

Synthesis and mesomorphic properties of glycolipids and neoglycolipids

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Abbreviations

The following abbreviations have been used in the text.

abs.	absolut
Ac	acetyl
AcCl	chloroacetyl
Bn	benzyl
CAN	ceric ammonium nitrate
ch	cholesteric
col	columnar
Cr	crystalline
cub	cubic
DCC	<i>N, N'</i> -dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
DMF	<i>N, N</i> -dimethylformamide
EtOAc	ethyl acetate
FAB	fast atom bombardment
Gal	galactose
Glc	glucose
Gen	gentiobiose
H ₁	normal hexagonal
H ₂	inverted hexagonal
I ₁	discontinuous cubic phase with a normal aggregate structure
I ₂	discontinuous cubic phase with an inverted aggregate structure
I	isotropic
Isomal	isomaltose
L _α	lamellar
Lac	lactose
Mal	maltose
Mel	melibiose
PMB	<i>para</i> -methoxybenzyl
<i>p</i> -TsOH	<i>para</i> -toluenesulfonic acid

S_A	smectic A
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
T_c	chain melting temperature (α -phase \leftrightarrow β -phase)
t.l.c.	thin layer chromatography
TMS	tetramethyl silane
V_1	bicontinuous cubic phase with a normal aggregate structure
V_2	bicontinuous cubic phase with an inverted aggregate structure
$\nu_s(\text{CH}_2)$	symmetric stretching vibration of the methylene groups
WAXS	wide-angle X-ray scattering
wt %	weight percent

1. Introduction

One of the most important prerequisites for life is a boundary as delimitation of the organised and ordered cell interior against the more or less chaotic outer world. However, this border has to be semipermeable, permitting a selective exchange of nutrients and metabolites with the environment, without which life as an open system would be impossible. This function is accomplished by the cell membranes, for which nature uses amphiphilic liquid crystals – the lipids – as building blocks. In the same manner the cytoplasm is divided by membranes into smaller substructures for special processes and reactions.

It was believed for a long time that the lipids only form an inert matrix embedding the important proteins. This view had to be changed within the last decade since a great deal of experimental evidence points towards an important functional role of membrane lipids and their supramolecular aggregates in many cell processes, e.g. cell fusion and exocytosis (Rilfors et al., 1989). A better understanding of the underlying principles of these processes may allow future development of liposomes as drug-carriers for tissue-specific drug delivery and lead to a better understanding of processes such as the virus-cell fusion as the first step of an infection. Thus, the first question is, how do lipids aggregate, and the second is which kind of supramolecular structures do they form?

1.1 Supramolecular structures and mesogenic properties of lipids

Lipids, due to their amphiphilic nature, form supramolecular structures in aqueous systems as well as in their pure state upon heating. The common structural feature of these aggregates is the separation of hydrophilic and hydrophobic molecular moieties at a plane which curves around the minor component, if the polar and unpolar moiety differ in size (Figure 1.1 A and C). The overall molecular shape is in this case wedge-shaped and leads to the formation of columnar mesophases. However, in the case of a comparable size of the hydrophilic and hydrophobic moieties the rod-like molecules pack to form the extensive planar bilayers of the lamellar phase (Figure 1.1 B), which stack one on top of the other, each separated in aqueous systems by a layer of water. Depending on concentration and/or temperature, amphiphilic molecules may thereby form one or more of the following supramolecular structures (mesophases):

1. lamellar liquid crystalline phases (L_α)
2. normal (H_1) or inverted (H_2) hexagonal phases.
3. a number of cubic phases.

Furthermore, in solution micelles with a normal (L_1) or an inverted aggregate structure (L_2) may occur. The well known structures of the *lamellar* and *hexagonal phases* are depicted in Figure 1.1 whereas the exact structure of *cubic phases* is in many cases still unclear.

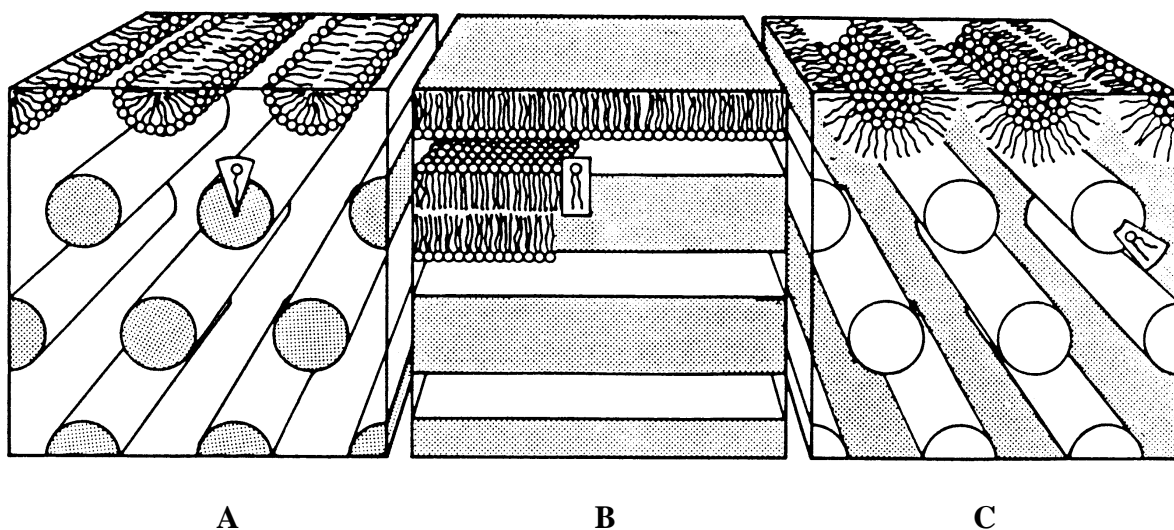


Figure 1.1: Structure of anisotropic liquid crystalline phases formed by amphiphilic molecules (from Rilfors et al., 1984). A: normal hexagonal (H_1) phase; B: lamellar (L_α) phase; C: inverted hexagonal (H_2) phase.

Note the various shapes of the amphiphilic molecules and the resulting supramolecular arrangement. Wedge-shaped molecules (A and C) give hexagonal phases whereas rod-like molecules (B) form lamellar phases.

Figure 1.2 displays the principle phase behaviour of an amphiphile, i.e. which kind of supramolecular structure (mesophase) may be observed with increasing concentration or temperature. The whole sequence of phases might theoretically be observed for a particular amphiphile, if the concentration or temperature is changed, but in many cases only some are found. The cubic phases are interspersed in the phase diagram between the other main phases, liquid crystalline or liquid. Depending on the type of the neighbouring phases it is possible to tentatively assign the type of a particular cubic phase, i.e. belonging to the normal or inverted

type as well as the differentiation between discontinuous and bicontinuous (see below). Phases on the water-rich side of the lamellar phase are considered to be of the „oil-in-water“ type and are given the subscript 1 („normal type“), while those on the water-poor side are considered to be of the „water-in-oil“ type and are given the subscript 2 (so called „inverted“ type). In phases of type 1, the polar/unpolar plane (the plane at which the hydrophilic and hydrophobic molecular moieties separate) is curved towards the fluid hydrocarbon chain region, which is surrounded by the hydrophilic headgroups (Figure 1.1 A). Just the opposite is true in the case of phases of type 2 (Figure 1.1 C). The polar/unpolar plane curves always towards the minor component, i.e. the molecular moiety with the smaller space demand.

