Synthesis of 3-O-Glycosyl-1,2-di-O-tetradecyl-sn-glycerol†

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Ten diether-type monoglycosyl and glycobiosyl glycerolipids, including 3-O-(4-O-β-D-galactopyranosyl-β-D-glucopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol, a synthetic analogue of lactosyl ceramide, were synthesized and their stereochemistry was assigned unambiguously by 13C NMR using the values of C–H one bond couplings. Their 13C NMR were further analysed to show the diagnostic effect of glycosylation in these compounds depending on the anomeric configuration of the glycosyl residue linked to C-3'-O atom.

Significant biological functions of glycoconjugates present as membrane components have recently promoted the synthesis of model glycolipids which do not have the naturally occurring structures in the lipid portion. As part of our project on the synthetic studies on cell surface glycans, we describe stereoselective synthesis of dialkyl ether type glycosylglycerolipids such as 1, a synthetic analogue of naturally occurring lactosyl ceramide which is a precursor for the various class of more complex glycosphingolipids, such as globo-, ganglio-, and blood group-related, glycosphingolipids. Recent isolation of dialkyl ether type glycosylglycerolipid 3 from Halobacterium cutirubrum by Kates and Deroo might suggest the future isolation of dialkyl glycosylglycerolipids such as 1 from natural sources.

A key glycosyl acceptor 6† was prepared according to the method of Kates et al. The glycosylation of 1,2-di-O-tetradecyl-sn-glycerol 6 with monosaccharide donors 7, 12 and 17 was first examined in the presence of HgBr₂ and powdered molecular sieve 4A. The reaction of 6 with 2,3,4,6-tetra-O-acetyl-a-D-glucopyranosyl bromide 7 led to the isolation of the mixture of β-anomer 8 and α-anomer 10 in 18.0 and 42.1% yield, respectively. Both 8 and 10 were deacetylated quantitatively to give free glucoglycerolipid 9 and 11, respectively. Stereochemistry of 8, 9, 10 and 11 was assigned by NMR data. A signal for H-1α of 8 appeared at δ 4.44 as a doublet with J = 8 Hz, while that of 10 appeared at δ 5.07 as a doublet with J = 3 Hz. A signal for C-1α of 9 appeared at δ 103.1 with 1JCH = 159.9 Hz, while that of 11 appeared at δ 98.7 with 1JCH = 165.6 Hz in agreement with the reported observations.

The reaction of 6 with 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bromide 12 also afforded a mixture of β-anomer 13 and α-anomer 15 in 23.1 and 34.6% yield, respectively. Deacetylation of 13 and 15 gave free galactoglycerolipid 14 and 16 quantitatively. Stereochemistry of 14 and 16 was determined by 13C NMR data. A signal for C-1α of 14 appeared at δ 103.6 with 1JCH = 155.3 Hz, while that of 16 appeared at δ 99.1 with 1JCH = 167.1 Hz.

The reaction of 6 with 2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl bromide 17 led to the isolation of α-anomer 18 in 60.1% yield and no β-anomer could be isolated in this case. Deacetylation of 18 gave free mannoglycerolipid 19. α-Configuration of 19 was assigned by 13C NMR data which showed a signal for C-1α at δ 100.1 with 1JCH = 169.1 Hz.
As the reaction of 12 with benzyl 2-acetamide-3-O-allyl-6-O-benzyl-2-deoxy-\(\alpha\)-D-glucopyranoside in the presence of HgBr\(_2\) and molecular sieve 4A was reported\(^{11}\) to give a 77\% yield of the \(\beta\)-glycoside and, similarly, 7 was reported\(^{12}\) to be condensed with 1-azido-2,3,4-tri-O-acetyl-1-deoxy-\(\alpha\)-D-glucopyranose to give a 72\% yield of the \(\beta\)-anomer, the formation of the \(\alpha\)-anomers as the major products in the glycosylation of 6 with the glycosyl donors 7 and 12 under the same condition was unexpected and might be ascribed to the presence of large lipophilic groups in the molecule of glycosyl acceptor 6.

