Synthesis and characterisation of a partially methylated dodecyl thiomaltotrioside derivative as a precursor of cyclodextrin analogue

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Abstract. Due to the enormous roles of cyclodextrin combining with small organic molecules, more recent interests study about the manipulation of cyclodextrin structure giving better performance for any kinds of field but they presented long synthesis steps as producing the precursors. This study points out the synthesis of precursor of β-cyclodextrin analogues with maltotriose as raw materials giving the short synthesis steps. The product structures were analysed by Fourier Transform Infrared (FTIR) Spectroscopy, and characterised by ¹H-, ¹³C-NMR, COSY NMR, and ESI Mass Spectroscopy. The result showed that O-acetylation reaction produced maltotriose derivative 1 (95%), thioglycosidation reaction produced maltotriose derivative 2 (54%), de-acetylation reaction produced maltotriose derivative 3 (97%), O-benzylidation reaction produced a mixture of maltotriose derivatives 4, O-methylation reaction produced maltotriose derivative 5 (46%) and de-benzylidation reaction produced maltotriose derivative 6 (85%).

1. Introduction

An α(1→4) glycosidic linkage of cyclodextrin (CDs) consist of six or more D(+)-glucose and form cyclic and chiral macromolecules [1]. Therefore, the classification of CDs are subjected to the amount of glucose units, namely α-CDs containing six units of glucose, β-CDs containing seven units of glucose and γ-CDs containing eight units of glucose. Recently, CDs have been regio or stereoselectively modified such as the applications in drug delivery system [2], chemical separations [3], adsorbents [4], food processing [5] and pharmaceutical excipients [6].

Based on unique properties of CDs, the structure of CDs has many possibilities of modifications, not only for academic purposes but also industrial purposes. The most important of modifying CDs is the specific position in macrocyclic CDs where it will be attacked by other functional groups. Moreover, Reactivity of the primary hydroxyl groups on one side of CDs and the secondary hydroxyl groups on the other side have allowed the purposive substitution in four, three, two or one positions in the macrocycle [7]. The placement of different functional groups will limit or maximise the potential of CDs as functional materials.
Wakao [8] proposed synthesis of a CD analogue by using intramolecular glycosylation. The glycosylation in their synthesis gives long synthetic sequences, i.e. twenty two steps. In the other side, Sakairi and Kazuhara [9] prepared a fully methylated (2-deoxy-2-iodo) cyclohexasaccharides by one-pot reaction method. The one-pot reaction method proposed by Sakairi and Kazuhara [9] used maltotriose as the starting material. This method has short synthetic sequences than the previous synthesis of CDs but the yield is low.

Maltotriose is obtained in good yield by enzymatic hydrolysis of polysaccharide [10]. Based on the Sakairi and Kazuhara’s [9] method, the use of trisaccharide such as maltotriose as the starting material of CD analogue synthesis can be an alternative to give the short synthetic sequences. However, the one-pot synthesis gives the low yield. Bodine et al. [7] proposed the CD analogues synthesis by using alkene and an azide from the molecule itself to produce a triazole through [3 + 2] Huisgen cyclisation. This reaction is chemoselective, high yielding and the precursors are otherwise stable to many reaction conditions.

Bodine et al. [7] successfully synthesised a β-CD analogue. The β-CD has the abilities to produce an inclusion complex with various kind of compounds in solid, liquid, or gas phase [11] and through some inter- and intramolecular interactions such as hydrogen bonding, electrostatic affinity, Van der Waals force, hydrophobic and dipole-dipole interaction [4]. The functionalised β-CD can be applied as drug delivery system, modifiers, reactors, molecular machines, enzyme mimics (catalyst), etc.

Due to the characteristics of β-CD, the synthesis of CD analogues from already-functionalized carbohydrates such our target compound, \( O-(4,6\text{-di-hydroxy-2,3-di-O-methyl-\( \alpha \)-D-glucopyranosyl})-(1\rightarrow4)O-(2,3,6-tri-O-methyl-\( \alpha \)-D-glucopyranosyl)-(1\rightarrow4)O-(2,3,6-tri-O-methyl-1-dodecyl-thio-\( \beta \)-D-glycopyranoside) \) 6 serves a profitable method. So, the precursor 6 will give a CD analogue with short synthetic sequences, high yielding, and chemoselective compound by an alkyne and an azide to form a triazole through [3 + 2] Huisgen cyclisation.