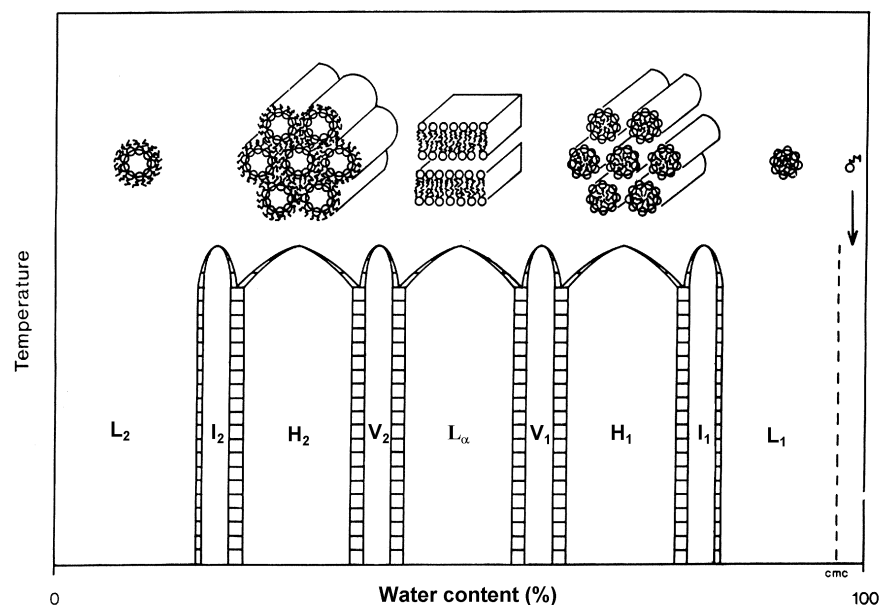


Figure 1.2: Principle phase behaviour of amphiphilic molecules

(adopted from Tiddy, 1980)

From a systematic point of view it is useful to divide the cubic phases into two subtypes (for reviews see: Lindblom and Rilfors, 1989; Fontell 1990):

discontinuous cubic phases formed by various packings of isotropic or slightly anisotropic micelles with a normal (I_1) or inverted (I_2) aggregate structure in a cubic elementary cell.

bicontinuous cubic phases with a normal (V_1) or inverted (V_2) structure. Most of the cubic phases formed by membrane lipids have been shown to have such a bicontinuous structure

(Rilfors et al., 1986). These structures can be described best by infinite periodic minimal surfaces (IPMS) known from differential geometry (Scriven, 1976). IPMS are surfaces where the average curvature is zero, i.e. concave and convex curvatures of the surface balance each other everywhere. In the case of the more frequent – and for the subsequent considerations more interesting – bicontinuous cubic phases the structure can be visualised by a lipid bilayer centred on such an infinite periodic minimal surface and separating two water filled channel systems. The IPMS is draped on either side with one leaflet of the bilayer and the methyl groups of the hydrocarbon chains touch each other on the IPMS. There are three basic infinite periodic minimal surfaces and one of them, the so-called Schwarz' surface of the space group $Im3m$ is depicted in Figure 1.3.

The normal state of a cell membrane is the lamellar L_{α} phase. Thus, the next question is, how can these bicontinuous cubic structures (i.e. non-lamellar structures) form and influence biological processes?

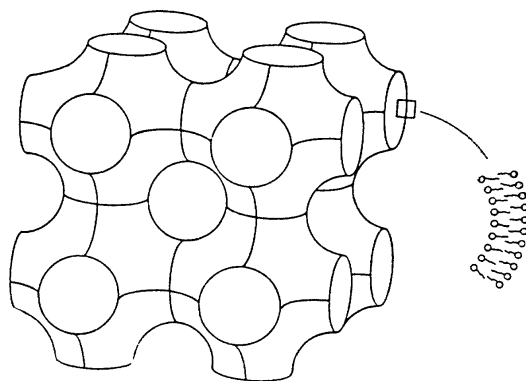


Figure 1.3: IPMS of the space group $Im3m$ (from Rilfors et al., 1989)

1.2 Biological relevance of non-bilayer structures

There is a great deal of experimental and theoretical evidence showing that bicontinuous cubic phases may play an important role in processes such as membrane fusion and membrane traffic (Siegel, 1986; Ellens et al., 1989; Siegel et al., 1989; Nivea et al., 1995), as they can be found for example during exocytosis or the virus-cell fusion in the course of an infection.

The molecular mechanism behind the fusion process is only poorly understood. It is known that the key step in a fusion process has to be the rearrangement of the lipid molecules of the formerly apposed two bilayers (i.e. the cell membranes of two neighbouring cells; see Figure

1.4) to form a single, continuous membrane connecting both cells.

Siegel (Siegel, 1986) describes in his theoretical considerations concerning the fusion process a number of inter-membrane structures which may participate at the $L_{\alpha} \rightarrow H_2$ (lamellar to non-lamellar) transition and which are in good accordance with the NMR, DSC and EM data of this transition.

The first structures to form in an $L_{\alpha} \rightarrow H_2$ transition are, according to Siegel, short-lived *inverted micellar intermediates* (IMI) within the two apposed bilayers (Figure 1.4). The IMI resemble inverted micelles and can diffuse freely within the plane between the two apposed bilayers and assemble into larger structures and finally transform thereby into an H_2 phase. There is however another possibility. The IMI are metastable structures in dynamic equilibrium with the original apposed bilayer structures and while reverting they can also revert to another bilayer structure, the *interlamellar attachment* (ILA) instead of reverting to the original bilayer. The ILA makes the two original bilayers continuous around the edge of an interlamellar pore and allows mixing of the aqueous content of two apposed vesicles or cells without leakage of the contents to the external medium, and exactly this is the crucial intermediate for membrane fusion.

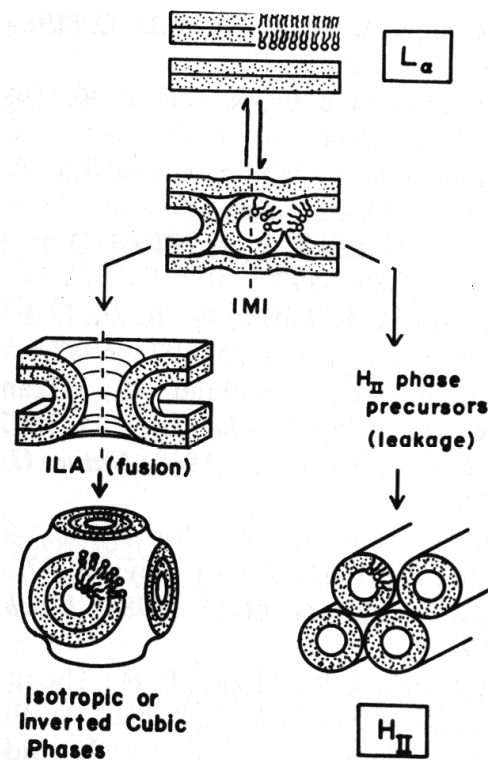


Figure 1.4: Mechanism and intermediates proposed by Siegel for membrane-membrane interactions leading to fusion or H_2 phase formation (from Ellens et al., 1989).

According to Siegels' kinetic theory of the $L_{\alpha} \rightarrow H_2$ transition, the ILA is a metastable state which cannot transform easily into the L_{α} phase nor into an IMI. The structure of the *interlamellar attachment* is similar to that of some bicontinuous cubic phases which can be formed under certain circumstances from them by assembly.

In the meantime, cubic phases have been reported for several lipids (Rilfors et al., 1986; Ellens et al., 1989; Seydel et al., 1989 and 1993; Brandenburg et al., 1990 and 1992). Additionally, Ellens (Ellens et al., 1986 and 1989) observed increased fusion of liposomes composed of N-methyl-dioleoyl-phosphatidylethanolamine (DOPE-Me) in the same temperature range in which isotropic ^{31}P -NMR resonances have been found in dispersions of this lipid. It is very likely that these isotropic signals belong to a liquid crystalline cubic structure as indicated by X-ray diffraction investigations by Gruner (Gruner et al., 1988), i.e. fusion occurs in the same temperature range as the formation of cubic structures. Furthermore, thermotropic cubic phases have been reported for alkyl glycosides (Fischer et al., 1994) and in the case of S,S-dialkyl acetals of inosose (Praefcke et al., 1990) a phase was found which is believed also to be cubic. The thermotropic cubic phase formed by alkyl glycosides was shown to be of the space group Ia3d (Fischer et al., 1994) which is also found for lyotropic cubic phases.

Another experiment by Siegel (Siegel et al., 1989) clearly demonstrated that membrane fusion and the formation of cubic phases proceed through a common intermediate, the ILA. Upon addition of 2 mol% diacylglycerol to a DOPE-Me model-system, the equilibrium $L_{\alpha} \rightarrow H_2$ transition temperature was lowered by 15 K as was the temperature of the occurrence of isotropic ^{31}P -NMR signals in multilamellar dispersions of the same model-system, being indicative for cubic phases. In addition, the isotropic signals occurred in the same temperature range in which increased fusion of unilamellar liposomes of the model-system was detected.

