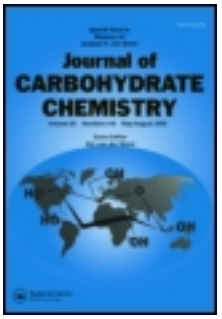

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Synthesis of Glycosyl Glycerols and Related Glycolipids

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SYNTHESIS OF GLYCOSYL GLYCEROLS AND RELATED GLYCOLIPIDS

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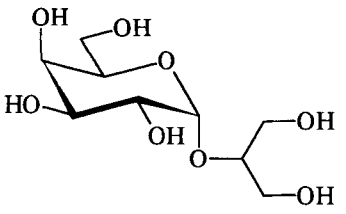
ABSTRACT

Several isomeric glycosyl glycerols were synthesized. Acetylated allyl glycosides of D-glucose and D-galactose were transformed into 1-*O*-(glycopyranosyl)-rac-glycerols in a three step procedure via the corresponding 2,3-epoxypropyl glycosides and the peracetylated glycosyl glycerols. Tetra-*O*-benzyl-D-glucose was glycosylated with 1,3-di-*O*-benzylglycerol to give the α-anomer preferentially. The 2-*O*-(tetra-*O*-acetyl-β-glycopyranosyl)-sn-glycerols and 2-*O*-(β-glycopyranosyl)-sn-glycerols of D-glucose, D-galactose and *N*-acetyl-D-glucosamine and the corresponding α-derivatives of D-mannose were synthesized by selective glycosylation methods from 1,3-di-*O*-benzylglycerol and 1,3-*O*-benzylideneglycerol, respectively, and activated sugar compounds followed by hydrogenolysis. After long chain acylation and selective deacetylation the 1,3-di-*O*-acyl-2-*O*-(β-glycopyranosyl)-sn-glycerols of D-glucose, D-galactose and *N*-acetyl-D-glucosamine and the corresponding α-derivative of D-mannose were synthesized.

INTRODUCTION

As early as 1930 Colin et al. reported galactosyl glycerols to occur in many red algae,[1,2] and later in 1953 Putman and Hassid observed the marine alga *Irideae*

laminarioides to contain 2-*O*-(α-D-galactopyranosyl)-sn-glycerol (**1**, fluridoside)[3] in 1 - 4 %.[4] Many different glycosyl glycerols have been found in lilies. For example the genus *Longiflorum* contains 2-*O*-(β-D-glucopyranosyl)-sn-glycerol (**2**, lilioside B) and the mono-acetylated derivative (lilioside A).[5] In the bulbs of other geni, 1-sn- (lilioside D) and 3-sn- (lilioside C) β-D-glucopyranosyl glycerols were found.[6]



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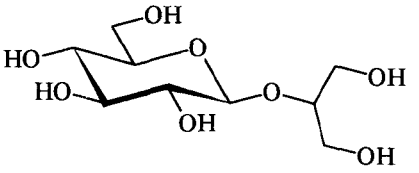

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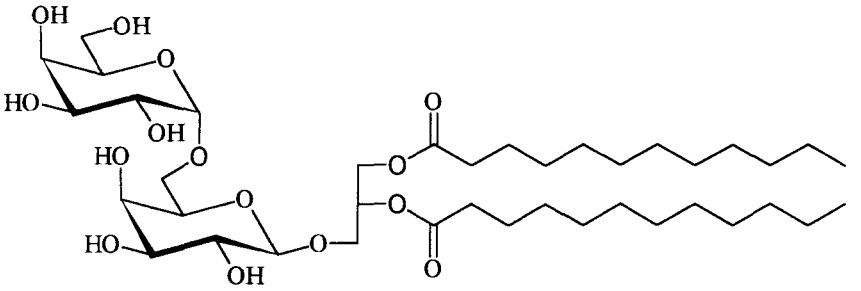

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Pocard et al. assumed that glycosyl glycerols, together with other substances, may have the ability to regulate the water balance of photosynthetic microorganisms, higher plants and bacteria.[7] Recently they observed the *de novo* synthesis of 2-*O*-(α-D-glucopyranosyl)-sn-glycerol in the salt tolerant (1.2 M NaCl) bacterium *Pseudomonas mendocina* SKB70 in adaption to osmotic stress. This is quite remarkable because thus far glycosyl glycerols have been known only in photosynthetic organisms. They function as the only osmolytes in cyanobacteria for example,[7-11] and cyanobacteria which cannot synthesize them are salt sensitive.[12,13] Also, the fluridoside in the above mentioned red alga serves as a means for adaption to salt stress.[14]

Glycosyl glycerols are highly water soluble, have a neutral net electric charge, and show no toxicity towards enzymes when assayed *in vitro* at high but physiologically relevant concentrations. These features make them useful as osmolytes in nature. They are also of particular interest, because they are very skin friendly and are suitable as moisturizers in cosmetics.[15,16] The outermost skin layer, the horn skin, is protected against dryness by water

binding substances which are called "natural moisturizing factor" (NMF, e.g., carbohydrates, amino acids, pyrrolidone carbonic acids, urea, etc.). The NMF may be dissolved by water during washing which results in a rough and chapped skin. Thus, moisturizing cremes are required to contain substances which are part of the NMF or have similar moisture-regulating effects.

One of the aims of this work was to synthesize isomeric glycosyl glycerols for tests of their moisturizing properties and to find suitable pathways for their facile synthesis avoiding toxic reagents, e.g., mercury salts in glycosylation reactions.

Glycosyl glycerols are also important as glycoconjugates, especially as diacylglycerol esters. These compounds demonstrate surfactant character, having a polar carbohydrate part and a nonpolar fatty acid ester part. Depending on their structure and the nature of the solvent, surfactants form micelles, mono layers, double layers, vesicles (liposomes), liquid crystalline phases and other associates. Glycosyl diglycerides also should show the ability to encapsulate other substances in solution. This makes them interesting as mild, skin friendly and biodegradable surfactants in shampoos and soaps and also as transporters of cosmetically or medically interesting components.

The glycosyl diglycerides play an important role in biological membranes, e.g., the thylacoid membrane. Galactosyl and sulphoquinovosyl diacylglycerols are the most important glycolipids in chloroplasts and plastids.[17,18] About 75 % of the lipids of the thylacoid membrane are galactolipids (50 % mono- and 25 % digalactosyl diacylglycerol, e.g., the 1,2-di-*O*-acyl-sn-glycerol derivative **3**). The remainder of the acyl lipid is comprised mostly of the anionic sulphoquinovosyl diacylglycerol and phosphatidyl glycerol.[19]

Simpler lipids with one to three sugar units are common components of cell membranes, whereas more complex species are involved in recognition processes. The glycerol part is esterified with saturated and unsaturated fatty acids. Carter et al. were the first to isolate glycosyl glycerol lipids from natural material and characterize mono and digalactosyl diglycerides from wheat flour.[20]

RESULTS AND DISCUSSION

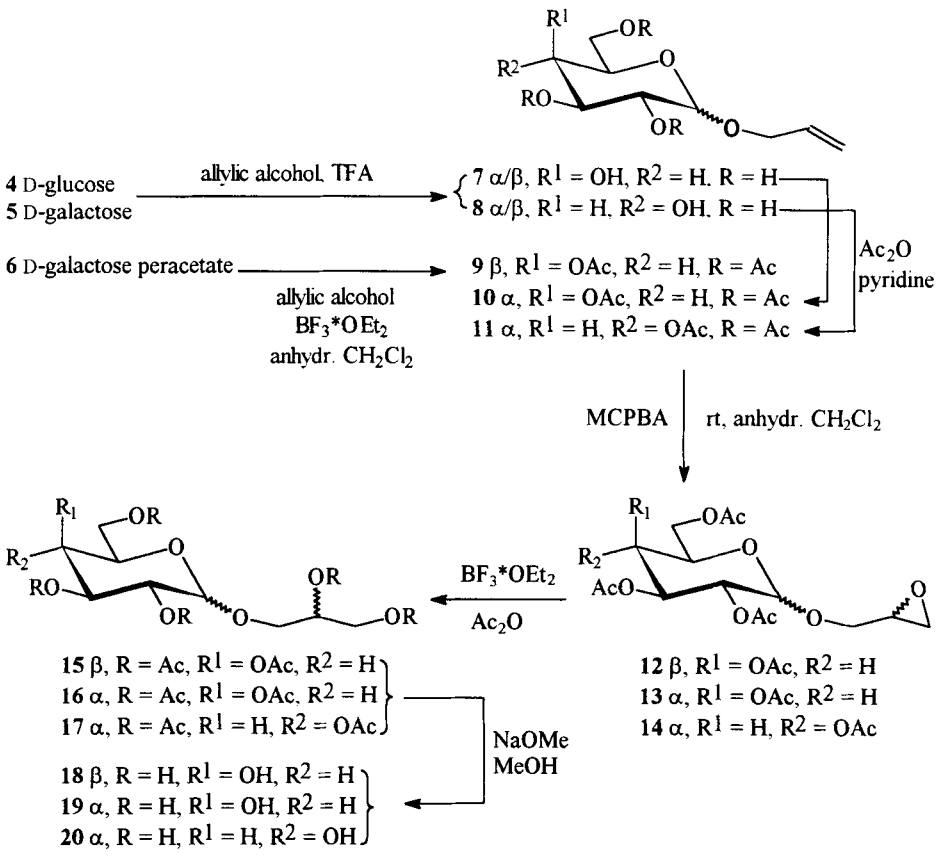
1. SYNTHESIS OF 1-*O*-(GLYCOPYRANOSYL)-RAC-GLYCEROLS

The isomeric allyl tetra-*O*-acetyl-glycosides **9**, **10** and **11** were converted to glycosyl glycerols[21] in a three step procedure, and further a new opening reaction of oxirane rings

was introduced. These glycosides and the following 2,3-epoxypropyl glycosides **12**, **13** and **14** were synthesized according to the literature. The β-D-galactoside **9** was easily available from β-D-galactose peracetate in a selective synthesis with allyl alcohol under boron trifluoride-etherate catalysis.[22] This cheap and high-yielding glycosylation method was introduced by Magnusson et al. in 1983.[23] The α-linked compounds were synthesized by a straightforward Fischer glycosylation, however, there was a considerable amount of β-product which was difficult to remove.[24,25] The epoxidation was done with *m*-chloroperbenzoic acid at room temperature, and the resulting 2,3-epoxypropyl-2,3,4,6-tetra-*O*-acetyl-D-glycopyranosides **12**, **13** and **14** were obtained with little diastereomeric selectivity (1:0.82; 1:0.72; 1:0.82). Recently, several other approaches towards sugar derivatives containing epoxide functions have been reported. Either components with double bonds were transformed with about the same diastereoselectivity or different pathways were followed.[26,27] The 2,3-epoxypropyl glycosides are interesting for example as affinity labels for (1-6)-β-D-galactopyran-binding monoclonal antibodies.[28]

The main step of this approach is the transformation of the epoxide to a protected or unprotected diol function. Björkling and Godtfredsen reported the transformation of the deacetyl derivative of **12** to monoacylated galactosyl glycerols.[29] Oxirane ring opening reactions under acidic or Lewis acid conditions are well known. For example, recently Tamura et al. reported the boron trifluoride-etherate catalyzed alkylation of epichlorohydrin to form (±)-1-chloro-3-ethoxy-2-hydroxypropane.[30] Isopropylidene-protected cis-diols were prepared from epoxides by Hanzlik and Leinwetter.[31] Henkel holds a patent on a procedure to prepare vicinal acyloxy groups from epoxides and acyl anhydrides under acetic acid/sulfuric acid catalysis.[32]

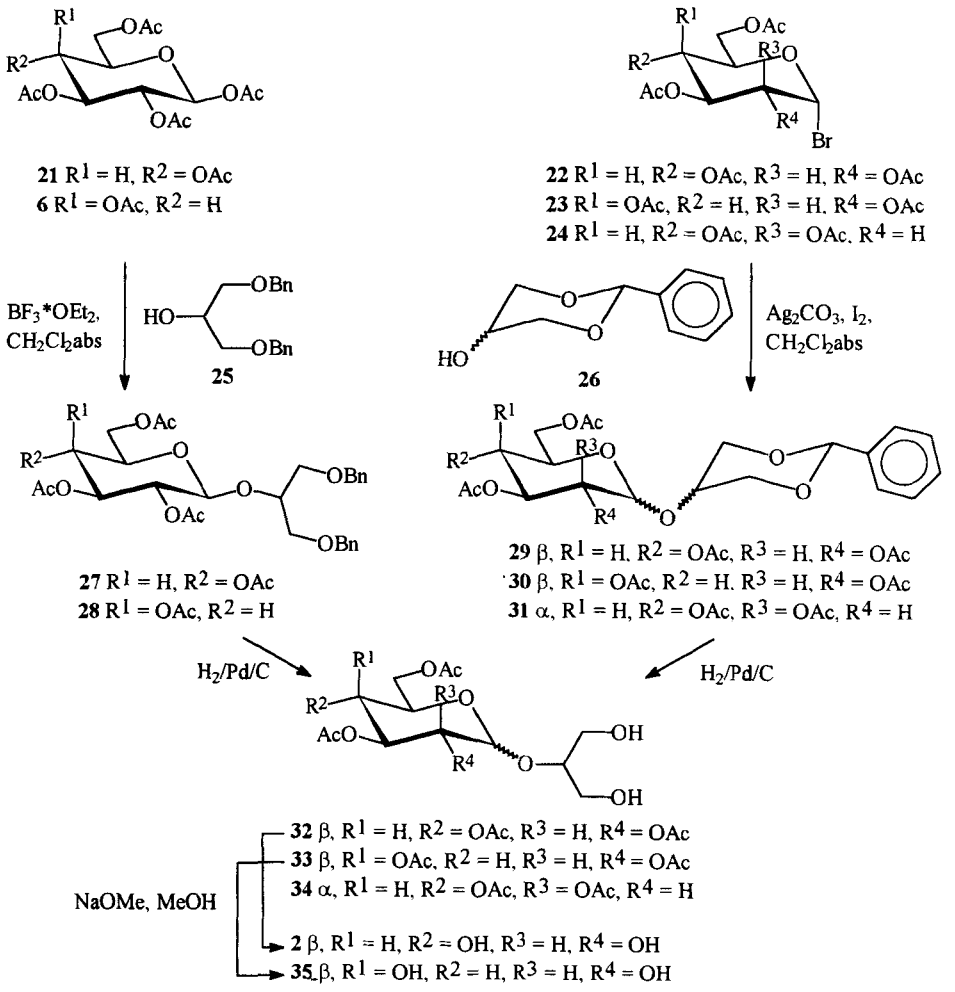
Our findings parallel this work, and here we report on the boron trifluoride-etherate catalyzed conversion of 2,3-epoxypropyl glycosides into 1,3-di-*O*-acetyl-(2,3,4,6-tetra-*O*-acetylglycopyranosyl)-rac-glycerols **15**, **16** and **17** in 70, 59 and 63 % yield, respectively. The reaction can be performed either under normal conditions or in an inert atmosphere. Whereas in the first case an immediate reaction occurs under the latter conditions 5 h are required. It is assumed that the presence of catalytically active water is the reason for this effect. Because of almost equal amounts of both diastereomers in compounds **12-14** and the nearly similar shift of the ^{1}H NMR signals of compounds **15-16**, it cannot be discriminated whether this reaction is accompanied by racemisation. The final deprotection to give the 1-*O*-(glycopyranosyl)-rac-glycerols **18** - **20** was carried out under the usual conditions with sodium methanolate in methanol.



