corresponding anomeric acetate, have recently received increased attention as donors.[16–18] When published conditions,[17] using tetrabutylammonium iodide as promoter, were tried in the coupling between acceptor **3** and iodide donor **4**, high yield was obtained in an initial attempt, but it was not possible to reproduce this first result. Similar problems have been encountered by Mukayiama and Kobashi, who advocated the use of triphenylphosphine oxide as promoter instead.[19] Also, in our coupling this afforded a high and reproducible yield of the desired α-linked disaccharide building block **5** (Scheme 2).

The 2-OH monosaccharide acceptor **9** and α-D-Man-(1→2)-α-D-Man disaccharide acceptor **11** were prepared



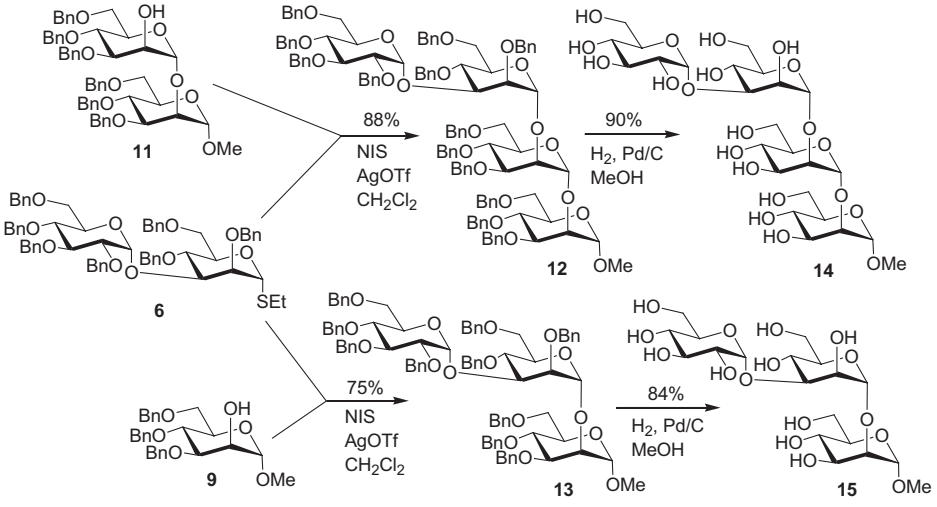
Scheme 2. Synthesis of the disaccharide donor block.



Scheme 3. Synthesis of the mono- and disaccharide acceptors.

from a common orthoester precursor according to the published procedures (Scheme 3).[20,21]

The final glycosidations were attempted to give the target structures using donor block **5** and NIS/AgOTf as promoter, but the yields were disappointing. Thus, the acetates in compound **5** were exchanged to benzyl groups to afford derivative **6** (Scheme 4). This slight change in the protecting group pattern of the donor proved most efficient. Now coupling between donor block **6** and the disaccharide acceptor **11** using NIS/AgOTf promotion yielded the tetrasaccharide **12** in 88% yield and with complete α-selectivity (Scheme 4). The coupling to monosaccharide acceptor **9** under the same conditions afforded trisaccharide **13** in 75% yield. One-step deprotection through catalytic hydrogenolysis then smoothly yielded the known target molecules **14** (90%) and **15** (86%).[5,7,8]



Scheme 4. Synthesis of target tetra- and trisaccharides.

In conclusion, an efficient synthesis of the thioglycoside disaccharide building block **6** has been performed. This derivative proved to be an efficient donor and has been used as a key intermediate in the synthesis of trisaccharide **15** and the title compound **14**, both valuable structures in interaction studies with the Calreticulin/Calnexin chaperone proteins.

1. Experimental

1.1. General

CH_2Cl_2 was distilled from calcium hydride. Organic solutions were concentrated under diminished pressure at <45 °C (bath temperature). NMR spectra were recorded at 400 MHz for ^1H and at 100 MHz for ^{13}C. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.26, δ_C (central of triplet) 77.0] or to CH_3OH [δ_H 3.35, δ_C (central of septet) 49.0] or to acetone as internal standard (D_2O). TLC was performed on a E. Merck Silica Gel 60 F254 with detection by charring with 8% H_2SO_4 acid. Silica gel (0.040–0.063 mm) was used for column chromatography.