In vivo diacylglycerols are formed in biomembranes by the second messenger systems of the phosphoinositol cascade. If one considers that the principal reaction to stimulation is an exocytosis in most tissues, it seems very likely that diacylglycerols play an important role in the stimulus-response coupling in addition to their role in protein kinase C activation (Nivea et al., 1995).

The great importance of these cubic phases is once more stressed by the fact that the composition of many biomembranes is at physiological conditions close to the bilayer \rightarrow non-bilayer transition. A small change in the local membrane composition due to some triggering mechanism can therefore induce locally a transient non-bilayer structure as it is

needed for a fusion or exocytosis event. However, non-bilayer structures are not allowed to occur permanently in the membrane, since this would destroy its barrier properties. After a short time, diffusion causes the locally changed membrane composition to return to its normal state even without a further biochemical regulation mechanism, and the preservation of the barrier function of the membrane is ensured. From this point of view it is not surprising that the ratio between bilayer forming and non-bilayer forming lipids is regulated by cells and adjusted according to the actual environmental conditions (Lindblom et al., 1986; Wieslander et al., 1980 and 1986; Goldfine et al., 1987). While it has been well known for a long time that membrane-bound enzymes have to be surrounded by membrane lipids to ensure their function (Sandermann, 1978), new investigations show that a definite amount of non-bilayer forming lipids is necessary for membrane-bound enzymes and proteins to show their normal activity (Wiedemann et al., 1988; Jensen and Schutzbach, 1988; Pick et al., 1987; Siefermann et al., 1987).

2. Aim of this work

The discussion in Chapter 1 clearly demonstrates the great importance of the supramolecular structures and in particular of cubic structures formed by lipids for processes in membranes. At present, there is very little knowledge of the prerequisites to chemical structure for cubic phases to occur, and a dearth of model-systems which enable the correlation of the chemical structures with the mesogenic properties. The extraordinary stability of cubic phases might be based on a new structural principle. Lamellar and columnar phases are destabilised by sterically problematic sugar headgroups, which thus selectively stabilise cubic phases. The basic idea of this concept is depicted in Figure 2.1.

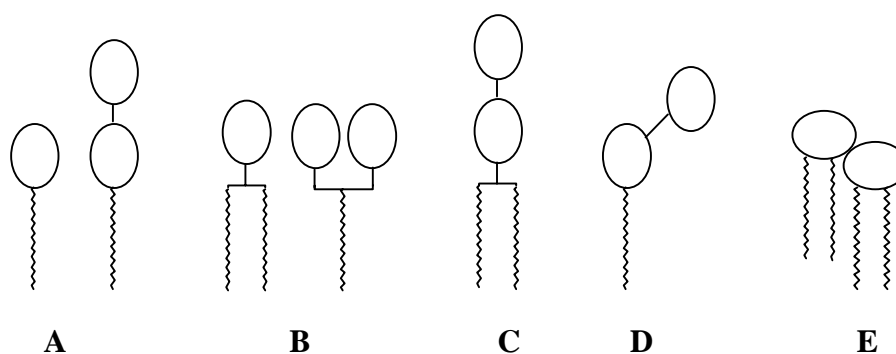


Figure 2.1: Structural concept

Amphiphiles of the general structure **A** display only smectic phases (Jeffrey and Wingert, 1992; Prade et al., 1995) and compounds of type **B** show columnar phases with the interfacial area being curved around the minor component (Mannock et al., 1987 and 1990; Jeffrey and Wingert, 1992; Prade et al., 1995). In the case of amphiphiles of type **C**, the headgroup prefers a lamellar structure while the aliphatic tails favour a hexagonal structure, but each is destabilised by the other moiety. As a result of frustration these molecules might form bicontinuous cubic structures. In the case of banana-shaped molecules of type **D** the situation is similar and thus cubic phases may be formed again (Fischer et al., 1994), and the same holds true for amphiphiles of type **E** (Brandenburg et al., 1990, 1992 and 1998) and many other naturally occurring glycolipids.

It is thus extremely interesting to discover, whether or not nature uses the demanding stereochemistry of carbohydrates in amphiphilic molecules to control the physical properties of membranes and in doing so also biological processes such as membrane traffic.

The aim of this work is to verify the concept sketched in Figure 2.1 and to derive

structure-property relationships governing the stability of cubic phases. Hence it is necessary to synthesise simple model-systems first which enable the correlation of the chemical structures with the mesogenic properties. The model systems to be synthesised are:

- * long-chain alkyl glycosides as the most simple model-systems (e.g. Figure 2.2)
- * glycosyl diacylglycerols (e.g. Figure 2.3).

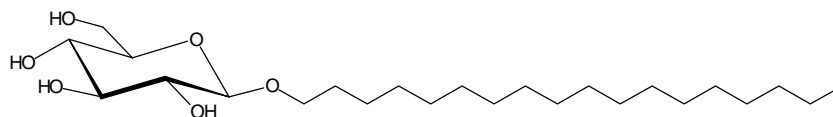


Figure 2.2: Stearyl-β-D-glucopyranoside

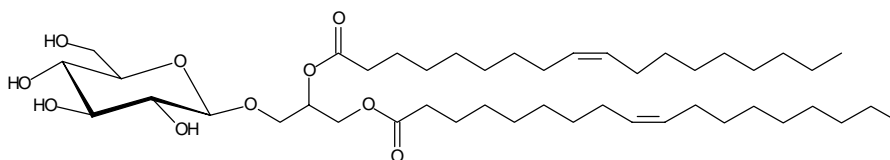


Figure 2.3: 1,2-Di-O-Oleoyl-3-O-(β-D-glucopyranosyl)-*sn*-glycerol

The structure of the sugar headgroup will be changed systematically, e.g. in:

- its length by using mono- and disaccharides
- its curvature by using 1→4 and 1→6 linked disaccharide headgroups.
- its configuration by using glucose or galactose

The thermotropic and lyotropic properties of these compounds will be determined by polarising microscopy and X-ray diffraction.

In doing so it should be possible to correlate the mesogenic properties and the stability of the observed phases with structural features, i.e. to derive structure-property relationships. In particular, the stability of bicontinuous cubic phases and the chemical structure prerequisites to their occurrence are of special interest.

In a second step the mixture properties of the synthesised compounds will be investigated in binary mixtures. The specific aim is to induce cubic phases in binary mixtures of compounds which do not show cubic phases in their pure state. In addition, the stability of these cubic phases shall be investigated in terms of composition of the mixture and temperature and to derive structure-property relationships for mixture systems.

3. Synthesis and mesogenic properties of alkyl glycosides

3.1 Introduction

The observation of a double melting of certain long-chain alkyl glucopyranosides, e.g. hexadecyl- β -D-glucopyranoside (Figure 3.1) by E. Fischer (Fischer and Helferich, 1911) was the first indication of thermotropic liquid crystalline properties in amphiphilic carbohydrates.

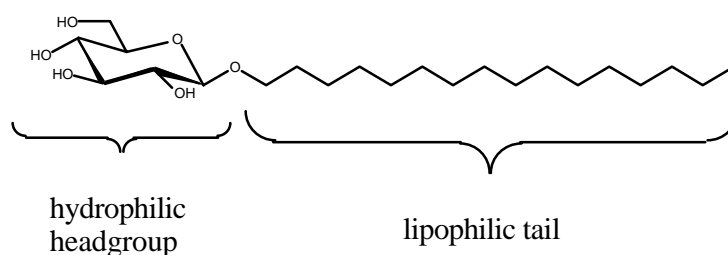


Figure 3.1: Hexadecyl- β -D-glucopyranoside

These amphotropic molecules form both thermotropic liquid crystalline phases in their pure state upon heating and lyotropic liquid crystalline phases upon addition of a solvent. The first observation of lyotropic behaviour is also related to studies on alkylated carbohydrates: while analysing the extracts from tuberculosis bacteria, R. Koch observed unusual optical textures of their aqueous dispersions (Koch, 1884).