2. Experimental

2.1. Materials

Materials used in this study were maltotriose 95% (C\(_{18}\)H\(_{32}\)O\(_{16}\)), ethyl acetate (EtOAc), toluene (PhCH\(_3\)), chloroform (CHCl\(_3\)), butanol (C\(_2\)H\(_5\)O), sodium bicarbonate (NaHCO\(_3\)), brine (NaCl), water, magnesium sulfate (MgSO\(_4\)), sodium sulfate (Na\(_2\)SO\(_4\)), acetic anhydride (Ac\(_2\)O), sodium acetate (NaOAc), ice, cool water, 1-dodecanethiol 98.5% (C\(_{12}\)H\(_{25}\)SH), boron trifluoride diethyl etherate (BF\(_3\)OEt\(_2\)), ethylene dichloride ((CH\(_2\))\(_2\)Cl), methanol (CH\(_3\)OH), sodium methoxide (NaOMe) in methanol 28%, amberlite IR 120 (H\(^+\)) resin, champhor sulfonic acid, anhydrous DMF (dimethyl formamide), tetrahydrofuran (THF), benzoic acid dimethyl acetal (BDA), triethylamine, sodium hydride (NaH), ammonia (NH\(_3\)), dimethyl sulfate (CH\(_3\))\(_2\)SO\(_4\), acetic acid (CH\(_3\)COOH), silica, silica glass, deuterated chloroform (CDCl\(_3\)), methanol (CD\(_3\)OD), benzene (C\(_6\)H\(_6\)) with tetra methyl silane (TMS) as the internal standard, and water (D\(_2\)O). All materials were produced by E. Merck.

2.2. Instrumentation

Equipment used in this research were set of flasks, Erlenmeyers and tubes, heater stirrer, magnetic stirrer, manual column chromatography equipment, automatic column chromatography machine, electronic scale, set of pippette volume, rotary evaporator, vacuum filter, Büchner filter, funnel, injector 1 mL, and rotary evaporator.

Analysis of structure’s equipments were Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu 4100 type A), \(^1\)H- 300 MHz NMR (Bruker Avance300), \(^1\)H- 400 MHz NMR (JEOL JNM-EX400), \(^13\)C- 100 MHz NMR (Bruker Avance300), and COSY DEPT 400 MHz NMR (JEOL JNM-EX400), and Electron Spray Ionisation Mass Spectroscopy Thermo Scientific Exactive.
2.3. Procedures

2.3.1. Synthesis of undeca-O-acetyl-maltotriose (1).
Synthesis of maltotriose derivative 1 is based on Sakairi and Kazuhara method [9]. Anhydrous sodium acetate (10 mL) and acetic anhydride (0.59 g, 5.77 mmol) were stirred in a fitted 100 mL of round bottomed flask and gently heated to 120°C. About 110°C – 119°C, maltotriose (0.62 g, 1.23 mmol) was poured to the solution. During keeping the temperature in 120°C, maltotriose should be added in small quantity but continuously to obviate excessive forming of unreacted sugar on the bottom. After all the sugar has been added, the solution is no longer exothermic and wait about an hour. The reaction was confirmed by Thin Layer Chromatography (TLC) with toluene : ethyl acetate (1:2) as eluent. If the TLC indicated the product, then put ice and ice water to change acetic anhydride to become acetic acid and occasionally scratching and stirring to encourage crystallisation and to prevent the formation of a block of solid respectively. Then, it was extracted with ethyl acetate and water. The organic phase was dissolved in ethyl acetate. Then, pH was adjusted to be neutral with sodium bicarbonate and added brine to remove water remaining. The product was dried with magnesium sulfate and filtered with Buchner Filter equipment. It was concentrated by rotary evaporator Buchii and vacuum filter. It was white solid. It was confirmed by FTIR and $^1$H NMR with CD$_3$OD as solvent.

2.3.2. Synthesis of O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-1-dodecyl-thio-β-D-glycopyranoside) (2).
1-Dodecanethiol (0.23 g, 1.16 mmol) was added to acetylated maltotriose 1 (1.12 g, 1.16 mmol) in 3 mL of ethylene dichloride. The mixture was stirred in temperature 0°C then boron trifluoride diethyl etherate 0.13 mL was poured. The reaction was kept in 0°C for about 15 minutes and changed the temperature to room temperature. The reaction was controlled by TLC. If the product has formed, the reaction was stopped by adding the number of chloroform. The crude was extracted with water and chloroform. The organic phase was dissolved in chloroform. Then, pH was adjusted to be neutral with sodium bicarbonate and added brine to remove water remaining. The extract was dried with magnesium sulfate then filtered with Buchner. The solvent removing was performed by evaporator Buchii. The product was yellow oil-like. The residue was subjected to column chromatography on silica gel using toluene : ethyl acetate (5:1) to toluene : ethyl acetate (1:2). The product was concentrated by evaporator Buchii and vacuum filter to give the pure product. It was confirmed by FTIR and $^1$H NMR with CD$_3$OD as solvent.