Scheme 1

2. PREPARATION OF 2-*O*-(β-GLYCOPYRANOSYL)-SN-GLYCEROLS

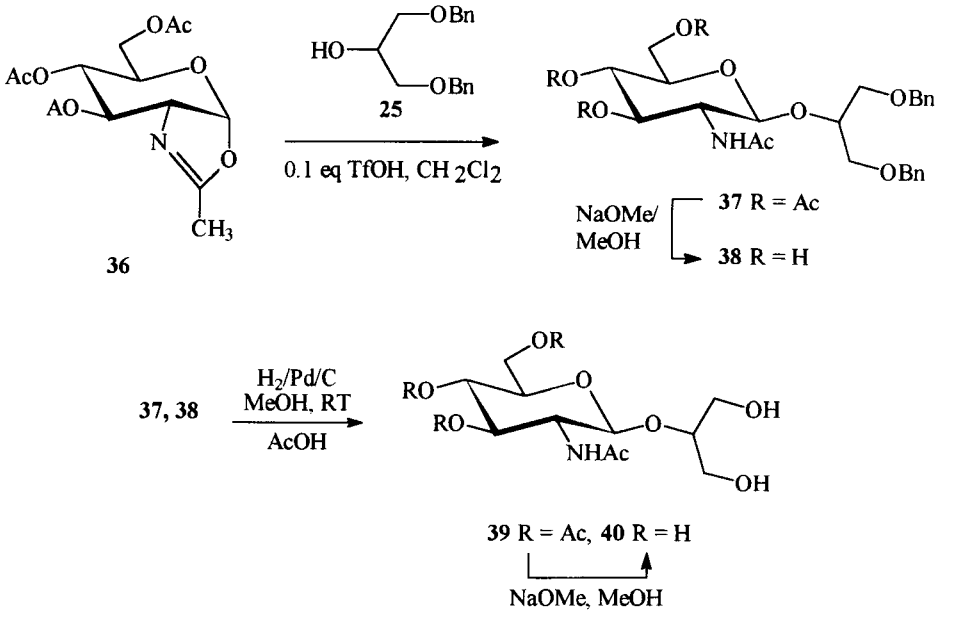
The preparation of 2-linked glycerol compounds with 1,2-*trans* glycosidic bonds was done in two converging ways in which various glycosylation methods and different glycerol derivatives were tested. The first and more advantageous route used the 1,3-di-*O*-benzyl-glycerol aglycon **25**,[33] which is stable under the Lewis acid conditions of the boron trifluoride-etherate catalyzed glycosylation of peracetates.[23] The 1,3-di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosyl)-sn-glycerols of glucose **27**[34] and galactose **28** were obtained in 61 and 54 %, respectively, with exclusive formation of the β-product. Even though Lewis acids catalyze the anomerization of glycosides, no α-products were found. The peracetylated α-anomer corresponding to **21** reacted very slowly and could easily be



Scheme 2

removed by column chromatography after hydrogenolysis. In this step acetic acid was added to avoid acetyl migration and thus the pure compounds **32** and **33** were obtained.

In the second route towards compounds **32**,[35] **33** and **34** an *endo/exo*-mixture of 2-phenyl-5-hydroxy-1,3-dioxolan (1,3-*O*-benzylideneglycerol) **26**[36,37] was used as aglycon. Because this glycerol derivative was more sensitive towards Lewis acids, the Koenigs-Knorr procedure had to be used. With 30 % for compound **29**, 19 % for compound **30** and 10 % for compound **31**, respectively, the yields in this glycosylation were less convincing than in the first route. This approach suffered from the formation of a mixture of diastereomers as

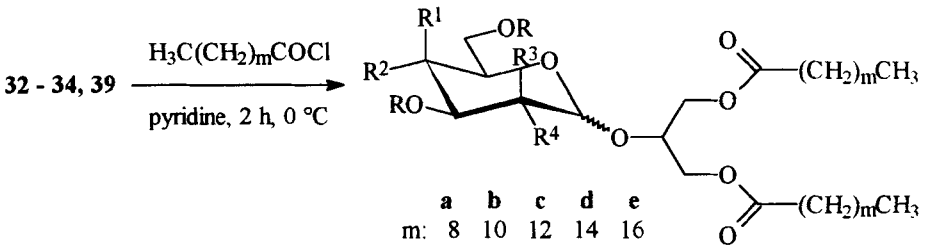


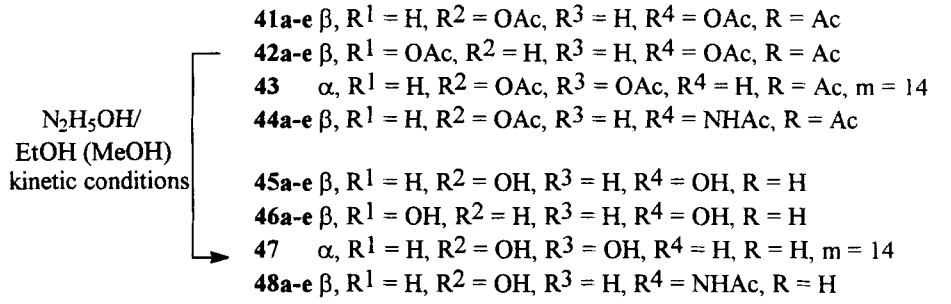
Scheme 3

well as use of expensive silver salts and unstable sugar derivatives and was thus not continued. Before deacetylation compounds **32** and **33** were purified and thus no further isolation of **2** and **35** was nessessary. The esterification of **32** and **33** with long chain fatty acids is described in chapter 4.

3. ACCESS TO 2-*O*-(-2-ACETAMIDO-2-DEOXY-β-D-GLUCOPYRANOSYL)-SN-GLYCEROL

1,2-*Trans*-glycosides of *N*-acetyl-D-glucosamine are easily and selectively available by the oxazoline method. 2-Methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyranoso)-[2,1-*d*]-1,3-oxazole (oxazoline, **36**)[38,39] can be activated for glycosylation under acidic conditions, e. g. with trifluoromethanesulfonic acid in anhydrous dichloromethane. Again compound **25** was used as aglycon because it was stable under these conditions. Thus 1,3-di-*O*-benzyl-2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-sn-glycerol



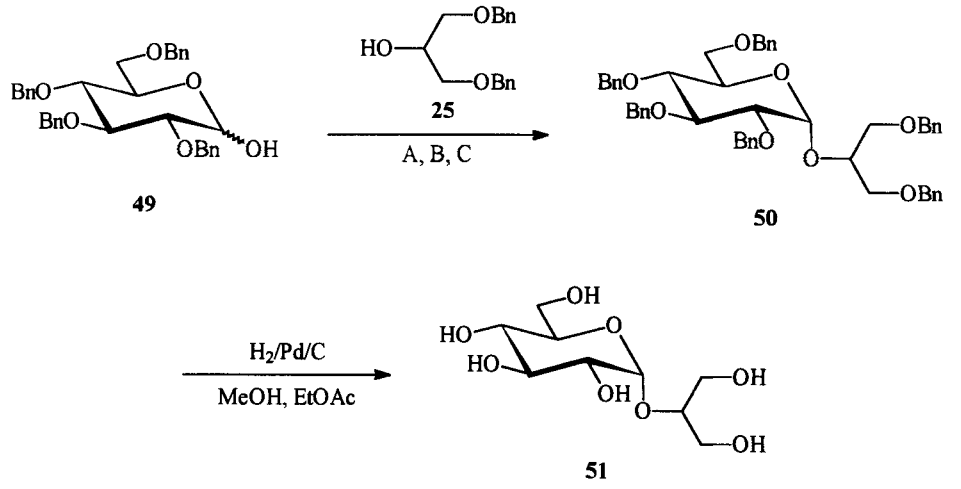


Scheme 4

(**37**) was obtained in 65 % yield. Deacetylation and hydrogenolysis, in both possible orders, led to 2-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-sn-glycerol (**40**), which represents a useful moisturizer.[15,16] The esterification of compound **39** with long chain fatty acids is described in section 4. Hydrogenolysis of **37** was carried out with H_2/Pd/C in methanol and acetic acid conditions to avoid acetyl migration.

4. FORMATION OF 1,3-DI-*O*-ACYL-2-*O*-(β-GLYCOPYRANOSYL)-SN-GLYCEROLS

Compounds **32** - **34** and **39** contain two primary hydroxy groups, which can be readily esterified with long chain fatty acids. The esterifications were carried out with decanoic, lauric, myristic, palmitic and stearic acid chloride and pyridine, and for the manno-derivative **34** only the palmitic acid ester was synthesized. Except for the didecanoate and dipalmitate of 1,3-di-*O*-acyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-sn-glycerol in their peracetylated form[40] 1,3-di-*O*-acyl-2-*O*-(glycopyranosyl)-sn-glycerols have not been described previously.



Scheme 5 A: 1. CCl_3CN, K_2CO_3, CH_2Cl_2; 2. Et_2O, TMSOTf, **25**
B: 1. Ac_2O, NaOAc, reflux; 2. **25**, BF_3*OEt_2, CH_2Cl_2
C: Amberlite IR 120 (H^+), **25**, toluene, 70 °C

The acylation, carried out with a slight excess (2.5 eq) of acyl chloride and pyridine, was straightforward. After about two hours the reaction had to be stopped, because a second product was formed, perhaps by transesterification. Depending on the purity of the acyl chloride, the yields varied from 60 % to quantitative.

A much more difficult step in this synthesis was the selective deacetylation of compounds **41a-e**, **42a-e**, **43** and **44a-e**. With 85 % ethanolic hydrazine hydrate solution (3 - 5 eq per acetate group) as a mild reagent and under kinetic reaction conditions, a fairly selective deacetylation with minor cleavage of the long chain fatty acid esters could be successfully applied.[41-44] The yields varied from about 20 to 70 %, dependent on the kinetic control. All these glycolipids exhibit interesting liquid crystalline properties which will be reported in due course.

5. SYNTHESIS OF 2-*O*-(α-D-GLUCOPYRANOSYL)-SN-GLYCEROL

There was further interest into synthetic pathways towards α-D-linked glycosyl glycerols as well as their α/β-mixtures. Previously Austin et al.[45] reported on the synthesis of **50** from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl chloride and **25** by Koenigs-Knorr

conditions. The intermediate **50** en route to **51** was not characterized. Activation of **49** with trichloroacetonitrile gave tetra-*O*-benzyl-D-glycopyranosyl trichloroacetimidate[46] as an inseparable α/β-mixture (α/β 1:4; with K_2CO_3 as base). Even though the chosen reaction conditions should support α-formation, this anomeric mixture of the glycopyranosyl donor led to an anomeric product mixture. Instead of the imidate, in a much simpler approach the acetate could be used and activation was by boron trifluoride-etherate. Compound **50** was obtained in 69 % yield with an α/β ratio of 77:23.

Further, glycosylation was done by the Fischer approach to obtain α/β-mixtures. Compound **49** was stirred with **25** and *p*-toluenesulfonic acid in toluene at 70 °C. Higher temperature led to a complex product mixture, whereas no reaction occurred at lower temperature. However, compound **50** was obtained as a mixture of anomers in poor yield (19 %). By hydrogenolysis of the benzyl ether groups the unblocked compound **51** could be prepared as a pure compound and as an anomeric mixture.

CONCLUSIONS

In this work the syntheses of isomeric 2-*O*-glycopyranosyl-sn-glycerols as well as the 1,3-di-*O*-acyl-2-*O*-glycopyranosyl-sn-glycerols of β-D-glucose, β-D-galactose, α-D-mannose and *N*-acetyl-β-D-glucosamine were reported and these compounds are at hand for subsequent studies. Furthermore, a novel pathway towards 1-*O*-glycopyranosyl-rac-glycerols of α- and β-D-galactose and α-D-glucose was introduced, including oxirane ring opening reactions. Finally, the α-glycosylation of 1,3-di-*O*-benzylglycerol was studied.