The driving force for the mesophase formation in the case of amphiphilic molecules is a micro phase separation, leading to an aggregate structure with separated regions for the lipophilic and hydrophilic molecular moieties, enabling the maintenance of van der Waals interaction in the hydrophobic region and of hydrogen bonding in the hydrophilic region, each stabilising the formed mesophase.

The principle phase behaviour of these compounds is shown in Figure 3.2 (Tiddy, 1980; Prade et al., 1995; Blunk et al., 1998). A typical amphiphile is represented in this diagram by a vertical line and usually exhibits only one mesophase, but in the case of an unusual geometry of the hydrophilic headgroup polymorphism can occur. In this case cubic phases may also be observed (S. Fischer et al., 1994), while simple amphiphiles such as the one shown in Figure 3.1 normally exhibit thermotropically only a S_A phase (G. A. Jeffrey and L. M. Wingert, 1992).

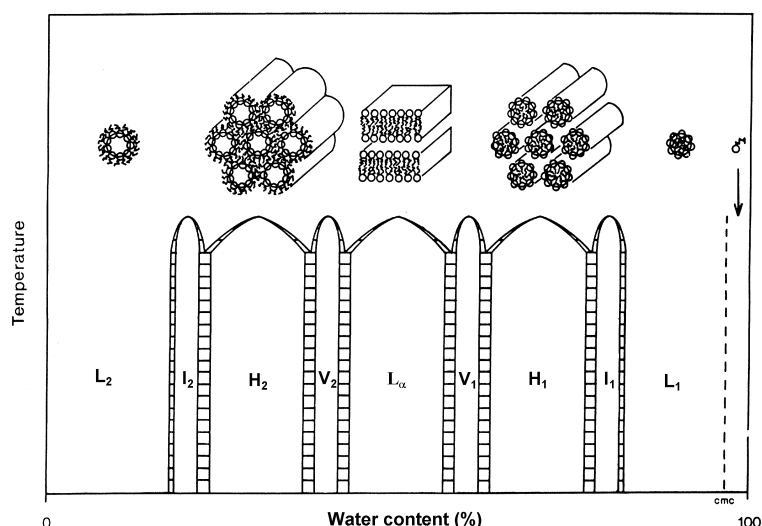


Figure 3.2: Principle phase behaviour of amphiphilic compounds

Deviation from the above-mentioned vertical line may also be seen upon the addition of solvents, the most common of which is water, because of its biological relevance. Whereas small amounts of water will not change the phase type and transition temperatures, larger amounts will introduce new phases such as cubic phases and columnar phases.

The discontinuous cubic phases are based upon various packings of spherical or slightly anisotropic micelles, while the bicontinuous cubic phases with interwoven fluid porous structures are based upon underlying infinite periodic minimal surfaces (Fairhurst et al., 1998). The first observation of liquid crystalline properties of alkylglycosides was related to long-chain compounds, but subsequent interest focused only on their shorter chain counterparts (Jeffrey, 1984; Jeffrey and Wingert, 1992; Prade et al., 1995) because of their interesting properties as surfactants (Böcker and Thiem, 1989; Vill et al., 1989; Boullanger, 1998). These compounds dissolve in water, whereas the long-chain glycosides will only swell.

To elucidate the structure-property relationships governing the occurrence of the above-mentioned polymorphism, long-chain alkyl glycopyranosides (in particular stearyl glycosides which can be incorporated in biomembranes) have been synthesised. These neoglycolipids are the simplest model system and therefore the starting point of these investigations. Further on, they will be used as components in binary mixtures (Chapter 5) with the more complex and more natural glycosyl diacylglycerols, the synthesis and mesogenic properties of which are discussed in Chapter 4.

3.2 Synthesis of long-chain alkyl glycopyranosides

In the literature two different procedures can be found that have been used for the synthesis of alkyl glycopyranosides:

- The first employs peracetylated glycosyl bromides as glycosyl donors using Koenigs-Knorr conditions (de Grip and Bovee-Geurts, 1979; Rosevar et al., 1980; Ma et al., 1994). This overall four-step procedure gives access only to products with β -configuration in the D-gluco and D-galacto series due to the neighbouring-group effect of the acetyl group at C-2, always forcing the aglycon into the trans position (Paulsen, 1982). The synthesis of the α -glycosides is possible via the *in situ* anomerisation procedure (Lemieux et al., 1975; Paulsen and Kolár, 1981). This procedure requires a neighbouring-group non-active substituent at C-2 and permits the synthesis of the α -glycosides of the D-gluco and D-galacto series via an *in situ* anomerisation of the α -glycosyl halide into the thermodynamically less stable β -halide and a subsequent nucleophilic S_N2 substitution of the halogen.
- The second procedure makes use of the peracetylated saccharides as glycosyl donors and the Lewis acid catalysed displacement of the acetoxy group at C-1 for glycoside synthesis. It has been known for some time that methyl- β -D-glycopyranoside may be prepared from penta-*O*-acetyl- β -D-glycopyranose under Lewis acid catalysis (Lemieux and Shyluk, 1953) and depending on the reaction conditions it is possible to obtain the β - or the α -glycoside (Banoub and Bundle, 1979). Under kinetic control the β -anomer can be isolated, which anomerises slowly under the reaction conditions giving the thermodynamically favoured α -anomer, enabling its preparation utilising thermodynamic control. Considerations concerning the mechanism of this glycoside synthesis can be found elsewhere (Banoub and Bundle, 1979; Böcker, 1989). This three-step procedure was later on used for the systematic synthesis of dodecyl glycosides to determine their possible use as detergents (Thiem and Böcker, 1989).

The aim of this work is to derive structure-property relationships and hence it is necessary to change the structure of the sugar headgroup systematically. An easy and quick synthetic strategy should therefore be used giving quick access to a huge number of glycosides. For this reason the second procedure was chosen despite its being characterised by lower yields, since

the starting materials are, with only a few exceptions, cheap. A great advantage of this procedure is the possibility to obtain, depending on the reaction conditions, both anomers of a particular glycoside from the same starting material, while the Koenigs-Knorr procedure gives access only to the glycosides with a 1,2-trans configuration (e.g. β -glycosides in the gluco and galacto series). For the synthesis of the glycosides with a 1,2-cis configuration the *in situ* anomerisation procedure with a different glycosyl donor has to be used. Furthermore the latter two procedures require the use of expensive silver or toxic mercury catalyst, the use of which can be prevented in the former case.

For example, in Figure 3.3 the synthesis of the α - and β -glucosides **4** and **6** using the chosen strategy is depicted. In the first step the saccharide is peracetylated with acetic acid anhydride and sodium acetate. The synthesis of the α -glycoside was accomplished using tin tetrachloride as Lewis acid and a reaction time of 48 hours, whereas the β -glycoside was obtained employing boron trifluoride ethyl etherate instead of tin tetrachloride together with a short reaction time of about two to four hours. Boron trifluoride ethyl etherate, which has already been used for the synthesis of alkyl thioglycosides (Ferrier and Furneaux, 1976), proved in this work to be superior to tin tetrachloride for the synthesis of alkyl- β -D-glycosides, since the rate of anomerisation was decreased. For example, after as much as 48 hours only a trace of α -anomer could be detected by t.l.c. in the reaction mixture for the synthesis of *cis*-9-octadecenyl-tetra-*O*-acetyl- β -D-glucopyranoside **5**, if boron trifluoride ethyl etherate was used, while this extended reaction time led exclusively to the formation of the α -anomer in all other cases, if tin tetrachloride was used.

The peracetylated glycosides were purified by silica gel chromatography prior to deprotection. In all cases except for the stearyl-hepta-*O*-acetyl- α -D-maltobioside **21** it was possible to isolate the desired product free of traces of the other anomer and hence no tedious ion exchange chromatography was necessary, which had to be used after a prepurification by silica gel chromatography by Böcker (Böcker and Thiem, 1989) to separate dodecyl glycosides.