1.2. Ethyl 6-*O*-acetyl-1-thio-α-D-mannopyranoside (2)

Ethyl 1-thio-α-D-mannopyranoside (**1**) (2.5 g, 0.011 mol) was dissolved in *sym*-collidine (25 mL) and the soln cooled to −35 °C. Acetyl chloride (1.5 mL, 0.021 mol) was then added dropwise over 30 min under vigorous stirring. After 1 h, MeOH (5 mL) was added, and the reaction was allowed to attain rt. The crude mixture was co-concentrated under diminished pressure several times with toluene. The residue was purified on a silica gel column (2:1 CH_2Cl_2–acetone) to afford **2** (2.5 g, 85%). $[\alpha]_D$ +128 (*c* 1.0, $CHCl_3$); ^1H NMR (CD_3OD): δ 1.29 (t, 3H, SCH_2CH_3), 2.04 (s, 3H, CH_3CO), 2.62 (q, 2H, SCH_2CH_3), 3.62–3.65 (m, 2H, H-3, H-4), 3.89 (dd, 1H, $J_{2,3}$ 3.0 Hz, $J_{2,1}$ 1.4 Hz, H-2), 4.08 (m, 1H, H-5), 4.23 (dd, 1H, $J_{6b,6a}$ 12.0 Hz, $J_{6b,5}$ 6.6 Hz, H-6b), 4.37 (dd, 1H, $J_{6a,6b}$ 12.0 Hz, $J_{6a,5}$ 2.0 Hz, H-6a), 5.22 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1). ^{13}C NMR (CD_3OD): δ 14.0 (SCH_2CH_3), 19.4 (CH_3CO), 24.6 (SCH_2CH_3), 63.8 (C-6), 67.7 (C-4), 71.0 (C-5), 71.8 (C-3), 72.2 (C-2), 84.9 (C-1), 171.5 (C=O).

1.3. Ethyl 2-*O*-acetyl-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (3)

Compound **2** (2.10 g, 7.9 mmol) was reacted with triethyl orthoacetate following the protocol of Pozsgay.[22] Once TLC showed complete conversion of the starting material into the 2,3-cyclic orthoester, additional DMF (10 mL) and sodium hydride (1.26 g of 60% dispersion in mineral oil, 31.0 mmol) were added at 0 °C. After additional 10 min, benzyl bromide (3 mL, 25.0 mmol) was added and the reaction mixture stirred at rt for 2 h. Ice was poured into the reaction mixture, and the aqueous phase was extracted with EtOAc. The organic phase was then left to stir for 1 h with 1 N HCl, washed with water, dried (Na_2SO_4), filtered and concentrated. The crude product was purified by silica gel chromatography (6:1 toluene–EtOAc) to give **3** (2.90 g, 82%). NMR data of the product were in agreement with the literature values.[23]