2.3.3. Synthesis of O-(2,3,4,6-tetra-hydroxy-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-hydroxy-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-hydroxy-1-dodecyl-thio-β-D-glycopyranoside) (3).
Maltotriose derivative 2 (13.97 g, 12.60 mmol) was dissolved in 50 mL of methanol [12,13]. Sodium methoxide 1 mL in methanol 28% was added to the solution. The mixture was stirred in room temperature. The reaction was checked by TLC (butanol:water, 9:1). The product was formed about three hours. The mixture was neutralized by adding the Amberlite IR 120 (H⁺) resin and stirred for about ten minutes. Then, the resin was filtered and concentrated the filtrate by evaporator and vacuum filter to afford the de-acetylated product as yellow oil-like. It was confirmed by FTIR and $^1$H NMR with CD$_3$OD as the solvent.

2.3.4. Synthesis of O-(2,3-di-hydroxy-4,6-di-O-benzyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-hydroxy-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-hydroxy-1-dodecyl-thio-β-D-glycopyranoside) (4).
Camphor sulfonic acid (0.30 g, 1.31 mmol) and benzaldehyde dimethyl acetal (0.20 mL) were added to the maltotriose derivative 3 (8.41 g, 12.22 mmol) in 50 mL of anhydrous DMF. The reaction mixture was performed in rotary evaporator Buchii at pressure 20 mmHg and the temperature 45 – 50°C. When TLC analysis (butanol:water, 9:1) indicated the reaction completed, triethylamine was added and concentrated the solution in evaporator Buchii employing toluene to remove residual DMF [14]. The product was yellow oil-like. It was confirmed by FTIR and $^1$H NMR with CD$_3$OD as solvent.
2.3.5. **Synthesis of O-(2,3-di-O-methyl-4,6-di-O-benzyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-methyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-methyl-1-dodecyl-thio-β-D-glycopyranoside)** (5). Maltotriose derivative 4 was dissolved in 100 mL of DMF and 60 mL of THF. The mixture was stirred at 0°C and added portion by portion 10.4 g, 0.25 mmol of sodium hydride 60%. It was stirred overnight at room temperature to give solid material. It was added portion by portion 16.41 g, 130 mmol of dimethyl sulfate and saponification of glycosidic bond was shown at 1026 and 1317 cm$^{-1}$. The product was quenched with methanol and aqueous ammonia. Then, it was extracted with chloroform and water. The organic phase was dissolved in the chloroform. Then, pH was adjusted to be neutral with sodium bicarbonate and added brine to remove water remaining. Then, the product was dried with magnesium sulfate. It was concentrated with Buchner filter and evaporator Buchii. The TLC showed three spots. Then, the column chromatography using toluene : ethyl acetate (1:2) to toluene : ethyl acetate (3:1) was performed. The product was confirmed by FTIR, $^1$H-, $^{13}$C-, COSY DEPT 135$^o$ NMR with acetone-D6-D2O as the solvent, and ESI Mass Spectroscopy.

2.3.6. **Synthesis of O-(4,6-di-hydroxy-2,3-di-O-methyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-methyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-methyl-1-dodecyl-thio-β-D-glycopyranoside)** (6). Maltotriose derivative 5 (730 mg, 0.82 mmol) was dissolved in acetic acid (2 mL) and water (0.5 mL) was added. The solution was stirred at 100°C for an hour, and evaporated to syrup. The residue was subjected to column chromatography using toluene : ethyl acetate (1:2). The product was confirmed by FTIR, $^1$H-, COSY DEPT 135$^o$ NMR with acetone-D6-D2O as the solvent, and ESI Mass Spectroscopy.

3. Results and Discussion

3.1. **Synthesis of maltotriose derivative 1**
Maltotriose derivative 1 was synthesised with acetic anhydride and anhydrous sodium acetate. The product was white solid and the yield was 95%. It was confirmed by using infrared spectra and $^1$H NMR data [15, 16]. FT-IR spectra data showed the following bands in cm$^{-1}$: 1743 (C=O stretching), C-O-C stretching of sugar rings was shown in 1211 and C-O stretching of glycosidic bond was shown at 1026. $^1$H NMR (300 MHz, CDCl$_3$), δ (ppm) were 2.00, 2.03, 2.04, 2.05, 2.06, 2.11, 2.16, 2.17 and 2.24 ppm (9s, each 3H, acetyl).