EXPERIMENTAL

General procedures. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.67 MHz) were recorded with a *Bruker AMX-400* spectrometer. Melting points were determined with an *Olympus BH-2* polarising microscope with a *Mettler FP 82* heating desk. Optical rotations were determined with a Perkin-Elmer 241 polarimeter. TLC was performed on precoated plates of silica gel 60 (*GF_{254}* by *Merck* or *ALUGRAM™ SIL G/UV254* by *Machery-Nagel)*, detection occured by UV-absorption or spraying with 15 %

ethanolic sulfuric acid and subsequent heating. Column chromatography was performed by the flash technique on silica gel 230-400 mesh (*Merck*). Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry of the University of Hamburg.

2,3-Epoxypropyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (12). Compound **9** (1.44 g, 3.71 mmol) and *m*-chloroperbenzoic acid (MCPBA) (0.96 g, 5.56 mmol) were dissolved in dichloromethane and stirred overnight at room temperature. Another portion of MCPBA (31 mg, 0.18 mmol) was added and stirring continued for another 23 h until no starting material remained. The solution was diluted with dichloromethane, washed successively with aqueous $Na_2S_2O_5$, saturated $NaHCO_3$-solution and water, dried and concentrated. TLC and separation by column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f (**9**) = 0.37, R_f (**12**) = 0.20 to give syrupy **12** (1.10 g, 2.72 mmol, 74 %) as a mixture of diastereomers.[47] $[\alpha]_D^{20}$ - 9.3 ° (*c* 1, $CHCl_3$), [ref.:[29] only ^1H NMR of 2-(*R*) derivative]; ^1H NMR ($CDCl_3$, TMS): δ = 5.39 (dd, 2H, 2x H-4), 5.27-5.17 (2x dd, 2H, 2x H-2), 5.03 (2x dd, 2H, 2x H-3), 4.61 (d, 1H, H-1-I), 4.51 (d, 1H, H-1-II), 4.22-4.10 (m, 4H, 2x CH_2-6), 4.07 (dd, 1H, H-1′a-I), 3.92 (ddd, 2H, 2x H-5), 3.87 (m, 2H, 2x H-1′-II), 3.50 (dd, 1H, H-1′b-I), 3.14 (m, 2H, 2x H-2′), 2.80 (dd, 1H, H-3′a-I), 2.77 (dd, 1H, H-3′a-II), 2.67 (dd, 1H, H-3′b-II), 2.56 (dd, 1H, H-3′b-I), 2.16, 2.08, 2.03, 1.98 (4s, je 3H, 4x $COCH_3$); $J_{1,2}$ = 7.6, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, $J_{4,5}$ = 1.8, $J_{5,6b}$ = 6.6, $J_{1'a\text{-}I,1'b\text{-}I}$ = 11.7, $J_{1'a\text{-}II,1'b\text{-}II}$ = 0, $J_{1'b\text{-}I,2'}$ = 2.8, $J_{1'\text{-}II,2'}$ = 6.6, $J_{2',3'a\text{-}I}$ = 4.3, $J_{2',3'a\text{-}II}$ = 4.1, $J_{2',3'b\text{-}I}$ = 2.6, $J_{2',3'b\text{-}II}$ = 3.1, $J_{3'a\text{-}II,3'b\text{-}II}$ = 5.1, $J_{3'a\text{-}I,3'b\text{-}I}$ = 4.6 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.4-169.6 (8x $COCH_3$), 101.6, 101.1 (2x C-1), 70.9, 70.8 (2x C-3, 2x C-5), 70.7, 69.0, (2x 1′-CH_2), 68.7 (2x C-2), 67.0 (2x C-4), 61.3 (2x C-6), 50.6, 50.2 (2x 2′-CH), 44.1 (2x3′-CH_2), 20.8-20.6 (8x $COCH_3$).

2,3-Epoxypropyl 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranoside (13). Compound **10** (284 mg, 0.73 mmol) and *m*-chloroperbenzoic acid (352 mg, 2.04 mmol) were converted by the same procedure as for compound **12**. TLC and separation by column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f (**9**) = 0.35, R_f (**12**) = 0.19 to give crystalline **13** (238 mg, 0.59 mmol, 81 %) as a mixture of diastereomers;[47] mp 103.2 °C; $[\alpha]_D^{20}$ 125.3 ° (*c* 1, $CHCl_3$), [ref.:[48] mp 91.5 - 92.5 °C; $[\alpha]_D^{20}$ 126.5 ° (*c* 1, $CHCl_3$)]; ^1H NMR ($CDCl_3$, TMS): δ = 5.46 (2x dd, 2H, 2x H-4), 5.40 - 5.35 (2x dd, 2H, 2x H-2), 5.19 (2x d, 2H, 2x H-1) 5.14 (2x dd, 2H, 2x H-3), 4.28 (ddd, 2H, 2x H-5), 4.13 - 4.07 (m, 4H, 4x CH_2-6), 3.92 (dd, 1H, H-1′a-II), 3.82 (m, H, H-1′a-I), 3.62 (dd, 1H, H-1′b-I), 3.49 (dd,

1H, H-1′b-II), 3.17 (m, 2H, H-2′-I, H-2′-II), 2.81 (dd, 2H, 2x H-3′a-II), 2.68 (dd, 1H, H-3′b-I), 2.61 (dd, 1H, H-3′b-II), 2.19, 2.15, 2.04, 1.99 (4s, je 3H, 4x COC$\underline{H}_3$); $J_{1,2}$ = 3.6, $J_{3,4}$ = 3.6, $J_{4,5}$ = 6.1, $J_{5,6b}$ = 6.6, $J_{1'a\text{-}II,1'b\text{-}II}$ = 11.7, $J_{1'a\text{-}I,1'b\text{-}I}$ = 11.7, $J_{1'aI/II,2'\text{-}I/II}$ = 2.8, $J_{1'bI/II,2'\text{-}I/II}$ = 6.1, $J_{2',3'}$ = 2.6, 3.6, $J_{3'a\text{-}I/II,3'b\text{-}I/II}$ = 5.1 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.4-169.9 (8x $\underline{C}OCH_3$), 96.6, 96.5 (2x C-1), 69.3, 68.4 (2x C-1′),68.1, 67.9, 67.4, 66.4 (2x C-2, C-3, C-4, C-5), 61.7, 61.6 (2x C-6), 50.3, 50.1 (2x C-2′), 44.3, 44.1 (2x C-3′), 20.7-20.6 (8x $CO\underline{C}H_3$).

2,3-Epoxypropyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (14). Compound **11** (1.83 g, 4.71 mmol) and *m*-chloroperbenzoic acid (1.22 mg, 7.07 mmol) were converted by the same procedure as for compound **12**. TLC and separation by column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f (**9**) = 0.35, R_f (**14**) = 0.19 to give syrupy **14** (1.21 g, 2.99 mmol, 64 %) as a mixture of diastereomers;[47] $[\alpha]_D^{20}$ + 99.9 ° (*c* 1, $CHCl_3$); [ref.:[49] $[\alpha]_D^{20}$ + 108 °, (*c* 1.7)]; ^{1}H NMR ($CDCl_3$, TMS): δ = 5.54 - 5.46 (2x dd, 2H, 2x H-3), 5.16 (d, 1H, H-1-II), 5.09 (d, 1H, H-1-I), 5.07 (dd, 2H, H-4), 4.92 - 4.86 (m, 2H, 2x H-2), 4.25 (2x ddd, 2H, 2x H-5), 4.13 - 4.06 (m, 4H, 2x H-6), 3.93 (dd, 1H, H-1′a-II), 3.85 (dd, 1H, H-1′a-I), 3.60 (dd, 1H, H-1′b-I), 3.50 (dd, 1H, H-1′b-II), 3.21 - 3.15 (m, 2H, H-2′), 2.84 - 2.80 (m, 2H, H-3′a-I/II), 2.69 (m, 1H, H-3′b-I), 2.63 (m, 1H, H-3′b-II), 2.12 - 2.00 (m, 24H, 8x COC$\underline{H}_3$); $J_{1,2}$ = 3.6, $J_{2,3}$ = 6.1, $J_{3,4}$ = 9.1, $J_{4,5}$ = 9.7, $J_{1'a\text{-}II,1'b\text{-}II}$ = 11.7, $J_{1'a\text{-}I,1'b\text{-}I}$ = 11.7, $J_{1'a\text{-}I/II,2'\text{-}I/II}$ = 2.6, $J_{1'b\text{-}I/II,2'\text{-}I/II}$ = 6.1, 5.6, $J_{2',3'}$ = 2.5, 3.6, $J_{3'a\text{-}I/II,3'b\text{-}I/II}$ = 5.5 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.6-169.6 (8x $\underline{C}OCH_3$), 96.1 (2x C-1), 70.7, 70.7, 70.0, 70.0, 68.5, 68.4, 67.4, 67.4 (each 2x C-2, C-3, C-4, C-5), 69.3, 68.5 (2x C-1′), 61.9, 61.8 (2x C-6), 50.3, 50.1 (2x C-2′), 44.3, 44.1 (C-3′), 20.7 - 20.6 (8x $CO\underline{C}H_3$).

1,2-Di-*O*-acetyl-3-*O*-(2,3, 4, 6-tetra-*O*-acetyl-β-D-galactopyranosyl)-rac-glycerol (15). Compound **12** (154 mg, 0.38 mmol) was dissolved in acetic anhydride (5 mL), and BF_3-etherate (2 μL, 0.02 mmol) was added. The reaction mixture was stirred for 30 min at rt. The reaction was stopped by stirring with saturated sodium hydrogen carbonate for 30 min. $CHCl_3$ was added and the solution was washed with sodium hydrogen carbonate and water, dried over sodium sulfate and concentrated to dryness. TLC and column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f(**15**) = 0.30, R_f(**12**) = 0.34, R_f (galactose peracetate) = 0.49 yielding **15** as a colourless syrup (137 mg, 0.27 mmol, 70 %). $[\alpha]_D^{20}$ - 9.2 ° (*c* 1, $CHCl_3$); [ref.:[29,50] (3-*O*-sn-derivative): $[\alpha]_D^{20}$ - 5.7 °, (*c* 0.3, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$, TMS): δ = 5.39 (m, 2H, 2x H-4), 5.18 (m, 4H, 2x H-2, 2x 2′-CH-glycerol), 5.02 (m, 2H, 2x H-3), 4.51 (2x d, 2H, 2x H-1), 4.30 (m, 2H, 2x 3′-CH_2-a-

glycerol), 4.21-4.07 (m, 6H, 2x CH_2-6, 3′-CH_2-b-glycerol), 4.01 (m, 4H, H-5, 1′-CH_2-a-glycerol), 3.70 (m, 2H, 1′-CH_2-b-glycerol), 2.16, 2.10-2.04, 1.98 (4x s, 36H, 12x $COCH_3$); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, $J_{4,5}$ = 2.0, $J_{5,6b}$ = 6.6 Hz. ^{13}C NMR ($CDCl_3$, TMS): δ = 170.5 - 169.3 (12x $COCH_3$), 101.6, 101.3 (2x C-1), 70.8, 70.8, 70.1, 69.9, 68.7, 68.6, 67.6, 67.0 (each 2x C-2, C-3, C-4, C-5, 2′-CH-glycerol), 62.5 (2x C-6), 61.3, 61.2 (2x 3′-CH_2-glycerol), 20.9-20.6 (12x $COCH_3$).

1,2-Di-*O*-acetyl-3-*O*-(2,3, 4, 6-tetra-*O*-acetyl-α-D-galactopyranosyl)-rac-glycerol (16). Compound **13** (154 mg, 0.38 mmol) was converted by the same procedure as compound **15** to yield **16** as a colourless syrup (136 mg, 0.27 mmol, 59 %). TLC and column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f(**16**) = 0.35, R_f(**13**) = 0.34, R_f (galactose peracetate) = 0.49. $[\alpha]_D^{20}$ - 93.9 ° (*c* 1, $CHCl_3$), [ref.:[51] mp 74 - 75 °C, $[\alpha]_D^{20}$ 132.0 °, (*c* 0.08, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$, TMS): δ = 5.46 (m, 2H, 2x H-4), 5.33, 5.30 (2x dd, 2H, 2x H-3), 5.21 - 5.08 (m, 6H, 2x H-1, 2x H-2, 2x 2′-CH-glycerol), 4.33, 4.30 (2x dd, 2H, 2x 3′-CH_2-a-glycerol), 4.21 (m, 2H, 2x H-5), 4.20 - 4.14 (m, 2H, 2x 3′-CH_2-b-glycerol), 4.12 - 4.08 (m, 2H, 2x H-6), 3.82 (m, 2H, 2x 1′-CH_2-a-glycerol), 3.64 (m, 2H, 1′-CH_2-b-glycerol), 2.30, 2.14, 2.11-2.05, 1.99 (4x s, 36H, 12x $COCH_3$); $J_{1,2}$ = 4.1, $J_{3,4}$ = 3.6, $J_{4,5}$ = 3.6 Hz.