1.4. Ethyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (5)

Triphenylphosphine oxide (375 mg, 1.35 mmol) was added to a stirred mixture of glucosyl iodide **4** (prepared by reaction of 360 mg, 0.67 mmol, of the corresponding glucosyl acetate with 1.1 equiv TMSI)[24] and acceptor **3** (100 mg, 0.22 mmol) in CH_2Cl_2 (2 mL) containing 4 Å MS. The reaction mixture was stirred at rt for 3 days, then filtered through a Celite pad and concentrated. Silica gel column chromatography (toluene–EtOAc 16:1) of the residue yielded **5** (145 mg, 70%). $[\alpha]_D$ +69 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.29 (t, 3H, SCH_2CH_3), 2.06 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3CO), 2.58–2.68 (q, 2H, SCH_2CH_3), 3.46 (t, 1H, $J_{4,3} = J_{4,5}$ 9.5 Hz, H-4_{Glc}), 3.49 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{2,1}$ 3.3 Hz, H-2_{Glc}), 3.68 (dd, 1H, $J_{6b,6a}$ 10.5 Hz, $J_{6b,5}$ 2 Hz, H-$6b_{Man}$), 3.84 (dd, 1H, $J_{6a,6b}$ 10.5 Hz, $J_{6a,5}$ 4.0 Hz, H-$6a_{Man}$), 3.88–3.92 (m, 1H, H-5_{Glc}), 3.99–4.09 (m, 4H, H-3_{Man}, H-4_{Man}, H-3_{Glc}, H-$6b_{Glc}$), 4.17–4.22 (m, 1H, H-5_{Man}), 4.33 (dd, 1H, $J_{6a,6b}$ 12.1 Hz, $J_{6a,5}$ 4.4 Hz, H-$6a_{Glc}$), 4.45–4.68 (m, 6H, CH_2Ph), 4.82–4.89 (dd, 2H, CH_2Ph), 4.94 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1_{Glc}), 4.99 (d, 1H, CH_2Ph), 5.17 (d, 1H, CH_2Ph), 5.22 (br s, 1H, H-2_{Man}), 5.39 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1_{Man}), 7.15–7.40 (m, 25H, aromatic). ^{13}C NMR ($CDCl_3$): δ 15.1 (SCH_2CH_3), 20.9 (CH_3CO), 21.4 (CH_3CO), 25.8 (SCH_2CH_3), 63.0, 68.9, 69.9, 72.0, 73.2, 73.5, 74.1, 74.2, 75.1, 75.2, 75.8, 77.3, 79.7, 80.5, 81.6 (C-2-6, 2′-6′, CH_2Ph), 81.9 (C-1), 99.7 (C-1′), 127.0–129.0, 137.9, 138.0, 138.2, 138.6, 138.8 (C-aromatic), 170.4, 170.9 (C=O). Anal. Calcd for $C_{53}H_{60}O_{12}S$: C, 69.11; H, 6.57. Found: C, 69.15; H, 6.64.

1.5. Ethyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (6)

To a solution of **5** (565 mg, 0.61 mmol) in MeOH (10 mL), a catalytic amount of 1 M sodium methoxide in MeOH was added. The reaction mixture was stirred for 1 day, then neutralized with Dowex H^+ ion exchange resin, filtered and evaporated under diminished pressure. The crude deacetylated product was dissolved in DMF

(15 mL) and sodium hydride (96 mg, 2.40 mmol) was added at 0 °C. After 15 min, benzyl bromide (1.80 mmol, 214 μL) was added and after another 3 h ice-cold water was poured into the reaction mixture. The aqueous phase was extracted with toluene and the organic phase washed twice with water before being dried and concentrated. After silica gel column chromatography (30:1 toluene–EtOAc), disaccharide **6** was isolated in 84% yield (500 mg). $[\alpha]_D$ +79 (*c* 0.45, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.28 (t, 3H, SCH_2CH_3), 2.58–2.68 (q, 2H, SCH_2CH_3), 3.49–3.57 (m, 3H, H-2_{Glc}, H-5_{Glc}, H-3_{Man}), 3.62 (t, 1H, $J_{4,3} = J_{4,5}$ 9.5 Hz, H-4_{Glc}), 3.70 (dd, 1H, $J_{6b,6a}$ 11.0 Hz, $J_{6b,5}$ 2.0 Hz, H-$6b_{Man}$), 3.80 (dd, 1H, $J_{6a,6b}$ 11.0 Hz, $J_{6a,5}$ 3.7 Hz, H-$6a_{Man}$), 4.01–4.10 (m, 5H, H-4_{Man}, H-3_{Glc}, H-2_{Man}, H-$6a_{Glc}$, H-$6b_{Glc}$), 4.17–4.21 (m, 1H, H-5_{Man}), 4.40–4.95 (m, 13H, CH_2Ph), 5.09 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1_{Glc}), 5.12 (d, 1H, CH_2Ph), 5.45 (s, 1H, H-1_{Man}), 7.1–7.3 (m, 35H, aromatic). ^{13}C NMR ($CDCl_3$): δ 15.1 (SCH_2CH_3), 25.5 (SCH_2CH_3), 68.7, 69.3, 71.2, 72.2, 73.0, 73.3, 73.6, 74.7, 74.8, 75.7, 76.4, 77.9, 79.3, 79.8, 81.0 (C-2-6, 2′-6′, CH_2Ph), 81.9 (C-1), 99.4 (C-1′), 127.0–129.0, 137.9, 138.2, 138.5, 138.6, 138.8, 139.0 (C-aromatic). Anal. Calcd for $C_{63}H_{68}O_{10}S$: C, 74.38; H, 6.74. Found: C, 74.31; H, 6.63.