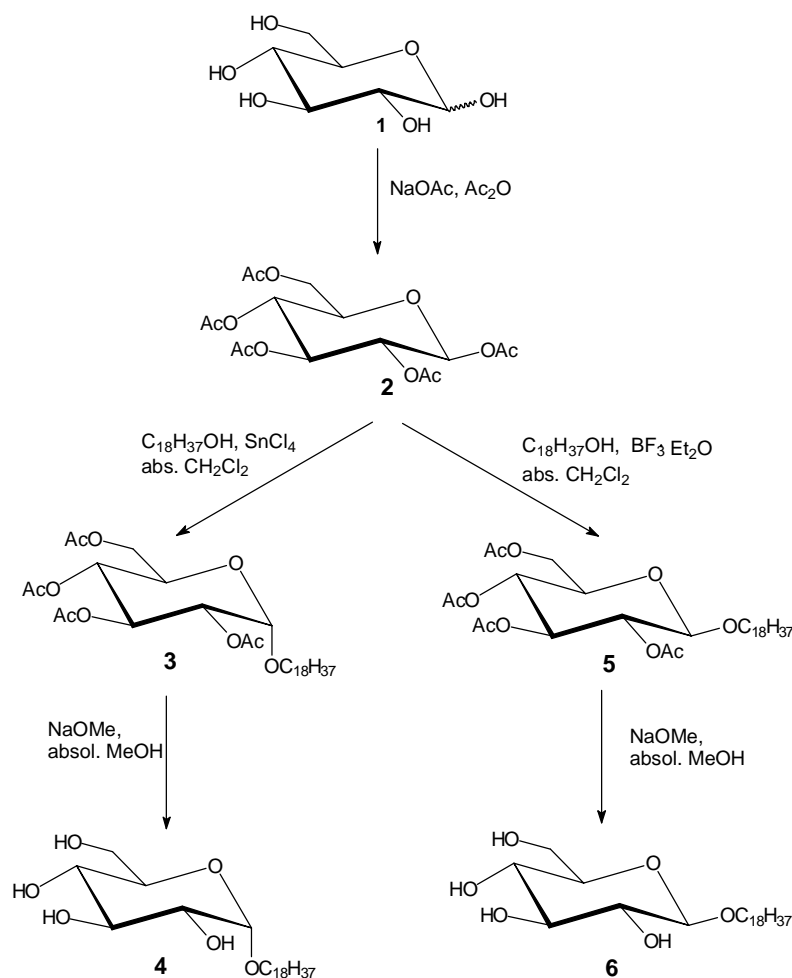


Figure 3.3: Synthesis of alkyl glycopyranosides

3.3 Mesogenic properties

3.3.1 Long-chain alkyl glycopyranosides with monosaccharide headgroups

Thermotropic behaviour

Figure 3.5 summarises the transition temperatures of some long-chain alkyl gluco- and galactopyranosides, determined by optical polarising microscopy.

In the case of the gluco derivatives **4** and **6** the introduction of 6 more CH₂ groups increases the clearing temperature slightly with respect to the dodecyl α- and β-glucosides (Glc-α-OC₁₂H₂₅ and Glc-β-OC₁₂H₂₅, Figure 3.4), but effects a slight decrease in the case of the galacto compound **16** relative to dodecyl-β-D-galactoside (Gal-β-OC₁₂H₂₅, Figure 3.4). This is in accordance with the general concept that the clearing temperature normally rises

with increasing chain length and reaches a plateau, where an optimal ratio between the polar and unpolar moieties is achieved and drops afterwards slightly. This optimum is reached in the case of monosaccharides with 14 to 16 CH₂ groups and the 12 and 18 chains are therefore close to this plateau. Since the galacto compounds with an axial OH group at C-4 are shorter than the gluco compounds, the optimal ratio of the polar and unpolar moieties should be reached somewhat earlier and the compound with 18 CH₂ groups is in the case of the galacto compounds therefore further beyond the plateau than in case of the gluco compounds.

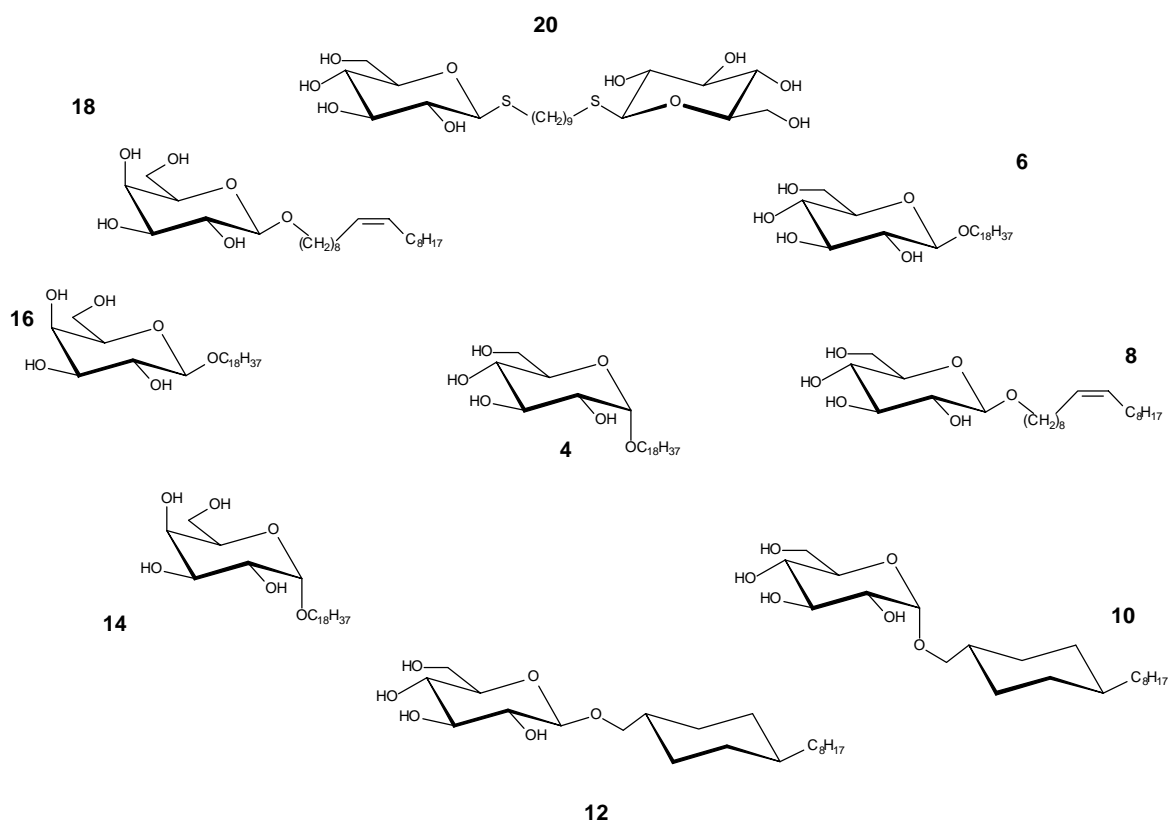
However it is remarkable that the gluco and galacto compounds exhibit the opposite behaviour: for the glucosides the α -anomer is the more stable one, whereas it is the less stable anomer in the case of the galacto compounds. There is also a remarkable difference in stability between the stearyl- α - and - β -galactosides **14** and **16**, while the stability of the glucosides **4** and **6** is almost the same. The reason for this quite different behaviour might be the different possibilities for hydrogen bonding in the polar headgroup region, which should be dependent on the configuration. In this context it is interesting to compare the clearing temperature of the β -glucosides (Glc- β -OC₁₈H₃₇ and Glc- β -OC_{18:1} ^{Δ^9} H₃₅; **6** and **8**) with the clearing temperature of the β -galactosides (Gal- β -OC₁₈H₃₇ and Gal- β -OC_{18:1} ^{Δ^9} H₃₅; **16** and **18**): If the unpolar part is kept constant, replacing the glucose by a galactose will stabilise the S_A in all cases by about 20 K.

Glc- α -OC ₁₂ H ₂₅	Cr	77.0	S _A	151.0	I
Glc- β -OC ₁₂ H ₂₅	Cr	80.0	S _A	143.0	I
Gal- β -OC ₁₂ H ₂₅	Cr	99.0	S _A	166.0	I

Figure 3.4: Literature data (Vill et al., 1989) for the transition temperatures of dodecyl- α - (Glc- α -OC₁₂H₂₅) and β -D-glucoopyranoside (Glc- β -OC₁₂H₂₅) and dodecyl- β -D-galactopyranoside (Gal- β -OC₁₂H₂₅).