3.2. **Synthesis of maltotriose derivative 2**
Maltotriose derivative 2 was synthesised from maltotriose derivative 1 and 1-dodecanthiol [17,18]. The product was yellow syrup and the yield was 54%. FT-IR spectra data showed the following bands in cm$^{-1}$: 602 (C=S stretching), 3025-2855 (C-H stretching), 1747 (C=O stretching), C-O-C of sugar rings was shown at 1241 cm$^{-1}$ and C-O of glycosidic bond was shown at 1037 cm$^{-1}$. The $^1$H NMR (300 MHz, CDCl$_3$), δ (ppm) were 2.77-2.60 (m, 2H, SCH$_2$), 2.36, 2.17, 2.16, 2.10, 2.06, 2.03, 2.00, and 1.99 (8s, each 3H, acetyl), 1.64-1.56 (m, 20H, SCH$_2$(CH$_2$)$_{10}$CH$_3$) and 0.86 (t, 3H, J 13.18 Hz, CH$_2$CH$_3$).

3.3. **Synthesis of maltotriose derivative 3**
Maltotriose derivative 3 was synthesised from maltotriose derivative 2 and sodium metoxide in methanol 28% [19]. The yield was 97%. FT-IR spectra data showed the following bands in cm$^{-1}$: 3000-3600 (O-H stretching), 2925, 2360, and 2341 (C-H stretching), C-O-C of sugar units was shown at 1026 and C-O of glycosidic bond was shown at 669. The $^1$H NMR (300 MHz, CD$_3$OD), δ (ppm) were 3.31 and 1.89 (OH), 2.78-2.64 (m, 2H, SCH$_2$), 1.65-1.29 (m, 20H, SCH$_2$(CH$_2$)$_{10}$CH$_3$) and 0.88 (t, 3H, J 13.11 Hz, CH$_2$CH$_3$).
3.4. Synthesis of maltotriose derivative 4
Maltotriose derivative 4 was synthesised from maltotriose derivative 3 and benzaldehyde dimethyl acetal. FT-IR spectra data showed the following bands in cm\(^{-1}\): 1150 and 1055 (C=C stretching), 2924 and 2853 (C-H aromatic), 2360 and 2341 (C-H stretching). C-O-C stretching of sugar units was shown at 1055 and 1028 and the peak of C-O stretching of glycosidic bond was shown at 698. The \(^1\)H NMR (300 MHz, CD\(_2\)OD), \(\delta\) (ppm) were 5.57 (s, PhCH, 1H) and 7.51–7.3 (m, Ar-H, 10H).

3.5. Synthesis of maltotriose derivative 5
Maltotriose derivative 5 was synthesised from maltotriose derivative 4 and dimethyl sulfate [20]. The product was yellow syrup-like and yield 46%. FT-IR spectra data showed the following bands in cm\(^{-1}\): 2854 and 2924 cm\(^{-1}\) (C-H stretching), C-O-C stretching of sugar units was shown at 1026 – 1088, 698 cm\(^{-1}\)(C-S stretching) and the peak of C-O stretching of glycosidic bond was shown at 656 cm\(^{-1}\). The \(^1\)H NMR (400 MHz, acetone-D\(_6\)), \(\delta\) (ppm) were 7.51 – 7.48 (m, 2H, H\(_{arom}\)), 7.40–7.36 (m, 3H, H\(_{arom}\)), 5.62 (s, 1H, PhCHO), 3.63, 3.57, 5.55, 3.53, 3.52, 3.51, 3.36, 3.32 (8s, each 3H, methyl), 2.78-2.61 (m, 2H, SCH\(_2\)), 1.69-1.17 (m, 20H, SCH\(_2\)(CH\(_3\))\(_{10}\)CH\(_3\)) and 0.86 (t, 3H, J 13.11 Hz, CH\(_2\)CH\(_3\)). \(^13\)C-NMR (101 MHz, CDC\(_1\)) \(\delta\) (ppm) were 128.64, 127.96, and 126.22 (CH\(_3\)), 101.07 (PhCHO), 59.77, 59.70, 59.50, 58.77, 58.41, 58.32, 58.01, 20.53 (OCH\(_3\)), 31.75, 29.98, 29.81, 29.50, 29.48, 29.10, 29.18, 29.06, 28.22, 22.45 (CH\(_2\) of dodecanethiol) and 13.45 (CH\(_3\) of dodecanethiol). ESI MS showed M+Na: 911.48.