1,2-Di-*O*-acetyl-3-*O*-(2, 3, 4, 6-tetra-*O*-acetyl-α-D-glucopyranosyl)-rac-glycerol (17). Compound **14** (0.931 g, 2.30 mmol) was converted, by the same procedure as for compound **15**, to **17** as a colourless syrup (0.739 g, 1.46 mmol, 63 %). TLC and column chromatography were carried out with petroleum ether/EtOAc 1:1, R_f(**17**) = 0.35, R_f(**13**) = 0.34, R_f (glucose peracetate) = 0.49. [ref.:[52] D-glycerol derivative: mp 90 °C, $[\alpha]_D^{20}$ + 87 ° (*c* 0.9, $CHCl_3$); L-glycerol derivative: mp 56 °C, $[\alpha]_D^{20}$ + 89 ° (*c* 1.5, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$, TMS): δ = 5.45 (dd, 2H, 2x H-3), 5.19 (m, 2H, 2x H-2′), 5.12 (d, 1H, H-1-I), 5.11 (d, 1H, H-1-II), 5.06 (dd, 2H, 2x H-4), 4.86 (dd, 2H, 2x H-2), 4.36 - 4.07 (m, 8H, 2x H-3′, 2x H-6), 4.03 (m, 2H, 2x H-5), 3.83 (m, 2H, H-1′a), 3.65 (m, 2H, H-1′b), 2.18, 2.11 - 2.00 (m, 36H, 12x OAc); $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.2, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.1, $J_{1'a,1'b}$ = 11.2, $J_{1'a,2'}$ = 4.1, $J_{1'b,2'}$ = 6.1 Hz; ^{13}C NMR ($CDCl_3$, TMS) = 170.6 - 169.6 (12x $COCH_3$), 96.2 (2x C-1), 70.7, 70.6, 70.0, 70.0, 69.9, 68.4, 67.6 (each 2x C-2, C-3, C-4, C-5, C-2′), 67.5, 66.6, 66.2 (each 2x C-1′), 62.3, 62.2, 61.8 (each 2x C-6, C-3′), 20.9 - 20.0 (12x $COCH_3$).

1-*O*-(β-D-Galactopyranosyl)-rac-glycerol (18). Compound **15** (135 mg, 0.26 mmol) was dissolved in dry methanol (10 mL) and sodium methanolate (1.62 mg, 0.03 mmol) was added. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2,

R_f (**15**) = 0.87, R_f (**18**) = 0.04. The solution was neutralized with ion exchange resin (Amberlite IR 120 (H^+)), filtered and concentrated to dryness to yield **18** as a mixture of diastereomers (56 mg, 0.22 mmol, 83 %); [ref.[51] (3-*O*-sn-derivative): mp 136 - 137 °C, $[\alpha]_D^{20}$ - 6.4 ° (*c* 0.5, H_2O)]; ^1H NMR (DMSO-d_6): δ = 4.69, 4.52, 4.47 (3x d, 3x 2H, 6x CH-OH), 4.43, 4.33, 4.17 (3x m, 3x 2H, 6x CH_2OH), 3.92, 3.90 (2x d, 2H, 2x H-1), 3.64 - 3.29 (m, each 2x H-2, H-3, H-4, H-5, H-6, 2′-glycerol, 1′-, 3′-glycerol); $J_{1,2}$ = 7.1, $J_{CH,OH}$ = 3.1, 5.1, 4.6 Hz; ^{13}C NMR (DMSO): δ = 2x 104.0 (2x C-1), 75.2, 73.3, 73.2, 70.7, 70.6, 70.6, 70.5, 68.1, (each 2x 2′-glycerol, C-2, C-3, C-4, C-5), 71.2, 71.1, 62.9, 62.8 (1′-, 3′-glycerol), 60.4 (2x C-6).

1-*O*-(α-D-Galactopyranosyl)-rac-glycerol (19). Compound **16** (827 mg, 1.63 mmol) was dissolved in anhydrous methanol (10 mL), and sodium methanolate (8.6 mg, 0.16 mmol) was added. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2. The solution was neutralized with acidic ion exchange resin (Amberlite IR 120 (H^+)), filtered and evaporated to dryness yielding **18** as a syrup (402 mg, 1.58 mmol, 97 %): $[\alpha]_D^{20}$ + 16.4 ° (*c* 1, H_2O); [ref.[51] (3-*O*-sn-derivative): mp 150 - 151 °C, $[\alpha]_D^{20}$ + 158 ° (*c* 0.5, H_2O)]; ^1H NMR (D_2O, acetone): δ = 4.86 (2x d, 2H, 2x H-1), 3.91 - 3.67 (m, 10H, each 2x H-2, H-3, H-4, H-5, H-2′), 3.74 (2x dd, 2H, H-1′a-I, H-1′a-II), 3.65 (d, 2H, 2x H-6), 3.59 - 3.45 (m, 4 H, each 2x H-3′, H-1′b-II), 3.39 (dd, 2H, H-1′b-I); $J_{1,2}$ = 3.6, $J_{5,6}$ = 5.6, $J_{1',2'}$ = 3.1, 10.7 Hz; ^{13}C NMR (D_2O, acetone): δ = 99.1, 99.9, (2x C-1), 70.8 - 68.8 (each 2x C-2, C-3, C-4, C-5, C-2′), 69.6 (C-1′), 69.3 (C-1′′), 62.9 (2x C-3′), 61.5 (2x C-6).

1-*O*-(α-D-Glucopyranosyl)-rac-glycerol (20). Compound **17** (739 mg, 1.46 mmol) was dissolved in dry methanol (10 mL), and sodium methanolate (8.1 mg, 0.15 mmol) was added. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2, R_f (**17**) = 0.87, R_f (**20**) = 0.04. The solution was neutralized with ion exchange resin (Amberlite IR 120 H^+), filtered and concentrated to dryness to yield **20** as a mixture of diastereomers (356 mg, 1.40 mmol, 96 %); [ref.[51] (3-*O*-sn-derivative): syrup, $[\alpha]_D^{20}$ + 97.1 ° (*c* 0.2, H_2O)]; ^1H NMR (400 MHz, CD_3OD): δ = 3.53 (d, 1H, H-1-I), 3.51 (d, 1H, H-1-I); $J_{1,2}$ = 3.6 Hz; ^{13}C NMR (CD_3OD) : δ = 98.1, 97.7 (2x C-1), 72.6, 71.2, 71.1, 69.8, 69.4, 69.2 (each 2x C-2, C-3, C-4, C-5, C-2′), 68.3, 67.5 (2x C-1′), 61.7, 61.6 (2x C-3′), 60.1 (C-6).

1,3-Di-*O*-benzyl-2-*O*-(2, 3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranosyl)-sn-glycerol (27). 1,2,3,4,6-Penta-*O*-acetyl-β-D-glucopyranose (**21**, 42.00 g, 0.108 mol) and 1,3-di-*O*-benzylglycerol (**25**, 73.00 g, 0.268 mol) were dissolved in anhydrous dichloromethane (50 mL) under argon atmosphere. After addition of boron trifluoride-etherate (13.5 mL, 0.107

mol) the mixture was stirred at room temperature with exclusion of light for 4 h. The mixture was neutralized with a saturated solution of sodium hydrogen carbonate and washed three times with water, dried over magnesium sulfate and filtered, followed by evaporation of the solvent. TLC and column chromatography were carried out with petroleum ether/ethyl acetate 2:1 to yield **27** as a powder (39.62 g, 65.7 mmol, 61 %): mp 55.5 °C; $[\alpha]_D^{20}$ - 5.0 ° (*c* 1, $CHCl_3$); [ref.:[34] mp 55 - 56 °C, $[\alpha]_D^{20}$ not given]; ^1H NMR ($CDCl_3$, TMS): δ = 7.37 - 7.25 (m, 10 H, 2x $CH_2C_6\underline{H}_5$) 5.19 (dd, 1H, H-3), 5.05 (dd, 1H, H-4), 4.99 (dd, 1H, H-2), 4.80 (d, 1H, H-1), 4.52, 4.49 (s, 2H, 2x $C\underline{H}_2C_6H_5$), 4.21 (dd, 2H, H-6a), 4.11 (dd, 1H, H-6b), 4.02 (m, 1H, H-2′), 3.69 - 3.60 (m, 3H, H-5, H-1′a, H-3′a),, 3.57 - 3.51 (2x dd, 2H, H-1′b, H-3′b), 2.04, 2.02, 2.00, 1.93 (4s, 4x 3H, 4x $COC\underline{H}_3$); $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.7, $J_{3,4}$ = 9.2, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 5.1, $J_{5,6b}$ = 2.6, $J_{6a,6b}$ = 12.2, $J_{1'a,1'b}$ = 10.7, $J_{1'a,2'}$ = 6.5, $J_{1'b,2'}$ = 2.5, $J_{2',3'a}$ = 5.1, $J_{2',3'b}$ = 2.0, $J_{3'a,3'b}$ = 10.7 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.2, 169.8, 169.0, 168.9 (4x $\underline{C}OCH_3$), 137.7, 137.6, 128.0 - 127.1 ($\underline{C}_6H_5$), 100.3 (C-1), 77.9 (C-2′), 73.1, 73.0 ($\underline{C}H_2C_6H_5$), 72.5 (C-3), 71.3 (C-5), 71.1 (C-2), 70.6, 69.7 (C-1′, -3′), 68.1 (C-4), 61.6 (C-6), 20.3, 20.2, 20.1, 20.1 (4x $CO\underline{C}H_3$).

1,3-Di-*O*-benzyl-2-*O*-(2, 3, 4, 6-tetra-*O*-acetyl-β-D-galactopyranosyl)-sn-glycerol (28). 1,2,3,4,6-Penta-*O*-acetyl-β-D-galactopyranose (**6**, 5.00 g, 12.8 mmol) and 1,3-di-*O*-benzylglycerol (**25**, 3.49 g, 12.8 mmol) were converted by the same procedure as used to convert compound **21** to **27**. TLC and column chromatography were carried out with petroleum ether/ethyl acetate 2:1, R_f (**6**) = 0.17, R_f (**28**) = 0.25, R_f (α-peracetate) = 0.19, R_f (1,3-di-*O*-benzylglycerol, **25**) = 0.53 to yield **28** as a syrup (4.34 g, 7.20 mmol, 56 %): $[\alpha]_D^{20}$ - 5.0 ° (*c* 1, $CHCl_3$) [ref.:[53] syrup, not characterized]; ^1H NMR ($CDCl_3$, TMS): δ = 7.37 - 7.27 (m, 10 H, 2x $CH_2C_6\underline{H}_5$) 5.37 (dd, 1H, H-4), 5.20 (dd, 1H, H-2), 5.01 (dd, 1H, H-3), 4.74 (d, 1H, H-1), 4.52, 4.51 (s, 2H, 2x $C\underline{H}_2C_6H_5$), 4.11 (d, 2H, H-6) , 4.04 (m, 1H, H-2′), 3.85 (ddd, 1H, H-5), 3.70-3.64 (2x dd, 2H, H-1′a, H-3′a), 3.58-3.52 (2x dd, 2H, H-1′b, H-3′b), 2.14, 2.01, 1.98, 1.93 (4s, 4x 3H, 4x $COC\underline{H}_3$); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, $J_{4,5}$ = 1.0, $J_{5,6a}$ = $J_{5,6b}$ = 6.6, $J_{6a,6b}$ = 0, $J_{1'a,2'}$ = 3.6, $J_{1'b,2'}$ = 2.5, $J_{1'a,1'b}$ = 10.7, $J_{2',3'a}$ = 5.1, $J_{2',3'b}$ = 2.0, $J_{3'a,3'b}$ = 10.2 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.3, 170.2, 169.5 (4x $\underline{C}OCH_3$), 138.2, 138.1, 128.5 - 127.6 (C_6H_5), 101.4 (C-1), 78.5 (C-2′), 73.5, 73.4 ($\underline{C}H_2C_6H_5$), 71.0 (C-3), 70.7 (C-5), 69.1 (C-2), 67.1 (C-4), 71.1, 70.1 (C-1′, C-3′), 61.3 (C-6), 20.7, 20.6 (4x $CO\underline{C}H_3$).

Anal. Calcd for $C_{31}H_{38}O_{12}$ (602.64): C, 61.79; H, 6.36. Found.: C, 61.25; H, 6.44.

1,3-*O*-Benzylidene-2-*O*-(2,3, 4, 6-tetra-*O*-acetyl-β-D-glucopyranosyl)-sn-glycerol (29). 1,3-*O*-Benzylideneglycerol (**26**, 1.43 g, 7.9 mmol) was dissolved in anhydrous

dichloromethane (30 mL) and silver carbonate (2.83 g, 10.1 mmol), iodine (0.66 g, 2.6 mmol) and freshly activated molecular sieves 3 Å were added. After stirring for 30 min at rt peracetylated glucopyranosyl bromide (**22**, 4.3 g, 10.56 mmol) dissolved in anhydrous dichloromethane (45 mL) was added dropwise within 1 h. The mixture was stirred under nitrogen with exclusion of light for 5 d. After filtration over Celite and washing of the residue with dichloromethane, the filtrate was washed with sodium thiosulfate solution (10 %) and water, dried and concentrated to dryness. TLC and purification by column chromatography were carried out with diethyl ether/hexane 1:1 to give crystalline **29** as a mixture of diastereomers (1.22 g, 30 %): mp 120 °C; $[\alpha]_D^{20}$ - 18 ° (*c* 1, $CHCl_3$); [ref.:[37] mp 133 °C, $[\alpha]_D^{20}$ - 33 ° (*c* 1, $CHCl_3$)]; ^1H NMR ($CDCl_3$, TMS): δ = 7.34 – 7.38 (m, 10H, 2x C_6H_5), 5.51 (s, 1H, H-2′-cis), 5.30 (s, 1H, H-2′-trans), 5.25 (dd, H-3), 5.07 – 5.14 (m, 2H, H-2, H-4), 4.82 (d, H-1), 4.01 – 4.35 (m, 6H, H-6a, H-6b, H-6′a/e, H-4′a/e), 3.71 (bs, 1H, H-5′), 3.69 (ddd, H-5), 1.95, 2.01, 2.02, 2.05 (s, 3H, OAc); $J_{1,2}$ = 7.6, $J_{2,3}$ = 10.7, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 5.7, $J_{5,6b}$ = 2.5, $J_{6a,6b}$ = 12.2 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.6, 170.3, 169.5, 169.4 (4x OAc), 101.4 (C-1), 98.8 (C-5′), 72.7, 72.0, 71.1 (C-5, C-3, C-2), 70.3 (C-3′), 69.5 (C-4), 68.5 (C-2′), 67.8 (C-1′), 61.9 (C-6), 20.7, 20.6, 20.5, 20.4 (4x OAc).