Next, glycosylation of 6 with typical disaccharide glycosyl donors 20, 25 and 29 were studied. The reaction of 6 with heptaacetyl-maltosyl bromide 20 in the presence of HgBr\(_2\) and molecular sieve 4A led to the isolation of the \(\beta\)-anomer 21 and the \(\alpha\)-anomer 23 in 64.4 and 6.4\% yields, respectively. Configurations of newly introduced anomeric centers in 21 and 23 were assigned by \(^{13}\)C NMR data: signals for two anomeric carbon atoms in 21 appeared at \(\delta\) 100.5 with \(1J_{CH} = 163.6\) Hz, for C-1a and at \(\delta\) 95.5 with \(1J_{CH} = 175.8\) Hz for C-1b, while signals for two anomeric carbons in 23 appeared at \(\delta\) 98.9 with \(1J_{CH} = 170.9\) Hz for C-1a and at \(\delta\) 95.4 with \(1J_{CH} = 175.8\) Hz for C-1b. Deacetylation of 21 and 23 afforded free maltosylglycerolipids 22 and 24, respectively. Anomeric configurations were confirmed by \(^{13}\)C NMR which revealed two signals for C-1a and C-1b at \(\delta\) 103.3 with \(1J_{CH} = 158.2\) Hz and at \(\delta\) 101.0 with \(1J_{CH} = 168.0\) Hz for 22, and two signals for C-1a and C-1b at \(\delta\) 98.6 with \(1J_{CH} = 167.0\) Hz and at \(\delta\) 100.6 with \(1J_{CH} = 167.0\) Hz for 24.
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* Chemical shifts were measured for solutions in DMSO-d₆ at 75 ~ 80° for all compounds, except that of 9 which was measured at 25°.
Glycosylation of 6 with heptaacetyl lactosyl bromide 25 under the same condition afforded a 61.5% yield of β-anomer 26 and 11.7% yield of α-anomer 27. In agreement with this assignment of stereochemistry, 13C NMR of 26 showed two signals at δ 100.8 with 1JCH = 159.9 Hz and δ 101.1 with 1JCH = 159.9 Hz for C-1α and C-1β, and that of 27 showed two signals for C-1α and C-1β at δ 99.0 with 1JCH = 170.9 Hz and at δ 101.1 with 1JCH = 161.1 Hz. Deacetylation of 26 and 27 led to the isolation of free lactosylglycerolipid 1 and its α-anomer 28, respectively. Anomeric configurations were confirmed by 13C NMR. Signals for C-1α and C-1β of 1 appeared at δ 103.0 with 1JCH = 158.2 Hz and at δ 103.7 with 1JCH = 158.2 Hz, respectively. Signals for C-1α and C-1β of 28 were observed at δ 98.7 with 1JCH = 168.0 Hz and at δ 103.7 with 1JCH = 156.3 Hz, respectively.

Finally, glycosylation of 6 with heptaacetyl cellobiosyl bromide 29 was examined under the same condition, and the β-anomer 30 was isolated in 58.6% yield. Anomeric configurations of 30 were assigned by 13C NMR which revealed the presence of signals at δ 100.8 with 1JCH = 161.1 Hz for C-1α and C-1β. Deacetylation of 30 afforded the free cellobiosylglycerolipid 31 in 95.5% yield. 13C NMR of 31 showed a signal for C-1α and C-1β at δ 103.0 with 1JCH = 157.4 Hz and confirmed two anomeric configurations as β-D.

13C NMR data (in DMSO-d6) for synthetic glycolipids were shown in Table I. Signals of these glycolipids were assigned for each carbon atoms based on the chemical shifts of carbon atoms of the corresponding free carbohydrates in DMSO-d6, which in turn were assigned by using the reported chemical shifts of carbon atoms for each free carbohydrates observed for solutions in D2O13. 13C NMR of 6 in DMSO-d6 showed signals at δ 79.0 and 61.1 which were assigned to C-2’ and C-3’, respectively. Signals at δ 69.0, 70.6, and 70.6 were tentatively assigned to C-1’, L-1 and L-1’, respectively.

From the data in Table I, following characteristic α-effect of glycosylation for the chemical shift of C-3’ of sn-glycerol moiety was observed. Upon β-D-glycosylation at C-3’-OH, the signals for C-3’ were deshielded by 7.1~7.7 ppm and appeared at δ 68.2~68.6, while upon α-D-glycosylation, the signals for C-3’ were deshielded by 5.7~5.9 ppm and appeared at δ 66.7~67.0. These observation may be useful for the assignment of the configuration at the anomeric carbon atom linked to C-3’-O. On the other hand, signals for C-2’ were shielded (β-effect) by 1.5~1.9 ppm and appeared at δ 77.1~77.5 indifferent to the configuration of the anomeric carbon atom introduced at C-3’-O.