3.6. Synthesis and characterisation of maltotriose derivative 6
The \(^1\)H NMR of maltotriose derivative 6 showed that there was not aromatic group attached stating the aromatic group spectra will appear in 7.5 – 7.3 ppm (B. Capron, et al., 1961). The others spectra appeared in the similar spectra of maltotriose derivative 5. The hydroxyl spectra of maltotriose derivative 6 appeared in the chemical shift 2.31 ppm as the singlet spectra.

The COSY NMR analysis was performed with acetone-D6-D\(_2\)O as the solvent. The hydroxyl signal disappeared in this analysis. This can be used to confirm which one was the signal of hydroxyl groups. Based on the Figure 2, the disappeared peaks were the singlet peaks in the chemical shift 2.84 and 2.80 ppm. It confirmed that those peaks were hydroxyl peaks.

### Table 1

| Type or Hydrogen number | Chemical shift (ppm) | J coupling constant (Hz) | Type of spectra |
|------------------------|----------------------|-------------------------|----------------|
| H-1”, H-1”             | 5.43                 | 3.53                    | dd             |
| H-1                    | 4.30                 | 4.17                    | dd             |
| H-6-H-6’, H-6”         | 3.72 - 3.67          | -                       | m              |
| H-5, H-5’,H-5”         | 3.46 – 3.35          | -                       | m              |
| O-CH\(_3\)             | 3.63, 3.57, 5.55, 3.53, 3.51, 3.59, 3.32, 3.31 | -                     | s              |
| H-4, H-4’, H-4”        | 3.11                 | 3.67, 9.77              | dd             |
| H-3, H-3’, H-3”        | 3.03                 | 3.67, 9.77              | dd             |
| H-2’, H-2”             | 2.93                 | 18.57                   | t              |
| -OH                    | 2.84, 2.80           | -                       | s              |
| SCH\(_2\)              | 2.76 – 2.61          | -                       | m              |
| H-2                    | 2.31                 | -                       | s              |
| SCH\(_2\)(CH\(_3\))\(_{10}\)CH\(_3\) | 1.69 - 1.17          | -                       | m              |
| -CH\(_2\)CH\(_3\) of dodecanethiol | 0.86 – 0.90          | -                       | t              |
Figure 1 $^1$H NMR of maltotriose derivative 6

Figure 2 The COSY NMR of maltotriose derivative 6
The ESI Mass Spectroscopy data was also confirmed the maltotriose derivative 6. The molecular weight of the maltotriose derivative 6 is 801.03 g/mole. Figure 3 showed the M+Na is 823.45.

The structure of maltotriose derivative 6 had been approved by $^1$H NMR, COSY NMR, and MS. The mechanism synthesis reaction of maltotriose derivative 6 was proposed as Figure 4. The first step of the synthesis of maltotriose derivative 6 was introducing an acetyl group into maltotriose as starting material. It gave the replacing of all of hydroxyl group into acetyl group. By replacing all of hydroxyl group into acetyl group, the C1 position of the fully acetylated product might easily attack by 1-dodecanethiol [9]. 1-Dodecanethiol might selectively protect C1 position. Therefore, other position which are acetyl could easily modified.

The next step was changing all of acetyl group to hydroxyl group. This step aims to selectively attack hydroxyl group in C”4 and C”6 position by benzaldehyde dimethyl acetal. The protection in this position proposed to protect C”4 and C”6 from methylation in the next step. After methylation, the C”4 and C”6 could be changed to hydroxyl group. So, the C’1 and C”4 could be replaced by azide and alkyne group respectively. Then, azide and alkyne group might give CD analouge by introducing triazole group as result of [3+2] Huisgen cyclisation.

The substitution nucleophilic 2 ($S_N2$-like) performed in this synthesis. The $S_N2$ reaction was followed by protonation and hydrolysis to form diol. The protonation will produce the first diol in the C-4” position and the hydrolisis will produce the second diol in the C-6” position. Due to Bodine et al. [7] proposed the CD analogues synthesis by using [3+2] Huisgen cyclisation. The maltotriose derivative 6 is potentially subjected as that cyclodextrin analogue through the triazole as connector since the hydroxyl group could be converted an alkyne by two steps and the thiol group could be changed to an azide group.
Figure 4 The reaction mechanism of maltotriose derivative 6 synthesis
4. Conclusion
Maltotriose as raw material gives a short step of synthesis of β-cyclodextrin analogues. The last step produced the yellow syrup product 84.45%.

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