1,3-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-sn-glycerol (30). 1,3-*O*-Benzylideneglycerol (**26**, 1.00 g, 5.5 mmol), silver carbonate (1.97 g, 7.06 mmol), iodine (0.46 g, 1.8 mmol) in anhydrous dichloromethane (25 mL) and peracetylated galactopyranosyl bromide (**23**, 4.3 g, 10.56 mmol) in anhydrous dichloromethane (35 mL) were converted by the same procedure as for compound **29**. Monitoring by TLC and purification by column chromatography were carried out with diethyl ether/hexane 1:1 to give crystalline **30** as a mixture of diastereomers (533 mg, 19 %): mp 69 °C; $[\alpha]_D^{20}$ - 32 ° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS): δ = 7.32 – 7.49 (m, 5H, C_6H_5), 5.52 (s, 1H, H-2′-cis), 5.40 (dd, H-4), 5.33 (dd, H-2), 5.06 (dd, H-3), 4.76 (d, H-1), 4.27 – 4.34 (m, H-6a, H-6b), 4.20 – 4.02 (m, 4H, H-6′a/e, H-4′a/e), 3.91 (ddd, H-5), 3.73 (bs, H-5′), 2.15, 2.04, 1.99, 1.95 (s, 3H, OAc); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, $J_{4,5}$ = 1.1, $J_{5,6a}$ = 6.6, $J_{5,6b}$ = 6.6, $J_{6a,6b}$ = 12.2, $J_{4'e,4'a}$ = $J_{6'e,6'a}$ = 12.7, $J_{4'e,5'}$ = $J_{5',6'e}$ = 12.7, $J_{5',4'a}$ = $J_{5',6'a}$ = 2.3 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.4, 170.3, 170.2, 169.6 (4x OAc), 101.5 (C-1), 99.3 (C-2′), 71.1, 70.9, 70.3 (C-5, C-3, C-2), 69.4 (C-3′), 68.5 (C-4), 67.8 (C-2′), 67.1 (C-1′), 61.4 (C-6), 20.7, 20.6, 20.5, 20.4 (4x OAc).

1,3-*O*-Benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-sn-glycerol (31). 1,3-*O*-Benzylideneglycerol (**26**, 1.00 g, 5.5 mmol), silver carbonate (1.97 g, 7.06

mmol), iodine (0.46 g, 1.8 mmol) in anhydrous dichloromethane (25 mL) and peracetylated mannopyranosyl bromide (**24**, 4.3 g, 10.56 mmol) in anhydrous dichloromethane (35 mL) were converted into **31** by the same procedure used to prepare compound **29**. Monitoring by TLC and purification by column chromatography were carried out with diethyl ether/hexane 1:1 to give crystalline **31** as a mixture of diastereomers (280 mg, 10 %): mp 152 °C; $[\alpha]_D^{20}$ - 68 ° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS): δ = 7.32 – 7.50 (m, 5H, C_6H_5), 5.52 (s, 1H, H-2′-cis), 5.30 (dd, H-4), 4.63 (dd, H-2), 5.15 (dd, H-3), 5.49 (d, H-1), 4.03 – 4.28 (m, H-6a, H-6b, H-6′a/e, H-4′a/e), 3.70 (ddd, H-5), 3.65 (bs, H-5′), 2.09, 2.07, 2.06, 1.99 (s, 3H, OAc); $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.1, $J_{5,6a}$ = 5.1, $J_{5,6b}$ = 2.5 Hz.

2-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-sn-glycerol (32). Method A: Compound **27** (10.08 g, 16.73 mmol) was dissolved in methanol (250 mL) and acetic acid (10 mL) was added. The solution was stored under argon and Pd/C (1 g, 10 %) was added and the atmosphere was changed to hydrogen. The reaction was monitored by TLC with ethyl acetate/toluene 5:1, R_f (**27**) = 0.78; R_f (**32**) = 0.2 and ethyl acetate /petroleum ether 2:1, R_f (**27**) = 0.65; R_f (**32**) = 0.09. Purification by column chromatography was carried out with ethyl acetate/petroleum ether/ethanol 2:10:1 and toluene/ethyl acetate 1:5 to give **32** as a colourless powder (6.44 g, 15.2 mmol, 91 %). Method B: Compound **29** (1.06 g, 2.08 mmol) in ethyl acetate/methanol (50 mL) was treated with Pd/C (132 mg) under argon and the atmosphere was changed to hydrogen to yield **32** (821 mg, mmol, 93 %): mp 100.3 - 103.7 °C; $[\alpha]_D^{20}$ + 4.7 ° (*c* 1, $CHCl_3$); [ref.:[34] mp 101 - 102 °C, $[\alpha]_D^{20}$ not given]; ^1H NMR ($CDCl_3$, TMS): δ = 5.25 (dd, 1H, H-3), 5.03 (m, 2H, H-2, H-4), 4.67 (d, 1H, H-1), 4.24 (dd, 1H, H-6a), 4.15 (dd, 1H, H-6b), 3.79 (m, 2H, H-2′, H-5), 3.63 (m, 4H, 1′-, 3′-CH_2-glycerol), 2.88 (dd, 1H, OH), 2.10, 2.07, 2.04, 2.02 (4s, 4x 3H, 4x $COC\underline{H}_3$); $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.7, $J_{3,4}$ = 9.7, $J_{5,6a}$ = 2.0, $J_{5,6b}$ = 6.1, $J_{6a,6b}$ = 12.2 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.7, 170.2, 169.8, 169.5 (4x $\underline{C}OCH_3$), 101.6 (C-1), 85.3 (2′-CH), 72.5, 72.1, 71.7, 68.5 (C-2, C-3, C-4, C-5), 62.9, 62.5, 62.1 (C-6, 1′-, 3′-CH_2), 20.8, 20.7, 20.6 (4x $CO\underline{C}H_3$).

Anal. Calcd for $C_{17}H_{26}O_{12}$ (422.39): C, 48.34; H, 6.20. Found.: C, 48.00; H, 6.25.

2-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-sn-glycerol (33). Method A: Compound **28** (1.96 g, 3.26 mmol) was converted into **33** by the same procedure used to prepare **32**. The reaction was monitored by TLC with ethyl acetate/toluene 5:1, R_f (**28**) = 0.71; R_f (**33**) = 0.10, R_f (α-peracetate) = 0.77 and ethyl acetate/petroleum ether 4:1, R_f (**28**) = 0.82, R_f (**33**) = 0.11, R_f (α-peracetate) = 0.77. Purification by column chromatography was carried out with ethyl acetate/petroleum ether/EtOH 2:10:1 and toluene/ethyl acetate

1:5 to give **33** as a colourless syrup (1.28 g, 3.03 mmol, 93 %). Method B: Compound **30** (0.50 g, 0.97 mmol) in ethyl acetate/methanol 1:1 (25 mL) was converted into **33** with Pd/C (70 mg) by the same procedure used to prepare **32;** yield of **33** (369 mg, 0.87 mmol, 90 %): $[\alpha]_D^{20}$ + 17.2° (*c* 1, $CHCl_3$) [ref.:[53] not characterized]; ^1H NMR ($CDCl_3$, TMS): δ = 5.41 (dd, 1H, H-4), 5.24 (dd, 1H, H-3), 5.06 (dd, 1H, H-2), 4.63 (d, 1H, H-1), 4.15 (m, 2H, H-6), 4.00 (ddd, 1H, H-5), 3.78 (m, 1H, 2′-CH-glycerol), 3.63 (m, 4H, 1′-, 3′-CH_2-glycerol), 2.97 (dd, 1H, OH), 2.17, 2.09, 2.08, 2.00 (4s, 4x 3H, 4x $COC\underline{H}_3$); $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, $J_{4,5}$ = 1.0, $J_{5,6b}$ = 6.1, $J_{6a,6b}$ = 11.7, $J_{1'/3',2'}$ = 5.1 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.7, 170.2, 169.8, 169.5 (4x $\underline{C}OCH_3$), 102.1 (C-1), 85.1 (2′-CH-glycerol), 71.2 (C-5), 70.7 (C-3), 69.3 (C-2), 67.0 (C-4), 62.9, 62.4 (1′-, 3′-CH_2-glycerol), 62.8 (C-6), 20.8, 20.6, 20.6, 20.5 (4x $CO\underline{C}H_3$).

Anal. Calcd for $C_{17}H_{26}O_{12}$ (422.39): C, 48.34; H, 6.20. Found.: C, 48.25; H, 6.17.

2-*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl)-sn-glycerol (34). Compound **31** (250 mg, 0.48 mmol) in ethyl acetate/methanol 1:1 (20 mL) was converted by method B as described for **30** with Pd/C (50 mg 5 %) to give crystalline **34** (182 mg, 90 %): mp 62 °C; $[\alpha]_D^{20}$ 89 ° (*c* 1, $CHCl_3$); ^1H NMR (methanol-d_4): δ = 5.35 (dd, 1H, H-4), 5.45 (dd, 1H, H-2), 5.48 (dd, 1H, H-3), 5.23 (d, 1H, H-1), 4.45 – 4.52 (m, 2H, H-5, H-6b), 4.23 (m, 1H, H-6a), 3.37 – 3.85 (m, 4H, 2x CH_2-glycerol), 3.90 – 3.95 (m, 1H, CH-glycerol), 3.70 (ddd, 1H, H-5), 2.26, 2.19, 2.16, 2.09 (4s, 4x 3H, 4x OAc); $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 3.6, $J_{5,6b}$ = 2.1, $J_{6a,6b}$ = 12.2, $J_{1'a/b,2'}$ = $J_{2',3'a/b}$ = 5.6, $J_{1'a,1'b}$ = $J_{3'a,3'b}$ = 12.2 Hz; ^{13}C NMR (D_2O): δ = 170.3, 170.0, 169.9, 169.8 (4x OAc), 97.1 (C-1), 79.7 (C-2′), 70.1 (C-3), 69.9 (C-5), 68.5 (C-2), 66.1 (C-4), 62.3, 61.4 (C-1′, C-3′), 60.5 (C-6), 20.7, 20.6, 20.4, 20.3 (4x OAc).

2-*O*-(β-D-Glucopyranosyl)-sn-glycerol (2). Compound **32** (1.46 g, 3.46 mmol) was dissolved in anhydrous MeOH (10 mL) and converted by the same procedure as for compound **18** to give crystalline **2**. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2, R_f (**32**) = 0.77, R_f (**2**) = 0.11. **2** was obtained as a colourless powder (0.85 g, 3.34 mmol, 97 %): mp 166.5 °C, $[\alpha]_D^{20}$ - 17.5 ° (*c* 1, DMSO); [ref.:[34] 166 - 167 °C, $[\alpha]_D^{20}$ - 30 ° (*c* 1, water)]; ^1H NMR (DMSO-d_6): δ = 5.00 (d, 2-OH), 4.91, 4.87 (d, 1H, 3-OH, 4-OH), 4.45 (dd, CH_2-O$\underline{H}$), 4.43 - 4.33 (m, 2H, 2x $CH_2O\underline{H}$), 4.25 (d, H-1), 3.66 (ddd, CH_2-OH), 3.56 (m, 1H, H-2′-glycerol), 3.52 - 3.34 (m, 5H, H-1′-, H-3′-glycerol, H-6), 3.17 - 3.08 (m, 2H, H-4, H-5), 3.03 (ddd, 1H, H-3), 2.96 (ddd, 1H, , H-2); $J_{1,2}$ = 7.6, $J_{2,3}$ = 9.2, $J_{2,OH}$ = 3.6, $J_{3,OH}$ = 5.1, $J_{4,OH}$ = 5.1, $J_{CH2,OH}$ = 5.6, 6.1, $J_{2',CH2'}$ = 5.6, $J_{2',CH2}$ = 5.1,

$J_{CH2a,CH2b}$ = 11.7 Hz; ^{13}C NMR (DMSO-d_6): δ = 103.9 (C-1), 82.7 (C-2′-glycerol), 77.7, 77.3 (C-4, C-5), 74.5 (C-2), 71.0 (C-3), 62.3, 62.0, 61.8 (C-6, C-1′-, C-3′-glycerol).

Anal. Calcd for $C_9H_{18}O_8$ (254.24): C, 42.52; H, 7.14. Found.: C, 42.29; H, 7.24.