In conclusion, ten diether type monoglycosyl and glycobiosyl glycerolipids, including the synthetic analogue 1 of factorosyl ceramide 2, were synthesized and their stereochemistry was assigned unambiguously by 13C NMR using the values of C-H one bond couplings. And their 13C NMR data were further analysed to show the diagnostic α-effect of glycosylation in these compounds depending on the anomeric configuration of the glycosyl residue linked to C-3’-O atom.

**EXPERIMENTAL**

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were determined with a Perkin-Elmer Model 141 polarimeter for solutions in CHCl3 at 25°, unless otherwise noted. IR spectra were recorded with an EPI-G2 Hitachi Spectrophotometer, as KBr disks for the crystalline samples and as neat films for the liquid samples. 1H-NMR spectra were recorded with a Varian HA-100 NMR spectrometer, using tetramethylsilane as the internal standard. 13C NMR spectra were recorded with a JNM-FX 100FT NMR spectrometer operated at 25.05 MHz. The values of δc and δh are expressed in ppm downward from the internal standard for the solutions in CDCl3 unless otherwise noted. Powdered molecular sieves 4Å employed for glycosylations was activated before use by heating in vacuo for 10~15 hr at 180~200°. Column chromatography was performed on columns of Silica Gel Merck (70~230 mesh; E. Merck, Darmstadt, Germany). Thin layer chromatography was performed on precoated plates (layer thickness, 0.25 mm; E. Merck, Darmstadt, Germany) of Silica Gel 60 F254.

3-O-Benzyl-1,2-di-O-tetradecyl-sn-glycerol 5. The mixture of 4 (19.1 g, 0.105 mol), 7) tetradecyl bromide (116.3 g,
0.42 mol, and powdered NaOH (23.6 g, 0.42 mol) in benzene (350 ml) was stirred under reflux for 20 hr with continuous azeotropic removal of water. The reaction mixture was poured into ice-water, and extracted with Et2O. Organic layer was washed with water, dried (MgSO4), and evaporated in vacuo. The residue was chromatographed over SiO2 (500 g, toluene-n-hexane, 3:2) to give 5 (47.5 g, 79.4%).

1,2-di-O-tetradecyl-sn-glycerol 6. The solution of 5 in EtOH was hydrogenolysed in the presence of 10% Pd-C to give 6 quantitatively. mp 42~43° (c=0.95), Rp 0.6 in toluene-EtOAc (3:1). Found: C, 76.89; H, 13.37. Calcd. for C31H64O3: C, 76.80; H, 13.31.

3-O-(2,3,4,6-tetra-O-acetyl-a-D-galactopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 7 and 3-O-(2,3,4,6-tetra-O-acetyl-a-D-galactopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 10. To the mixture of 6 (4.8 g, 0.01 mol), HgBr2 (3.6 g, 0.01 mmol) and molecular sieve 4A (10 g) in CH2Cl2 (50 ml) was added dropwise a solution of 7 (4.5 g, 0.011 mmol) in CH2Cl2 (20 ml) with stirring at 5~10° under argon. The mixture was further stirred for 5 hr at 15~20° and was filtered through celite bed. The filtrate was washed with aq. NaHCO3 and H2O, dried (MgSO4) and evaporated. The residual oil was chromatographed over SiO2 (500 g, n-hexane-EtOAc, 5:1) to give an oily 10 (3.43 g, 42.1%). [a]D +4.51 (1H, d, J = 8 Hz, H-1), 2.13 (3H, s, OAc), 2.05 (3H, s, OAc), 2.02 (3H, s, OAc), 1.98 (3H, s, OAc). 1.23 (48H, bs, CH2), 0.86 (6H, t, J = 6 Hz, CH3 x2). mp 43~44° (EtOH), [a]D +2.5° (c = 0.665). Rp 0.30 in hexane-EtOAc (3:1) (2.13 (3H, s, OAc), 2.03 (6H, s, OAc x2), 1.96 (3H, s, OAc), 1.23 (48H, bs, CH2), 0.86 (6H, t, J = 6 Hz, CH3 x2). [a]D +10.7° (c = 161.1 Hz, C-1). (Found: C, 66.69; H, 10.22. C45H82O12 requires: C, 66.31; H, 10.14%)