The introduction of an unsaturation (compound **8**) decreases the clearing and melting temperature as expected, yielding liquid crystallinity already at ambient temperature. If the glucose headgroup is replaced by galactose, the transition temperatures are also lowered, but compound **18** is crystalline and not liquid crystalline at ambient temperature, showing again that a much more effective network of hydrogen bonding is present in the galactosides.

Replacing the stearyl chain by a *cis*-9-octadecenyl chain lowered in both cases (compounds **8** and **18**) the clearing temperature by 20 K.



4			Cr	98.0	S_A	151.2	I^a
6	Cr_2	87.0	Cr_1	93.3	S_A	146.8	I^a
8			Cr	< 20.0	S_A	126.0	I^a
10			Cr	109.7	S_A	181.5	I^a
12			Cr	124.1	S_A	182.5	I^a
14			Cr	89.0	S_A	145.9	I^a
16			Cr	106.0	S_A	164.2	I^a
18			Cr	80.6	S_A	145.0	I^a
20			Cr	108.9			I^b

Figure 3.5: Transition temperatures of alkyl monoglycosides.

(a) Myelin figures (Bouligand, 1998) in the contact preparation with water.

(b) While this compound did not show any liquid crystalline phases, it stabilised the S_A -phase of compounds **2** and **4** in the contact preparation by 5 and 8.4 K, respectively.

The introduction of a stiff cyclohexyl group in compounds **10** and **12** increases the clearing temperatures as should be expected. It is somewhat surprising that there is more or less no difference in stability between the two different anomers **10** and **12** in this case.

The bola amphiphile **20** did not show any liquid crystalline behaviour, since the linker might be too short, but it stabilised the liquid crystalline phase of compounds **4** and **6** in the contact preparation by 5 and 8.4 K, respectively. The reason for this might be the increased amount of sugar in the mixture due to the incorporation of the bola amphiphile with two sugars and only a short linking chain, which shifted the ratio between the polar and unpolar moieties in the mixture towards the sugar. Whereas the optimum ratio and the maximum clearing temperature is reached in case of monosaccharide headgroups with 14 to 16 CH₂ groups, it is reached in case of disaccharide headgroups with longer alkyl chains. The stearyl glycosides **4** and **6** are already beyond this optimal ratio because of the excessively long chain. Upon addition of the bola amphiphile, the amount of sugar is increased and the better ratio between the polar and unpolar moieties leads to an increased clearing temperature.

Lytropic behaviour

Beyond the critical micellar concentration (CMC), glycolipids form supramolecular aggregates in aqueous media. The type of aggregate structure can be assumed to play a biologically relevant role and is determined by the conformation (shape) of the contributing molecules, which is in turn determined primarily by their chemical structure and is influenced by ambient conditions such as pH and concentration of mono- and divalent cations (Israelachvili, 1991). Moreover, the molecular shape of a given glycolipid molecule depends on the state of order of the chains, which can assume two main phase states, the gel (β -phase) and the liquid crystalline (α -phase) states. Between these two phase states a reversible transition can take place at a given phase transition temperature T_c . The value of T_c is dependent in the first place on the number, length and degree of unsaturation of the acyl chains, the conformation and the charge density and its distribution within the headgroup region and the nature and size of the saccharide moiety. A closer characterisation of the main types of supramolecular aggregate structures (micellar, lamellar L, cubic Q and inverted hexagonal H₂) occurring in glycolipid/water systems is given by Curatolo (1987). More general information about structural polymorphism can be found elsewhere (Luzzati et al., 1986; Israelachvili, 1991; Seddon, 1990; Seydel et al., 1993). A comprehensive overview of the phases and phase

transitions (including the three-dimensional aggregate structures L, Q and H₂) adopted by glycolipids is given by Koynova and Caffrey (Koynova and Caffrey, 1994).

The formation of lyotropic phases was investigated by means of X-ray diffraction, small-angle neutron scattering and the contact preparation technique (van Doren and Wingert, 1994). If water penetrates the sample, one or more lyotropic phases are formed, which can be identified by polarising microscopy based on their characteristic textures. Because a gradient of water concentration forms, the whole range of phases starting from the anhydrous bulk in the middle to the completely hydrated sample at the outermost region can be observed. Depending on the position of a particular phase with respect to the other phases, it is even possible to classify it tentatively as belonging to the normal or inverted type in the case of cubic or columnar phases; for the same reason it is possible to differentiate between a bicontinuous and a discontinuous (micellar) cubic phase. For example, a cubic phase, observed at a higher water concentration than the lamellar phase and followed by a columnar phase should be of the normal bicontinuous type.

The lyotropic behaviour of the compounds presented in Figure 3.5 was studied by polarising microscopy, FTIR spectroscopy and X-Ray diffraction.

All compounds visualised in a contact preparation with water in the polarising microscope exhibited only myelin figures, because of the very low water solubility. Myelin figures are mobile tubular structures, which are considered to consist of cylindrical or helical arrangements of many (300-5000) of the bilayers that constitute the lamellar phase (Jeffrey and Wingert, 1992; Bouligand, 1998).

Phase transition of the hydrocarbon chains

In Figure 3.6, the results of the alkyl chain phase transition – presented as the peak position of the symmetric stretching vibration $\nu_s(\text{CH}_2)$ versus temperature – are given for the stearyl glycosides. These compounds melt in the temperature range 55 to 70 °C. Interestingly, the β -glucoside **6** exhibits higher wavenumber values – higher fluidity or lower state of order, respectively – at all temperatures and also a significantly lower phase transition temperature T_c than the α -anomer **4**. This is just the opposite for the galactosides (compare analogous results above for thermotropic phase behaviour), for which T_c of the α -anomer **14** is more than 10°C lower than that of the β -anomer **16**, while the fluidity is similar in particular in the gel phase.

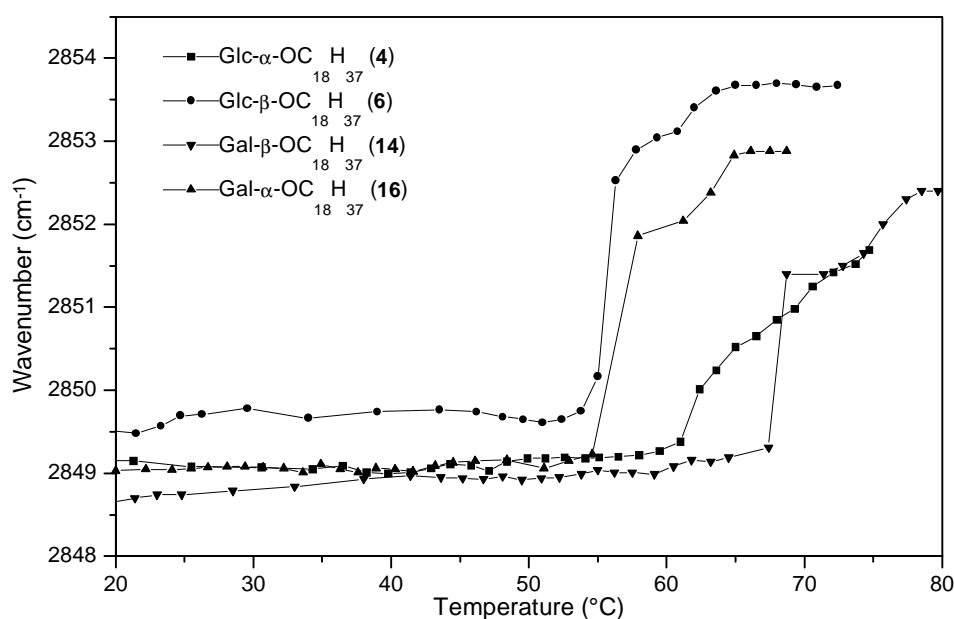


Figure 3.6: Phase transition of the hydrocarbon chains of stearyl gluco- and galactosides. The peak position of the symmetric stretching vibration of the methylene groups is in the range 2848 to 2850 cm^{-1} in gel or crystalline phases and in the range 2852 to 2854 cm^{-1} in liquid crystalline states.