2-*O*-(β-D-Galactopyranosyl)-sn-glycerol (35). Compound **33** (542 mg, 1.28 mmol) was dissolved in anhydrous MeOH (10 mL) and converted by the same procedure used to prepare compound **18** to give crystalline **35**. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2, R_f (**33**) = 0.77, R_f (**35**) = 0.11. **35** was obtained as a colourless powder (395 mg, 1.20 mmol, 94 %): mp 119.4 - 123.2 °C, $[\alpha]_D^{20}$ + 3.6 ° (*c* 1, DMSO) [ref.:[53,54] 126 - 127 °C, $[\alpha]_D^{20}$ - 2 ° (*c* 1, water)]; ^1H NMR (DMSO-d_6): δ = 4.88 (d, 1H, 2-OH), 4.68 (d, 1H, 3-OH), 4.54 (dd, 1H, CH_2-O<u>H</u>), 4.39 (m, 2H, 2x CH_2O<u>H</u>), 4.34 (d, 1H, 4-OH), 4.20 (d, 1H, H-1), 3.60 (m, 1H, H-4), 3.54 (m, 1H, H-2′-glycerol), 3.51 - 3.37 (m, 6H, H-1′-, H-3′-glycerol, H-6), 3.37 - 3.26 (m, 3H, H-2, H-3, H-5); $J_{1,2}$ = 7.6, $J_{2,OH}$ = 3.1, $J_{3,OH}$ = 4.6, $J_{4,OH}$ = 4.6, $J_{CH2,OH}$ = 5.6, $J_{2',CH2'}$ = 5.6 Hz; ^{13}C NMR (DMSO): δ = 104.6 (C-1), 82.6 (C-2′-glycerol), 76.1 (C-5), 74.0 (C-3), 71.7 (C-2), 69.0 (C-4), 62.3, 62.0, 61.3 (C-6, C-1′-, C-3′-glycerol).

Anal. Calcd for $C_9H_{18}O_8$ (254.24): C, 42.52; H, 7.14. Found.: C, 41.85; H, 7.19.

1,3-Di-*O*-benzyl-2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-sn-glycerol (37). Oxazoline **36** (40.0 g, 120 mmol) and 1,3-Di-*O*-benzylglycerol (**25**, 65.36 g, 240 mmol) were dissolved under argon atmosphere in anhydrous dichloromethane (250 mL) and trifluoromethane sulfonic acid (1.05 mL, 12 mmol, 0.1 eq) was added. The reaction mixture was boiled under reflux for 3 h, then neutralized with sodium hydrogen carbonate and the salts extracted with water. The combined organic layer was dried with sodium sulfate and concentrated to dryness. Purification by column chromatography was carried out with ethyl acetate/toluene 1:1 to give **37** as a colourless powder (46.93 g, 78 mmol, 94 %): mp 126 °C; $[\alpha]_D^{20}$ - 2.0 ° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$, TMS): δ = 4.85 (d, H-1), 3.86 (ddd, 1H, H-2), 5.18 (dd, H-3), 5.05 (dd, H-4), 3.65 (m, 1H, H-5), 4.22 (dd, 1H, H-6a), 4.09 (dd, 1H, H-6b), 5.48 (d, NH), 7.35 (m, 10H, CH_2C_6<u>H</u>$_5$), 4.52 (m, 4H, 2x - $CH_2C_6H_5$), 4.03 (m, H-2′-glycerol), 3.71 - 3.48 (m, 5H, H-1′-, H-3′-glycerol, H-5), 2.05, 2.01, 2.00, 1.74 (je s, 4x Ac); $J_{1,2}$ = 8.7, $J_{2,3}$ = 10.7, $J_{NH,2}$ = 8.7, $J_{3,4}$ = 9.2, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 5.1, $J_{5,6b}$ = 2.0, $J_{6a,6b}$ = 12.2 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.3 - 168.9 (4x Ac), 137.6, 137.5 (2x tert. C from C_6H_5), 128.1 - 127.1 (10x <u>C</u>-H, C_6H_5), 100.6 (C-1), 77.7, 72.4, 71.4, 68.2, 54.3 (C-2, C-3, C-4, C-5, C-2′-glycerol), 73.1, 73.0, 71.0, 69.5, 61.8 (C-6, 2x <u>C</u>$H_2C_6H_5$, C-1′-, C-3′-glycerol), 22.7, 20.3, 20.2, 20.2 (4x Ac).

Anal. Calcd for $C_{31}H_{39}NO_{11}$ (601.65): C, 61.89; H 6.53; N, 2.33. Found: C, 61.78; H, 6.53; N, 2.74.

1,3-Di-*O*-benzyl-2-*O*-(2-acetamido-2-deoxy-β- D - glucopyranosyl)-sn-glycerol (38). Compound **37** (3 g, 4.99 mmol) was converted by the same procedure used to prepare **18** to give **38** (2.25 g, 4.74 mmol, 95 %): mp 103 °C; $[\alpha]_D^{20}$ - 10.6 ° (*c* 1, DMSO); ^{1}H NMR (DMSO): δ = 7.68 (d, NH), 7.32 - 7.20 (m, 10H, $CH_2C_6\underline{H}_5$), 5.15 - 5.30, 4.55 (3H, 3 OH), 4.50 - 4.40 (m, 5H, H-1, 2 $C\underline{H}_2C_6H_5$), 3.87 (ddd, 1H, H-5), 3.65 (dd, 1H, H-6a), 3.58 - 3.40 (m, 5H, H-6b, H-1′-, H-3′-glycerol), 3.40 - 3.20 (m, 2H, H-2, H-2′-glycerol), 3.10 - 3.00 (m, 2H, H-3, H-4), 2.81 (s, 3H, $NHCOC\underline{H}_3$); $J_{NH,2}$ = 9.1, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 2.5, $J_{5,6b}$ = 2.5, $J_{6a,6b}$ = 11.5 Hz; ^{13}C NMR (DMSO): δ = 137.6, 137.5, 129.1 - 128.2 (C_6H_5), 101.8 (C-1), 77.9 (C-3), 77.3 (C-5), 71.6 (C-4), 74.9 (C-2′-glycerol), 73.3, 73.1 (2x $\underline{C}H_2C_6H_5$), 70.5, 70.2 (C-1′-, C-3′-glycerol), 62.0 (C-6), 56.7 (C-2), 23.9 ($NHCOC\underline{H}_3$).

2-*O*-(2-Acetamido-3, 4, 6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-sn-glycerol (39). Compound **37** (8.00 g, 13.3 mmol) was hydrogenated by the same procedure used to prepare **32**. The reaction was monitored by TLC with ethyl acetate/toluene 10:1, R_f(**37**) = 0.37; R_f(**39**) = 0 and ethyl CH_2Cl_2/MeOH 5:1, R_f(**37**) = 0.73, R_f(**39**) = 0.46. Purification by column chromatography was carried out with ethyl acetate/EtOH 10:2 to give **39** as a colourless powder (5.29 g, 12.6 mmol, 94 %): mp 173 °C; $[\alpha]_D^{20}$ + 12.0 ° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, TMS): δ = 6.50 (d, 1H, NH), 5.22 (dd, 1H, H-3), 5.03 (dd, 1H, H-4), 4.79 (d, 1H, H-1), 4.22 (dd, 1H, H-6a), 4.17 (dd, 1H, H-6b), 3.99 (ddd, 1H, H-2), 3.79 (m, 2H, H-2′-glycerol, H-5), 3.62 (m, 4H, H-1′-, H-3′-glycerol), 3.30, 3.09 (each dd, 1H, OH), 2.09, 2.05, 2.04, 1.97 (4s, 4x 3H, 4x $COC\underline{H}_3$); $J_{1,2}$ = 8.7, $J_{2,3}$ = 10.7, $J_{2,NH}$ = 8.7, $J_{3,4}$ = 9.4, $J_{4,5}$ = 9.7, $J_{5,6a}$ = 2.0, $J_{5,6b}$ = 6.1, $J_{6a,6b}$ = 12.2 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 171.7, 171.2, 170.8, 169.5 (4x $\underline{C}OCH_3$), 102.1 (C-1), 84.8 (C-2′-glycerol), 72.3 (C-3), 72.0 (C-5), 68.6 (C-4), 62.9, 62.3, (C-6, C-1′-, C-3′-CH_2-glycerol), 54.9 (C-2), 23.4, 20.7, 20.7, 20.6 (4x $CO\underline{C}H_3$).

Anal. Calcd for $C_{17}H_{27}NO_{11}$ (421.40): C, 48.45; H 6.46; N, 3.32. Found: C, 48.43; H, 6.43; N, 3.30.

2-*O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-sn-glycerol (40). Method A: Compound **38** (466 mg, 0.98 mmol) was converted into **40** by the same procedure used to prepare **32** employing Pd/C (70 mg), acetic acid (0.5 mL) and MeOH (10mL). **40** was obtained as a colourless syrup (260 mg, 0.88 mmol, 90 %); Method B: Compound **39** (2.11 g, 5.02 mmol) was dissolved in anhydrous MeOH (10 mL) and converted by the same

procedure as for compound **18** to give crystalline **40**. The reaction was monitored by TLC with ethyl acetate/ethanol 3:2, R_f (**37**) = 0.59, R_f (**40**) = 0.07. **40** was obtained as a colourless powder (1.45 g, 4.91 mmol, 98 %): mp 159.9 °C; $[\alpha]_D^{20}$ - 29.8 ° (*c* 1, DMSO); ^{1}H NMR (DMSO-d_6): δ = 7.67 (d, NH), 4.53 - 4.24 (m, 7H, 6x OH, H-1), 4.44 (d, H-1), 3.68 (dd, CH_2), 3.49 (m, 1H, 2′-CH-glycerol), 3.45 - 3.34 (m, 5H, 1′-, 3′-CH_2-glycerol, H-6), 3.34 - 3.25 (m, 2H, H-2, H-3), 3.12 - 3.00 (m, 2H, H-4, H-5), 1.68 (1s, 3H, NHCOC<u>H</u>$_3$); $J_{1,2}$ = 8.1, $J_{2,NH}$ = 7.6, $J_{2',CH2'}$ = 5.6, $J_{2',CH2'}$ = 5.1, $J_{CH2a,CH2b}$ = 11.5 Hz; ^{13}C NMR ($CDCl_3$, TMS): δ = 170.4 (NH<u>C</u>OCH$_3$), 102.0 (C-1), 82.7 (2′-CH-glycerol), 77.8 (C-4), 75.1 (C-3), 71.6 (C-5), 62.4, 62.0, 61.6 (C-6, 1′-, 3′-CH_2-glycerol), 57.0 (C-2), 23.9 (NHCO<u>C</u>H$_3$).

1,3-Di-*O*-acyl-2-*O*-(2, 3, 4, 6- tetra -*O*- acetyl -β- D -glucopyranosyl)-sn-glycerol (41a-e). Compound **32** (1 eq) was dissolved in dry dichloromethane and pyridine (8 eq) was added. The solution was cooled to 0 °C and the acyl chloride (2.5 eq) was added dropwise. The solution turned yellow and a precipitate of pyridinium chloride was formed. The reaction terminated after ½ h as monitored by TLC with toluene/ethyl acetate 5:1. The mixture was dissolved in dichloromethane, neutralized with sodium hydrogen carbonate solution and washed with water (3 times). The combined organic layers were dried over Na_2SO_4 and the solvent removed. For complete removel of the pyridine it was codistilled with toluene and the solvent was removed in high vacuum. The raw product was crystallized from methanol or purified by column chromatography with toluene/ethyl acetate 1:5. Table 1 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 7 and 8.

1,3-Di-*O*-acyl-2-*O*-(2, 3, 4, 6-tetra -*O*- acetyl-β- D-galactopyranosyl)-sn-glycerol (42a-e). Compound **33** (1 eq) was acylated by the same procedure used to prepare compounds **41a-e**. The reaction was monitored by TLC with toluene/ethyl acetate 5:1. Table 2 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 7 and 8.

1,3-Di-*O*-hexadecyl-2-*O*-(2,3,4, 6-tetra-*O*-acetyl-α-D-mannopyranosyl)-sn-glycerol (43). Compound **34** (70 mg, 0.16 mmol) was dissolved in toluene (15 mL) and pyridine (0.1 mL) was added. Palmitoyl chloride (0.124 mL, 0.41 mmol) was added dropwise at 0 °C and stirring was at 0 °C for 3 h and another 7 h at 65 °C. TLC was carried out with hexane/diethyl ether 1:1. The precipitate was filtered and the solvent removed in vacuo. The product was crystallized from methanol to yield **43** (108 mg, 88 %): mp 65 °C; $[\alpha]_D^{20}$ - 76 °

Table 1: Data for preparation of compounds **41a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	41a (m = 8)	**41b** (m = 10)	**41c** (m = 12)	**41d** (m = 14)	**41e** (m = 16)
32	4.80 g (11.4 mmol)	6.80 g (16.1 mmol)	8.40 g (19.9 mmol)	4.94 g (11.7 mmol)	4.20 g (9.94 mmol)
anhydr. CH_2Cl_2	35 mL	50 mL	55 mL	50 mL	40 mL
Pyridine	6.9 mL	9.8 mL	12.03 mL	7.07 mL	6.01 mL
$H_3C(CH_2)_mCOCl$	5.8 mL (2.5 eq)	9.60 mL (2.5 eq)	13.50 mL (2.5 eq)	8.83 mL (5 eq)	8.27 mL (2.5 eq)
R_f in tol/EtOAc 5:1	0.40	0.41	0.43	0.48	0.49
Yield	6.67 g (9.12 mmol) 80 %	10.64 g (13.5 mmol) 84 %	15.29 g (17.3 mmol) 87 %	8.61 g (9.75 mmol) 83 %	6.67 g (7.10 mmol) 71 %
mp	85 °C	104.7 °C	syrup	syrup	syrup
$[\alpha]^{20}_D$ ($CHCl_3$)	- 4.2 ° (*c* 1)	- 7.7 ° (*c* 1)	-	-	- 5.7 ° (*c* 1)
Molecular formula	$C_{37}H_{62}O_{14}$	$C_{41}H_{70}O_{14}$	$C_{45}H_{78}O_{14}$	$C_{49}H_{86}O_{14}$	$C_{53}H_{94}O_{14}$
Calcd MW	(730.89)	(787.00)	(843.11)	(899.21)	(955.32)
C	Calcd: 60.80 Found: 61.21	Calcd: 62.57 Found: 65.40	-	-	Calcd: 66.64 Found: 66.96
H	Calcd: 8.55 Found: 9.51	Calcd: 8.96 Found: 9.45	-	-	Calcd: 9.92 Found: 10.00

(*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 5.38 (dd, 1H, H-4), 5.24 (dd, 1H, H-2), 5.30 (dd, 1H, H-3), 5.05 (d, 1H, H-1), 4.20 – 4.35 (m, 6H, H-6a, H-6b, 1′-, 3′-CH_2), 3.68 – 3.76 (m, 1H, 2′-CH), 3.95 (ddd, 1H, H-5), 2.34 (m, 4H, α-CH_2), 1.58 - 1.64 (m, 4H, β-CH_2), 2.15, 2.10, 2.05, 1.99 (s, 3H, OAc), 1.25 (bs, 48H, -$(CH_2)_{12}$-), 0.88 (t, 6H, 2x CH_3); $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 3.6, $J_{5,6b}$ = 2.1 Hz.