1,2-di-O-tetradecyl-sn-glycerol 8 and 3-O-(2,3,4,6-tetra-O-acetyl-a-L-Mannopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 11. The mixture of 6 (4.8 g, 0.01 mol), HgBr2 (3.6 g, 0.01 mmol) and powdered NaOH (23.6 g, 0.42 mol) in benzene (350 ml) was stirred under reflux for 20 hr with continuous azeotropic removal of water. The reaction mixture was poured into ice-water, and extracted with Et2O. Organic layer was washed with water, dried (MgSO4), and evaporated in vacuo. The residue was chromatographed over SiO2 (500 g, toluene-n-hexane, 3:2) to give 11 (47.5 g, 79.4%).

1,2-di-O-tetradecyl-sn-glycerol 13 and 3-O-(2,3,4,6-tetra-O-acetyl-a-D-galactopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 15. 6 (0.01 mol) was glycosylated with 2,3,4,6-tetra-O-acetyl-a-D-galactopyranosyl bromide 12 (0.02 mol) as described for the preparation of 8 and 10. Purification of the reaction product by SiO2 column chromatography afforded 15 (2.82 g, 34.6%), mp 42~43° (EtOH), [a]D +67.4° (c = 0.655). Rp 0.42 in hexane-EtOAc (3:1). (2.13 (3H, s, OAc), 2.05 (3H, s, OAc), 2.02 (3H, s, OAc), 1.98 (3H, s, OAc), 1.24 (48H, bs, CH2), 0.88 (6H, t, J = 6 Hz, CH3 x2). [a]D +59.8° (c = 0.567), Rp 0.30 in hexane-EtOAc (3:1), Rp 0.27 in CHCl3-MeOH (10:1). Sc (DMSO-d6, 80°): 100.1 (VCH=167.1 Hz, C-1). (Found: C, 66.69; H, 10.22. C45H82O12 requires: C, 66.31; H, 10.14%). Further elution afforded 13 (1.88 g, 23.1%), mp 43~44° (EtOH), [a]D +2.5° (c = 0.655). Rp 0.30 in hexane-EtOAc (3:1). [a]D +4.51 (1H, d, J = 8 Hz, H-1), 2.13 (3H, s, OAc), 2.03 (6H, s, OAc x2), 1.96 (3H, s, OAc), 1.23 (48H, bs, CH2), 0.86 (6H, t, J = 6 Hz, CH3 x2). [a]D +10.7° (c = 161.1 Hz, C-1). (Found: C, 66.69; H, 10.22. C45H82O12 requires: C, 66.31; H, 10.14%).

3-O-(2,3,4,6-Tetra-O-acetyl-a-D-Galactopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 14. 13 was deacetylated as described for 11 to give quantitatively, mp 129~130° (MeOH), [a]D +3.9° (c = 0.665, THF). Rp 0.22 in CHCl3-MeOH (10:1). [a]D (DMO9-d6, 80°): 103.6 (VCH=155.3 Hz, C-1). (Found: C, 66.91; H, 11.35. C37H74O8.CH3OH requires: C, 67.22; H, 11.57%).

3-O-(a-D-Galactopyranosyl-1,2-di-O-tetradecyl-sn-glycerol 16. 15 was deacetylated as described for 11 to give quantitatively, mp 108~110° (MeOH), [a]D +52.0° (c = 0.74), Rp 0.31 in CHCl3-MeOH (10:1). [a]D (DMO9-d6, 80°): 99.1 (JCH = 165.3 Hz, C-1). (Found: C, 67.53; H, 11.56. C37H74O8.CH3OH requires: C, 67.22; H, 11.57%).

3-O-(2,3,4,6-Tetra-O-acetyl-a-D-Mannopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 18. 6 was glycosylated with 17 as described for the preparation of 8 and 10. Purification of the reaction product by SiO2 column chromatography afforded 18 (4.9 g, 60.1%), mp 40~42° (EtOH), [a]D +18.9° (c = 1.04), Rp 0.40 in hexane-EtOAc (3:1). [a]D +4.86 (1H, d, J = 2 Hz, H-1), 2.12 (3H, s, OAc), 2.09 (3H, s, OAc), 2.02 (3H, s, OAc), 1.98 (3H, s, OAc), 1.24 (48H, bs, CH2), 0.86 (6H, t, J = 6 Hz, CH3 x2). (Found: C, 66.40; H, 10.23. C45H82O12 requires: C, 66.31; H, 10.14%).