The glycolipids with a cyclohexane, but only a short lipid chain (C8) undergo surprisingly an alkyl chain melting at relatively high temperatures (Figure 3.7). Furthermore, the α - and β -anomers behave similarly. The chain melting, however, takes place over a very broad temperature range (> 20 °C), not allowing the statement of a definite T_c . At the high temperature end, the chain melting is still not completed. This extremely broad range probably results from the presence of the stiff cyclohexane group directly linked to the flexible alkyl chain. This group, which is itself hydrophobic, dramatically increases the hydrophobic moiety relative to the other substances and is thus responsible for the high T_c . Concomitantly, the broadness of the transition may be understandable. A favourable molecular packing of the hydrophobic moiety, necessary for a cooperative melting, is impeded drastically because of the voluminous cyclohexyl group.

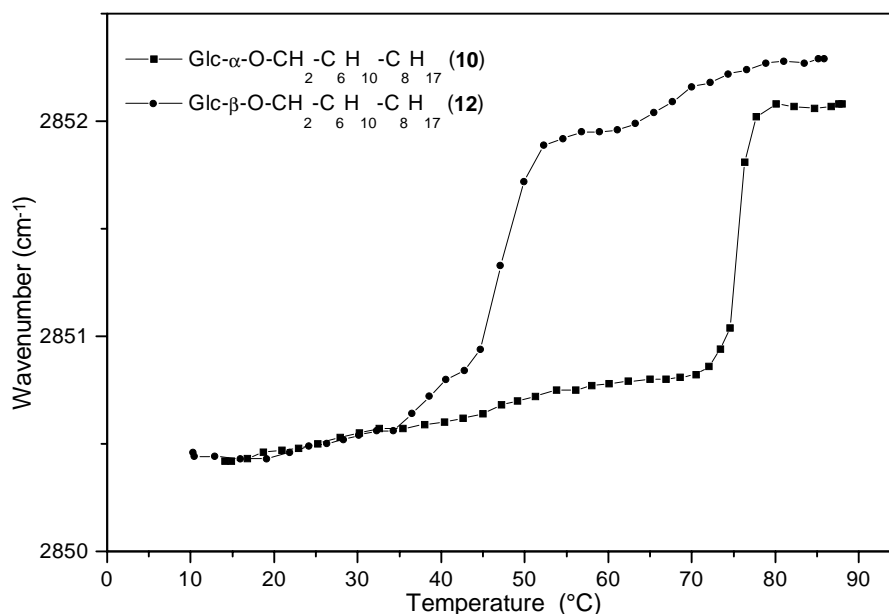


Figure 3.7: Phase transition of the hydrocarbon chains of glucose-containing glycolipids **10** and **12** bound in α - and β -linkage to a 4'-octylcyclohexyl group (see also legend of Figure 3.6).

To determine the packing density of the alkyl chains and to verify or disprove the above hypotheses, X-ray wide-angle diffraction measurements were also performed using Gal- α -OC₁₈H₃₇ (stearyl- α -galactoside **14**, Figure 3.8). Between 5 and 60 °C, sharp reflections are observed at 0.367 to 0.370 nm, 0.452 nm and 0.248 nm. From the appearance of these peaks (in the L _{β} phase usually only one reflection at 0.415 nm is observed), the existence of a 'crystalline' L_c phase can be concluded, which for example is found for diacyl glucoses. At 80 °C, the peaks at the lower spacing ratios have vanished and the remaining weak and broad reflection at 0.455 nm is typical for the occurrence of the α -phase.

Also, the cyclohexyl glucosides exhibit various sharp diffraction maxima, typical for the occurrence of the L_c-phase. In particular, the α -linked anomer has maxima at 0.333, 0.357, 0.426, 0.451 and 0.486 nm at 5 °C. These reflections are basically present – with slight shifts of the peak position – up to 60 °C and vanish above this temperature.

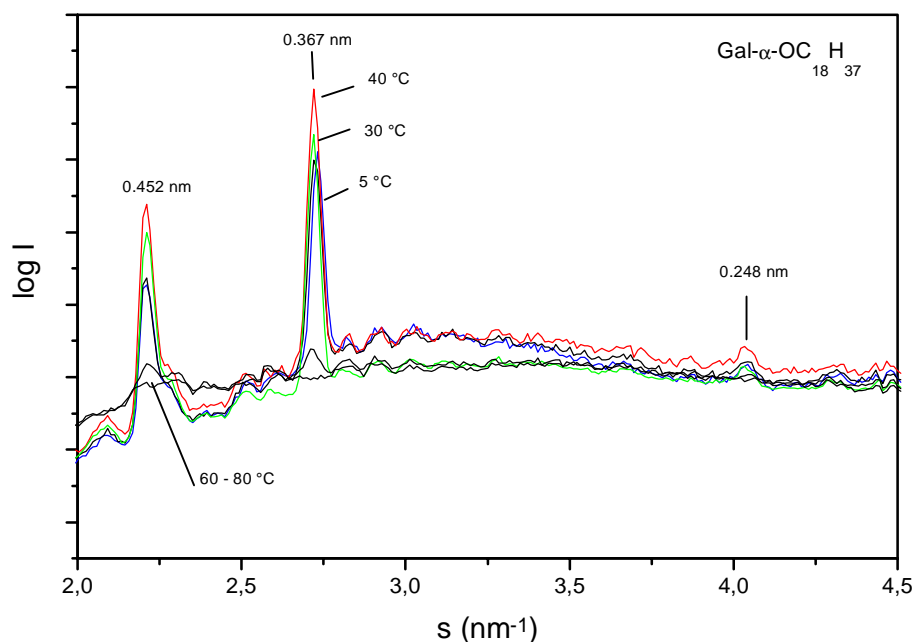


Figure 3.8: Wide-angle X-ray scattering (WAXS) patterns of Gal- α -OC₁₈H₃₇ **14** at 90 % buffer content and selected temperatures.

Supramolecular aggregate structures

Figure 3.9 shows X-ray diffraction patterns for stearyl- α -glucoside **4** and stearyl- β -glucoside **6** in 90 % buffer and at different temperatures.

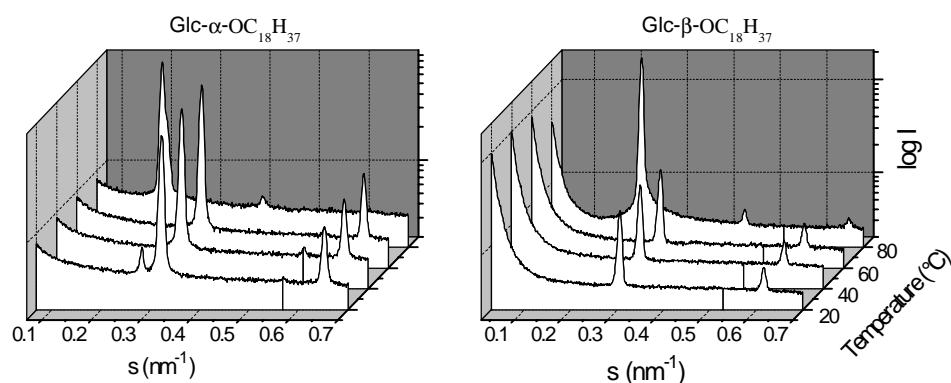


Figure 3.9: Small-angle X-ray scattering (SAXS) patterns of Glc- α -OC₁₈H₃₇ **4** and Glc- β -OC₁₈H₃₇ **6** in 90 % buffer at selected temperatures

Both samples exhibit similar patterns with reflections at equidistant ratios in the temperature range 20 to 60 °C, which convert at 80 °C into diffraction patterns with reflections lying again in equidistant spacing ratios, but with a much higher periodicity. For a more exact characterisation, in Figure 3.10 the pattern of stearyl- α -glucoside at 90 % buffer content at the temperatures 40 and 80 °C, i.e., below and above T_c are presented together with the respective

patterns obtained at 50 % buffer content. At 90 % buffer content and 40 °C (Figure 3.10A), two periodicities at 3.53 nm and 3.11 nm and the corresponding second order reflections are clearly observed. This is similarly true for the sample at 50 % buffer content and 40 °C (periodicities at 3.51 nm and 3.07 nm, Figure 3.10B and Table 3.1). However, this pattern contains further reflections, which may indicate another substructure. For example, the reflection at 1.43 nm = 3.51 nm / $\sqrt{6}$ might be indicative of a cubic substructure. This interpretation seems to be improbable because it is usually believed that cubic phases occur exclusively in the fluid phase of the hydrocarbon chains (Luzzati et al., 1986). However, for particular glycolipids, bacterial lipid A and lipopolysaccharide, the existence of cubic phases could be proven already in the gel phase of the acyl chains (Brandenburg et al., 1990 and 1998). Of course, because of the lack of further reflections, indexing on such cubic structures, in the moment no nearer characterisation of this phase is possible.