1,3-Di-*O*-acyl-2-*O*-(2-acetamido- 3, 4, 6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-sn-glycerin (44a-e). Compound **39** was acylated by the same procedure as for compounds **41a-e**. The reaction was monitored by TLC with toluene/ethyl acetate 1:1. The raw product was crystallized from methanol or ethanol or purified by column chromatography with toluene/ethyl acetate 1:1. Table 3 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 7 and 8.

1,3-Di-*O*-acyl-2-*O*-(β-D-glucopyranosyl)-sn-glycerol (45a-e). Compounds **41a-e** were dissolved in methanol, hydrazine hydrate (80 %, 2 eq per OAc group) was added and the mixture refluxed for 1 h. After stirring overnight the reaction mixture was neutralized with formic acid under cooling, followed by concentration of the solvent. The compounds were purified by column chromatography (chloroform/methanol 20:1) followed by

Table 2: Data for preparation of compounds **42a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	42a (m = 8)	**42b** (m = 10)	**42c** (m = 12)	**42d** (m = 14)	**42e** (m = 16)
33	4.40 g (10.4 mmol)	4.64 g (11.0 mmol)	5.70 g (13.5 mmol)	4.46 g (10.6 mmol)	13 g (30.8 mmol)
anhydr. CH_2Cl_2	35 mL	30 mL	40 mL	30 mL	70 mL
Pyridine	6.3 mL	6.64 mL	8.16 mL	6.4 mL	18.6 mL
$H_3C(CH_2)_mCOCl$	5.34 mL	6.53 mL	9.15 mL	7.97 mL	25.6 mL
R_f in tol/EtOAc 5:1	0.45	0.47	0.47	0.49	0.52
Yield	4.24 g (5.80 mmol) 56 %	6.12 g (7.78 mmol) 71 %	9.40 g (11.1 mmol) 83 %	6.55 g (7.28 mmol) 69 %	21.48 g (22.5 mmol) 73 %
mp	syrup	syrup	syrup	58 °C	syrup
$[\alpha]^{20}_D$ ($CHCl_3$)	-	+ 2.0 ° (*c* 1)	+ 1.0 ° (*c* 1)	0 ° (*c* 1)	+ 2.2 ° (*c* 1)
Molecular formula	$C_{37}H_{62}O_{14}$	$C_{41}H_{70}O_{14}$	$C_{45}H_{78}O_{14}$	$C_{49}H_{86}O_{14}$	$C_{53}H_{94}O_{14}$
Calcd MW	(730.89)	(787.00)	(843.11)	(899.21)	(955.32)
C	-	-	-	Calcd: 65.49 Found: 65.63	Calcd: 66.62 Found: 67.44
H	-	-	-	Calcd: 9.57 Found: 9.67	Calcd: 9.83 Found: 10.19

Table 3: Data for preparation of compounds **44a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	44a (m = 8)	**44b** (m = 10)	**44c** (m = 12)	**44d** (m = 14)	**44e** (m = 16)
39	3.13 g (7.4 mmol)	3.41 g (7.8 mmol)	3.45 g (7.9 mmol)	3.09 g (7.3 mmol)	2.81 g (6.7 mmol)
anhydr. CH_2Cl_2	5 mL	5 mL	5 mL	100 mL	10 mL
Pyridine	4.8 mL	4.5 mL	4.5 mL	4.5 mL	4.3 mL
$H_3C(CH_2)_mCOCl$	3.81 mL	4.65 mL	4.5 mL	4.5 mL	4.3 mL
R_f in tol/EtOAc 1:1	0.42	0.43	0.45	0.46	0.47
Yield	3.53 g (4.8 mmol) 65 %	3.79 g (4.8 mmol) 61 %	4.95 g (5.9 mmol) 74 %	6.46 g (7.2 mmol) 98 %	5.27 g (5.5 mmol) 83 %
mp	109.1 - 115.5 °C	107.4 - 110.9 °C	106.8 - 110.3 °C	101.1 - 108.8 °C	100.5 - 109.5 °C
$[\alpha]^{20}_D$ ($CHCl_3$)	-7.7 (*c* 1)	-7.7 (*c* 1)	-6.7 (*c* 1)	-5.9 (*c* 1)	-5.5 (*c* 1)
Molecular formula	$C_{37}H_{63}NO_{13}$	$C_{41}H_{71}NO_{13}$	$C_{45}H_{79}NO_{13}$	$C_{49}H_{87}NO_{13}$	$C_{53}H_{95}NO_{13}$
Calcd MW	(729.91)	(786.01)	(842.12)	(898.23)	(954.34)
C	Calcd: 60.89 found: 59.92	Calcd: 62.65 Found: 62.57	Calcd: 64.18 Found: 64.14	Calcd: 65.52 Found: 64.98	-
H	Calcd: 8.70 Found: 8.68	Calcd: 9.10 Found: 9.05	Calcd: 9.46 Found: 9.42	Calcd: 9.76 Found: 9.76	-
N	Calcd: 1.92 Found: 1.84	Calcd: 1.78 Found: 1.80	Calcd: 1.66 Found: 1.69	Calcd: 1.56 Found: 1.65	-

crystallisation from methanol. Table 4 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 9 and 10.

1,3-Di-*O*-acyl-2-*O*-(β-D-galactopyranosyl)-sn-glycerol (46a-e). The preparation of compounds **42a-e** followed the procedure as for compounds **45a-e**. Table 5 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 9 and 10.

1,3-Di-*O*-hexadecyl-2-*O*-(β-D-mannopyranosyl)-sn-glycerol (47). Compound **43** (90 mg, 0.1 mmol) was dissolved in anhydrous $MeOH/CH_2Cl_2$ 1:1 (10 mL) and ethanolic hydrazine hydrate (24 %, 255 μL) was added and stirred for 25 min at 60 °C and another 15 h at rt. The reaction mixture was neutralized with formic acid (2 - 3 drops), the precipitate was filtered and the solution was concentrated. The reaction was monitored by TLC with chloroform/methanol/acetone 8:1:1. The product was crystallized from methanol to yield crystalline **47** (22 mg, 30 %): mp 67 °C; $[\alpha]_D^{20}$ - 67 ° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 4.81 (d, H-1), 5.08 (dd, H-4), 4.19 - 4.33 (m, 6H, H-6a, H-6b, 2x CH_2 - glycerol), 3.63 - 3.78 (m, 4H, H-2, H-3, H-5, C-H-glycerol), 2.35 (m, 4H, α-CH_2), 1.55-1.61 (m, 4H, β-CH_2), 1.23 (bs, 48H, 2 -$(CH_2)_{12}$-), 0.86 (t, 6H, 2 -CH_3); $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.1, $J_{3,4}$ = 9.7, $J_{4,5}$ = 10.2, $J_{5,6a}$ = 3.6, $J_{5,6b}$ = 2.1 Hz.

Anal. Calcd for $C_{41}H_{76}O_{10}$ (729.00): C, 67.54; H 10.51. Found.: C, 66.70; H, 10.73

1,3-Di-*O*-acyl-2-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-sn-glycerol (48a-e). Compounds **48a-e** were dissolved in chloroform (20 mL) and ethanol (85 %, 20 mL) and hydrazine hydrate (100 %, 2 eq per OAc group) was added and the mixture refluxed for 3 h. After complete conversion the reaction mixture was neutralized with formic acid under cooling, followed by evaporation of the solvent. The compounds were purified by column chromatography (chloroform/methanol 20:1) followed by crystallisation from methanol. Table 6 shows the reaction data and the characteristics for the compounds, ^{1}H and ^{13}C NMR data are found in Tables 9 and 10.

1,3-Di-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-sn-glycerin (50). Method A (Imidate method):[46] 2,3,4,6-Tetra-*O*-benzyl-D-glucose (**49**, 2.58 g, 4.77 mmol) was dissolved under argon atmosphere in anhydrous dichloromethane (35 mL). The reaction mixture was cooled to 0 °C and trichloroacetonitrile (2.58 mL, 25.7 mmol) was added. After addition of dry K_2CO_3 (2.58 g, 18.7 mmol) the reaction mixture was stirred for 5 h. The reaction was stopped by separation of the potassium carbonate from the solution by centrifugation (5000 rpm, 2 min, three times) and decantation. The solution was

Table 4: Data for the preparation of compounds **45a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	45a (m = 8)	**45b** (m = 10)	**45c** (m = 12)	**45d** (m = 14)	**45e** (m = 16)
41a-e	577 mg (0.79 mmol)	3.00 g (3.81 mmol)	3.43 g (4.06 mmol)	8.61 g (9.58 mmol)	6.60 g (6.91 mmol)
MeOH	19 mL	20 mL	50 mL	60 mL	50 mL
CH_2Cl_2	1 mL	5 mL	-	10 mL	
hydrazine hydrate	0.29 mL	2.19 mL	2.04 mL	5.50 mL	4.00 mL
Yield	138 mg (0.25 mmol) 31 %	0.40 g (0.65 mmol) 17 %	0.98 g (1.45 mmol) 36 %	2.01 g (2.75 mmol) 29 %	2.50 g (3.17 mmol) 46 %
mp	70.5 °C	76 °C	82.2 °C	87.7 °C	91.5 °C
$[\alpha]^{20}_D$ ($CHCl_3$)	- 4.5° (*c* 1)	- 6.6 (*c* 1)	- 1.1 (*c* 1)	- 1.8 (*c* 1)	-
Molecular formula	$C_{29}H_{54}O_{10}$	$C_{33}H_{62}O_{10}$	$C_{37}H_{70}O_{10}$	$C_{41}H_{78}O_{10}$	$C_{45}H_{86}O_{10}$
Calcd MW	(562.74)	(618.85)	(674.96)	(731.06)	(787.17)
C	-	Calcd: 64.05 Found: 63.85	Calcd: 65.84 Found: 66.81	Calcd: 67.36 Found: 67.44	Calcd: 68.66 Found: 68.33
H	-	Calcd: 10.10 Found: 10.01	Calcd: 10.45 Found: 10.58	Calcd: 10.75 Found: 10.60	Calcd: 11.01 Found: 10.88

Table 5: Data for preparation of compounds **46a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	46a (m = 8)	**46b** (m = 10)	**46c** (m = 12)	**46d** (m = 14)	**46e** (m = 16)
42a-e	11.00 g (15.05 mmol)	15.00 g (19.06 mmol)	8.50 g (10.08 mmol)	6.20 g (6.89 mmol)	10.00 g (10.47 mmol)
MeOH	70 mL	50 mL	60 mL	45 mL	70 mL
hydrazine hydrate	8.68 mL (9.5 eq)	10.95 mL (9.5 eq)	5.80 mL (9.5 eq)	4.00 mL (9.5 eq)	6.10 mL (9.5 eq)
Yield	2.50 g (4.44 mmol) 30 %	3.30 g (5.33 mmol) 28 %	2.00 g (2.96 mmol) 29 %	1.70 g (2.33 mmol) 34 %	1.90 g (2.41 mmol) 23 %
mp	59.5 °C	74 °C	81.7 °C	80.5 °C	82 °C
$[\alpha]^{20}_D$ ($CHCl_3$)	- 1.0 (*c* 1)	- 1.3 (*c* 1)	- 2.9 (*c* 1)	- 0.6 (*c* 1)	- 0.5 (*c* 1)
Molecular formula	$C_{29}H_{54}O_{10}$	$C_{33}H_{62}O_{10}$	$C_{37}H_{70}O_{10}$	$C_{41}H_{78}O_{10}$	$C_{45}H_{86}O_{10}$
Calcd MW	(562.74)	(618.85)	(674.96)	(731.06)	(787.17)
C	Calcd: 61.90 Found: 62.53	Calcd: 64.05 Found: 64.91	Calcd: 65.84 Found: 66.09	Calcd: 67.36 Found: 67.70	Calcd: 68.66 Found: 67.14
H	Calcd: 9.67 Found: 10.13	Calcd: 10.10 Found: 10.30	Calcd: 10.45 Found: 10.36	Calcd: 10.75 Found: 10.65	Calcd: 11.01 Found: 10.92

Table 6: Data for preparation of compounds **48a-e** (acyl: **a** = decanoyl; **b** = dodecanoyl; **c** = tetradecanoyl; **d** = hexadecanoyl; **e** = octadecanoyl).