1.6. Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (12)

To a suspension of **11**[21] (159 mg, 0.18 mmol) and **6** (150 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) containing 4 Å MS were added NIS (46 mg, 0.21 mmol) and a catalytic amount of AgOTf (2 mg, 0.01 mmol). After 0.5 h, the reaction mixture was neutralized with Et_3N and filtered through Celite. Silica gel chromatography of the crude material (30:1→20:1 toluene–EtOAc) furnished product **12** (240 mg, 88%), whose NMR-spectra were in agreement with the published data.[7]

1.7. Methyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (13)

Donor **6** (125 mg, 0.12 mmol) and acceptor **9**[20] (86 mg, 0.18 mmol) were dissolved in 5 mL absolute CH_2Cl_2 and stirred with 4 Å MS for 15 min. NIS (41 mg, 0.18 mmol) and a catalytic amount of AgOTf (2 mg, 0.01 mmol) were subsequently added and the reaction mixture was stirred for 1 h. Neutralization of the reaction mixture with Et_3N and removal of molecular sieves through Celite followed. The mixture was then concentrated and purified on a silica gel column (20:1 toluene–EtOAc), to afford **13** (130 mg, 75%). $[\alpha]_D$ +24 (*c* 0.36, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 3.27 (s, 3H, OCH_3), 3.38–3.56 (m, 3H), 3.68–3.86 (m, 7H), 3.91–4.08 (m, 6H), 4.12–4.19 (m, 2H), 4.26–4.69 (m, 15H), 4.76–4.94 (m, 5H), 5.06 (br s, 1H, H-1″), 5.14 (br s, 1H, H-1), 5.27 (d, 1H, $J_{1,2'}$ 2.2 Hz, H-1′), 7.1–7.4 (m, 50H, aromatic). ^{13}C NMR ($CDCl_3$): δ 54.8 (OCH_3), 68,4, 69.4, 69.8, 70.9, 71.6, 72.2, 73.3, 73.4, 73.5, 74.2, 74.9, 75.1, 75.2, 75.3, 77.6, 77.7, 79.9, 80.2, 81.9 (C-2-6, 2′-6′, 2″-6″, CH_2Ph), 100.0, 100.1, 100.2 (C-1, 1′, 1″), 127.0–129.0, 137.9, 138.3, 138.4, 138.4, 138.5, 138.7, 138.8, 138.9 (C-aromatic). Anal. Calcd for $C_{89}H_{94}O_{16}$: C, 75.29; H, 6.67. Found: C, 75.34; H, 6.61.

1.8. Methyl α-D-glucopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (14)

Compound **12** (185 mg, 0.10 mmol) was dissolved in a mixture of EtOAc–MeOH (1:5, 10 mL). 1 N Hydrochloric acid (200 μL) and a catalytic amount of Pd/C were added and the reaction mixture was stirred under an H_2 atmosphere (1 atm) for 2 h. The mixture was filtered through Celite and the solvent co-evaporated with toluene. The residue was purified on a Bio-Gel P2 column eluted with 1% butanol in water, followed by a short reversed phase column (eluted with water) to give **14** (61 mg, 90%), with NMR data in agreement with the published values.[7]

1.9. Methyl α-D-glucopyranosyl-(1→3)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (15)

Compound **13** (125 mg, 0.09 mmol) was deprotected as described above for compound **12** to give **15**[5,25] (40 mg, 86%). $[\alpha]_D$ +49 (*c* 1.0, H_2O); ^1H NMR (D_2O): δ 3.40 (s, 3H, OCH_3), 3.41 (m, 1H), 3.54–3.96 (m, 16H), 4.24 (m, 1H), 4.99 (br s, 1H), 5.02 (br s, 1H), 5.25 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1_{Glc}). ^{13}C NMR (D_2O): δ 55.0 (OCH_3), 60.6, 60.8, 60.9, 65.5, 67.1, 69.8, 69.9, 70.4, 71.9, 72.5, 72.7, 73.0, 73.5, 78.5, 78.7 (C-2-6, 2′-6′, 2″-6″), 99.5, 100.6, 102.3 (C-1, 1′, 1″).

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