3-O-(2,3,4,6-Tetra-O-acetyl-a-D-Galactopyranosyl)-1,2-di-O-tetradecyl-sn-glycerol 19. 18 was deacetylated as described previously to give 19, mp 113~114° (MeOH), [a]D +29.0° (c = 0.49). Rp 0.27 in CHCl3-MeOH (10:1). [a]D (DMO9-d6, 80°): 100.1 (JCH = 169.1 Hz, C-1). (Found: C, 67.13; H, 11.33. C37H74O8.CH3OH requires: C, 67.22; H, 11.57%).
glucopyranosyl)-β-D-glucopyranosyl]-1,2-di-O-tetradecyl-
sm-glycerol 21 and 3-O-[2,3,6-tri-O-acetyl-4-O-[2,3,4,6-
tetra-O-acetyl-α-D-glucopyranosyl]-α-D-glucopyranosyl]-
1,2-di-O-tetradecyl-sm-glycerol 23. To the mixture of 6
(1.5 g, 3 mmol), powdered molecular sieve 4A (12 g), and
HgBr2 (2.2 g, 6 mmol) in CH2Cl2 (20 ml) was added dropwise
with stirring a solution of 20 (6 mmol) in CH2Cl2 (10 ml) at
-10° during 15 min. The mixture was stirred at nr
for 22 hr and was filtered. The filtrate was washed with
aq. NaHCO3, aq. NaCl, dried (MgSO4) and evaporated.
The residual oil was chromatographed over SiO2 (300 g)
toluene–EtOAc (3:1) to give 21 (2.2 g, 64%), mp
80–81° (EtOH), [α]D +30.2° (c =0.43). Rf 0.37 in
toluene–EtOAc (3:1). δH: 2.13 (3H, s, OAc), 2.09 (3H, s,
OAc), 2.04 (3H, s, OAc), 2.02 (6H, s, OAc), 1.99 (6H, s,
OAc), 1.23 (48H, bs, CH2), 0.88 (6H, t, J = 6 Hz, CH3). δC:
100.5 (1JCH =163.6 Hz, C-1a), 95.5 (1JCH =175.8 Hz, C-1b).

Further elution with the same solvent afforded 27 (0.4 g,
11.7%). [α]D +38.2° (c =1.135), Rf/0.26 in toluene–EtOAc
(3:1). δH: 2.14 (3H, s, OAc), 2.11 (9H, s, OAc), 2.04 (6H, s,
OAc), 1.96 (3H, s, OAc), 1.23 (48H, bs, CH2), 0.88 (6H, bt,
J =6 Hz, CH3). δC: 101.1 (1JCH =161.1 Hz, C-1b), 99.0
(1JCH =170.9 Hz, C-1a). (Found: C, 61.62; H, 8.95. C57H98O20
requires: C, 62.05; H, 8.95%).

3-O-[4-O-β-D-galactopyranosyl-β-D-glucopyranosyl]-
1,2-di-O-tetradecyl-sm-glycerol 22. A suspension of 21 (1.0 g)
in MeOH (20 ml), Et3N (2 ml) and H2O (2 ml) was refluxed
for 10 hr and processed as in the case of 21 to give
crystalline 22 (70 mg, 95.5%), mp (dec) 203–205° (MeOH–H2O),
[α]D +6.9° (c =0.26, THF). Rf/0.26 in CHCl3–MeOH (3:1). δC
(DMSO-d6): 103.7 (1JCH =158.2 Hz, 1b), 103.0 (1JCH =158.2 Hz,
1a). (Found: C, 63.67; H, 10.50. C43H84O13-0.5
CH3OH requires: C, 63.82; H, 10.46%).

3-O-[4-O-α-D-glucopyranosyl-β-D-glucopyranosyl]-1,2-
 di-O-tetradecyl-sm-glycerol 31. 30 (1.0 g) was treated as in
the case of 21 to give crystalline 31 (0.7 g, 95.5%), mp (dec)
225–226° (MeOH–H2O), [α]D −8.5° (c =0.485, THF). Rf/0.33 in
CHCl3–MeOH (5:1). δC: 103.0 (1JCH =157.4 Hz, 1a and
1b). (Found: C, 63.38; H, 10.48. C57H98O20 requires: C, 62.05;
H, 8.95%).
requires: C, 63.32; H, 10.38\%.

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