	48a (m = 8)	**48b** (m = 10)	**48c** (m = 12)	**48d** (m = 14)	**48e** (m = 16)
44a-e	2.00 g (2.7 mmol)	2.00 g (2.54 mmol)	3.54 g (4.20 mmol)	5.00 g (5.57 mmol)	5.00 g (5.24 mmol)
hydrazine hydrate	0.81 mL (16.2 mmol)	0.76 mL (15.2 mmol)	1.26 mL (25.2 mmol)	1.67 mL (33.4 mmol)	1.57 mL (31.4 mmol)
Yield	1.06 g (1.75 mmol) 65 %	1.00 g (1.52 mmol) 60 %	1.43 g (2.00 mmol) 49 %	3.00 g (3.89 mmol) 70 %	1.95 g (2.35 mmol) 45 %
mp	133 °C	135.5 °C	136 °C	136.5 °C	138 °C
$[\alpha]^{20}_D$ ($CHCl_3$)	- 16.0 (*c* 0.5)	- 15.9 (*c* 0.5)	- 41 (*c* 1)	- 9.1 (*c* 0.5)	- 8.7 (*c* 0.5)
Molecular formula	$C_{31}H_{57}NO_{10}$	$C_{35}H_{65}NO_{10}$	$C_{39}H_{73}NO_{10}$	$C_{43}H_{81}NO_{10}$	$C_{47}H_{89}NO_{10}$
Calcd MW	(603.79)	(716.01)	(772.12)	(828.22)	(954.34)
C	Calcd: 61.67 Found: 60.87	Calcd: 63.70 Found: 63.07	Calcd: 65.41 Found: 65.29	Calcd: 66.89 Found: 67.00	-
H	Calcd: 9.52 Found: 9.48	Calcd: 9.93 Found: 9.91	Calcd: 10.28 Found: 10.28	Calcd: 10.57 Found: 10.87	-
N	Calcd: 2.32 Found: 2.23	Calcd: 2.12 Found: 2.14	Calcd: 1.95 Found: 1.95	Calcd: 1.81 Found: 1.86	-

concentrated to dryness and the raw imidate and 1,3-di-*O*-benzylglycerol (**25**, 1.35 g, 4.96 mmol) were dissolved under argon in anhydrous diethyl ether, cooled to 0 °C and a solution of TMS triflate in anhydrous diethylether (120 µL of 0.72 mL in 10 mL diethyl ether) was added. The reaction was monitored by TLC with PE/Et_2O 1:1 and stopped after 50 min by addition of solid sodium hydrogen carbonate. The reaction mixture was neutralized with saturated sodium hydrogen carbonate, washed two times with water dried over sodium sulfate, filtered and concentrated to dryness. The anomers were separated by column chromatography with petroleum ether/chloroform/diethylether 10:3:3 to give the syrupy α-anomer **50** (0.796 g, 1.00 mmol, 21 %) and an unseparated anomeric mixture (1.24 g, 1.55 mmol, 32 %).

Method B: 1-*O*-acetyl-2,3,4,6-tetra-*O*-benzyl-D-glucopyranose[45] (118 mg, 0.20 mmol) was dissolved under argon in anhydrous dichloromethane and 1,3-di-*O*-benzyl-glycerol (70.0 mg, 1.1 eq) and BF_3-etherate (28 µL, 1.1 eq) were added. The reaction was stopped after stirring for 2 ½ h with exclusion of light by addition of saturated sodium hydrogen carbonate solution. Dichloromethane was added and the mixture was washed two times with water. The organic layer was dried over magnesium sulfate and concentrated to dryness. The raw material was separated by column chromatography with petroleum

Table 7: ^{13}C NMR data: Chemical shifts δ ($CDCl_3$, TMS) of compounds **41a**, **42a**, **44a**.

	41a	**42a**	**44a**
C-1	100.8	100.9	99.6
C-2	71.3	68.8	54.8
C-3	71.9	70.8	72.3
C-4	68.4	66.3	68.4
C-5	72.8	70.9	71.8
C-6	61.9	61.3	62.9
glycerol-C-1′,-C-3′	63.2, 63.0	63.2, 63.1	62.6, 62.1
glycerol-2′-CH	75.7	75.2	74.8
2x COO-acyl	173.4, 173.2	173.4, 173.3	173.7, 173.4
2x α-CH_2	34.1	34.0	33.9, 33.8
2x β-CH_2	24.9	24.8	24.7, 24.6
2x $(CH_2)_{m-2}$	24.6 - 34.1	24.6 – 35.3	31.6, 29.5-29.1
2x acyl-CH_3	14.1	14.1	13.9
4x $\underline{C}OCH_3$	170.7, 170.2, 169.4, 169.1	170.7, 170.1, 169.5, 169.2	170.6-169.2
4x $CO\underline{C}H_3$	20.8, 20.6, 20.5, 20.4	22.3, 20.8, 20.7, 20.6	22.5-20.2

ether/chloroform/diethyl ether 10:3:2 to yield the α-anomer **50** as a colourless syrup (92.4 mg, 53 %) and the β-product as a wax (26.9 mg, 16 %).

Method C: Compounds **49** (2.59 g, 4.79 mmol) and **25** (1.44 g, 1.1 eq) and *p*-toluene sulfonic acid (0.91 g, 1 eq) were dissolved in toluene (120 mL) and stirred in an oil bath (70 °C) for 7 h. The reaction was stopped by stirring with saturated sodium hydrogen carbonate solution. The mixture was neutralized with saturated sodium hydrogen carbonate solution, washed with water, and the organic layer was dried with magnesium sulfate, filtered and concentrated to dryness. The raw material was purified by column chromatography with petroleum ether/chloroform/diethyl ether 10:3:2 to yield a mixture of anomers (0.74 g, 0.93 mmol, 19 %).

α-Anomer: $[\alpha]_D^{20}$ + 39.4 ° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ = 7. 33 - 7.21, 7.14 - 7.10 (m, 30H, $CH_2C_6\underline{H}_5$), 5.21 (d, 1H, H-1), 4.98, 4.81, 4.79, 4.67, 4.62, 4.56, 4.44, 4.36 (d, 1H, $C\underline{H}_2C_6H_5$), 4.53, 4.46 (s, 2H, $C\underline{H}_2C_6H_5$), 4.14 (m, 1H, 2′-CH-glycerol), 4.03 (ddd, 1H, H-5), 3.98 (dd, 1H, H-3), 3.68 - 3.52, 3.46 - 3.41 (m, 8H, H-2, H-4, H-6, 1′-, 3′-CH_2-glycerol); $J_{1,2}$ = 3.6 Hz; ^{13}C NMR ($CDCl_3$): δ = 139.4 - 138.5, 128.8 - 127.9 (C_6H_5), 96.6 (C-1), 82.4 (C-3), 80.0 (C-2), 78.1 (C-4), 75.2 (C-2′-glycerol), 76.0 - 72.8 ($CH_2C_6H_5$), 71.1, 70.9 (1′-, 3′-glycerol), 68.8 (C-6).

β-Anomer: $[\alpha]_D^{20}$ + 11.0 ° (*c* 1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ = 137.6 - 137.1, 127.4 - 126.4 (C_6H_5), 102.4 (C-1), 82.4 (C-3), 80.0 (C-2), 78.1 (C-4), 75.2 (C-2′-glycerol), 76.0 - 72.8 ($CH_2C_6H_5$), 71.1, 70.9 (1′-, 3′-glycerol), 68.8 (C-6).

Table 8: ^{1}H NMR data: Chemical shifts δ ($CDCl_3$, TMS) and coupling constants J (Hz) of compounds **41a**, **42a**, **44a**.

	41a	**42a**	**44a**
H-1	4.64, d	4.59, d	4.86, d
H-2	4.99, dd	5.19, dd	3.77, ddd
H-3	5.20, dd	5.00, dd	5.32, dd
H-4	5.07, dd	5.37, dd	5.05, dd
H-5	3.69, ddd	3.91, ddd	3.70, m
NH	-	-	5.57, d
glycerol-1′-a			4.38, dd
glycerol-1′-b			4.01, dd
H-6a, H-6b, glycerol-3′-CH_2, glycerol-2′-CH_2	4.05 – 4.26, m	4.02 – 4.28, m	4.29-4.04, m
2x α-CH_2	2.31, m	2.31, m	2.32, m
2x β-CH_2	1.55-1.65, m	1.61-1.65, m	1.61, m
2x $(CH_2)_{m-2}$	1.30, bs	1.25, bs	1.27, bs
2x alkyl-CH_3	0.88, t	0.89, t	0.88, dd
4x $COCH_3$	2.26, 2.19, 2.16, 2.09, 4s	2.15, 2.05, 2.04, 1.98, s	2.09, 2.02, 2.01, 1.94, s
$J_{1,2}$	8.1	8.1	8.1
$J_{2,3}$	9.7	10.7	10.2
$J_{2,NH}$	-	-	8.7
$J_{3,4}$	10.7	3.6	9.7
$J_{4,5}$	10.7	1.1	9.7
$J_{5,6a}$	5.1	6.6	5.1
$J_{5,6b}$	2.5	6.6	2.6
$J_{6a,6b}$			12.2
$J_{1'a,1'b}$			11.7
$J_{1'a,2}$			3.6
$J_{1'b,2}$			5.1

2-*O*-(α-D-Glucopyranosyl)-sn-glycerin (51). Compound **50** (2.24 g, 2.82 mmol) was dissolved in ethyl acetate/methanol 1:1 under argon and Pd/C (10 %, 0.23 g) was added. The atmosphere was changed to hydrogen and the mixture was stirred for 8 h. Pd/C was filtered over Celite and the solution was concentrated to dryness. The crude product was dissolved in bidistilled water and filtered. Lyophilisation gave syrupy **51** (0.65 g, 2.56 mmol, 91 %): $[\alpha]_D^{20}$ 130 ° (*c* 1, H_2O) [ref.:[54] $[\alpha]_D^{20}$ 121 ° (*c* 1, H_2O)]; ^{1}H NMR (D_2O/acetone): δ = 5.22 (d, 1 H, H-1, $J_{1,2}$ = 3.56 Hz), 3.97 - 3.78 (m, 9 H, H-3, H-5, H-6a, H-6b, 1′-, 3′-CH_2, H-2′-CH), 3.65 (dd, 1 H, H-2, $J_{2,3}$ = 9.66 Hz), 3.52 (dd, 1 H, H-4, $J_{3,4}$ = 9.15 Hz). ^{13}C NMR (D_2O/acetone): δ = 98.2 (C-1), 79.1 (C-2′), 73.3 (C-3), 72.3 (C-5), 71.9 (C-2), 69.9 (C-4), 61.7 (C-6), 60.8, 60.7 (C-1′, C-3′).

Table 9: ^{1}H NMR data: Chemical shifts δ ($CDCl_3$, TMS) and coupling constants J (Hz) of compounds **45a**, **46a** and **48a**.

	45a	**46a**	**48a**
H-1	4.41, d	4.36, d	4.52, d
H-3		3.83, m	3.60, dd
H-4	3.59-3.50, m, 3.41, 3.33	3.68-3.55, m	3.49, dd
H-2, H-5			3.42, m
NH	-	-	6.55, d
H-6a	3.92, m	3.99	3.92, m
H-6b	3.77, m	3.96	3.75, m
2-OH			-
3-OH	2.96, 3.82, 3.67, 3.52	2.87 - 2.63	6.05, m
4-OH			3.42, m
6-OH			2.87, t
Glycerol-1′-CH_2-a			4.65, dd
Glycerol-1′-CH_2-b	4.38, 4.27,	4.37, 4.34, 4.18,	3.98, dd
Glycerol-3′-CH_2-a	4.20, 4.16	4.16	4.27, dd
Glycerol-3′-CH_2-b			4.10,
Glycerol-2′-CH	4.03, m	4.05, m	m
2x α-CH_2	2.32, m	2.33, m	2.34, m
2x β-CH_2	1.60, m	1.60, m	1.61, m
2x $(CH_2)_{m-2}$	1.28, bs	1.28, bs	1.27, bs
2x Alkyl-CH_3	0.88, t	0.88, t	0.88, t
NHCOCH_3	-	-	2.09, s
$J_{1,2}$	7.6	8.1	8.1
$J_{2,3}$	9.7	10.7	8.7
$J_{2,NH}$	-	-	3.6
$J_{3,4}$	10.7	3.5	9.7
$J_{4,5}$	10.7	1.5	9.2
$J_{5,6}$	5.1, 2.5	6.6	
$J_{6a,6b}$	11.2		11.7
$J_{1'a,1'b}$			12.2
$J_{1'a,2}$			2.0
$J_{1'b,2}$			3.6
$J_{2',3'a}$			8.6
$J_{3'a,3'b}$			14.2
$J_{6a,OH}$	-		7.2
$J_{6b,OH}$	-		6.6

Table 10: ^{13}C NMR data: Chemical shifts δ of compounds **45a** (CD_3OD), **46a** (CD_3OD) and **48a** ($CDCl_3$, TMS).

	45a	**46a**	**48a**
C-1	103.3	100.6	99.2
C-2	74.1	70.9	58.1
C-3	75.3	71.8	75.8
C-4	74.1	68.2	71.8
C-5	76.6	72.5	75.5
C-6	63.0	62.7	62.4
Glycerin-C-1', -C-3'	63.7, 63.4	63.4, 63.1	61.6, 62.1
Glycerin-2'-CH	70.5	74.9	74.0
2x COO-Alkanoyl	172.5	173.4	173.3, 173.3
2x α-CH_2, 2x β-CH_2, 2x $(CH_2)_{m-2}$	33.8 - 19.6	33.8 - 19.6	34.0, 33.8 24.5, 24.4 31.4, 29.0-28.7, 22.2
2x Alkyl-CH_3	13.2	14.2	13.6
$NHCOCH_3$	-	-	174.3
$NHCOCH_3$	-	-	22.6

Tables 7-10 exemplarily show the NMR data of the decanoyl substituted glycolipids **41a**, **42a**, **44a**, **45a**, **46a** and **48a**. The other homologues have the same chemical shifts and coupling constances and give corresponding spectra, except for the integration of the alkyl hydrogen section.

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