The periodicities at 80 °C – 4.90 to 4.95 nm – may be assumed to be typical for the occurrence of a ‘normal’ L multilamellar phase, whereas the values below 80 °C indicate an interdigitated lamellar phase. The occurrence of interdigitated phases is observed for diacyl phospholipids only at high ionic concentration or by adding polar substances, as found by Boggs and Rangaraj (1985). However, for particular glycolipids, i.e., lipid A, such interdigitation has been observed also for the pure lipid in the gel phase (Brandenburg et al., 1990). In the case of the investigated monoalkyl glycolipids, the reason for the occurrence of such an interdigitated phase is the disproportion between the cross-section of the polar and unpolar moieties allowing two packing organisations: as micelles with the unpolar chains packed together in the interior of a sphere and the polar headgroups lying on the surface, or the packing in a lamellar arrangement with interdigitated chains, which now resembles the situation of a ‘normal’ diacyl phospholipid. In both cases, a minimisation of the hydrophobic free energy is guaranteed. Although interdigitated phases for monoacyl glycolipids have not been described to date, the existence of such a phase has been proven for 1-stearoyl-lysophosphatidylcholine (Mattei and Shipley, 1986), a compound resembling the investigated glycolipids with respect to the disproportion of polar and unpolar moieties. In accordance with the occurrence of such interdigitation is the known tendency of lyso phospholipids to incorporate spontaneously into target cell membranes, thus again minimising the Gibbs free energy.

In the liquid crystalline phase the tight packing is lost due to the strong occurrence of gauche conformers, leading eventually to a ‘normal’ L_α-phase with the terminal methyl groups facing

each other. This general behaviour was found to be true for all other stearyl monosaccharides and the values for the measured periodicities are listed in Table 3.1.

The reason for the occurrence of two sets of lamellar reflections in case of the stearyl- α -glucoside **4** (Figure 3.10) is not completely clear. An inhomogeneity of the chemical structure as well as an inhomogeneous hydration can be excluded, the latter because of the repeated heating/cooling cycles prior to measurement, guaranteeing complete hydration. The observation that the two sets of lamellar reflections are invariant in the temperature range from 20 to 60 °C also speaks against this hypothesis. Interestingly, this effect is very specific for the stearyl- α -glucoside and is not found for any other investigated compound.

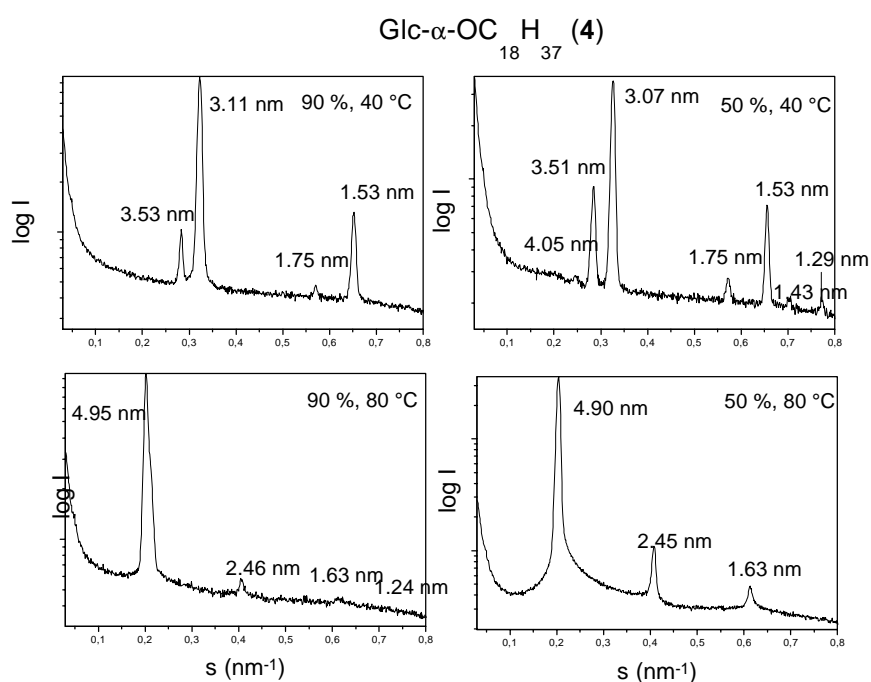


Figure 3.10: SAXS patterns of Glc- α -OC₁₈H₃₇ (compound **4**) at two buffer contents (A: 50 % and B: 90 %) and two temperatures (40 and 80 °C).

Stearyl- α -glucoside (4)	3.52 3.11	4.95	3.51 3.07	4.90
Stearyl- β -glucoside (6)	3.26	4.46	3.26	4.00 3.26
Stearyl- α -galactoside (14)	3.45	4.49	3.44	4.46
Stearyl- β -galactoside (16)	3.51	4.58	3.51	4.49 4.24

Table 3.1: Values for the measured periodicities of the stearyl-monosaccharides in nm.

The two cyclohexane-containing glycolipids adopt multilamellar structures under all investigated conditions (Figure 3.11). For the β -linked compound the change of the lamellar

periodicity from 3.69 nm to 4.39 or 4.50 nm, respectively, between 40 and 60 °C (Figure 3.11B) apparently indicates a transition from an interdigitated to a ‘normal’ lamellar phase. This transition is not observed for the α -linked compound (Figure 3.11A), although both isomers have a similar state of order in the investigated temperature range (Figure 3.7).

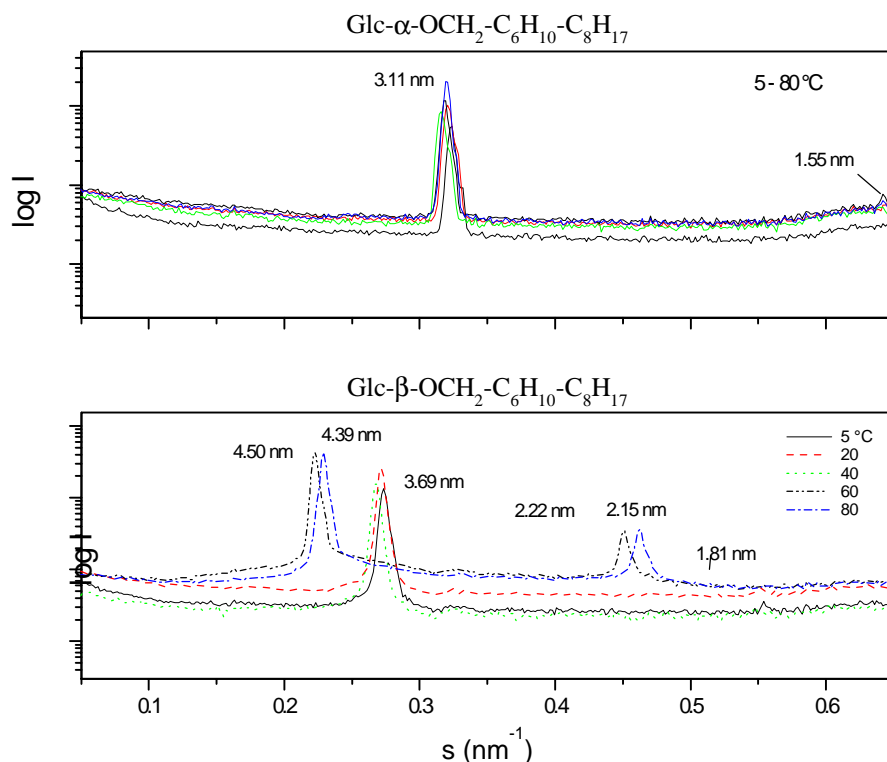


Figure 3.11: SAXS patterns of Glc- α - and Glc- β -cyclohexyl compounds **10** and **12** in 90 % buffer at selected temperatures.

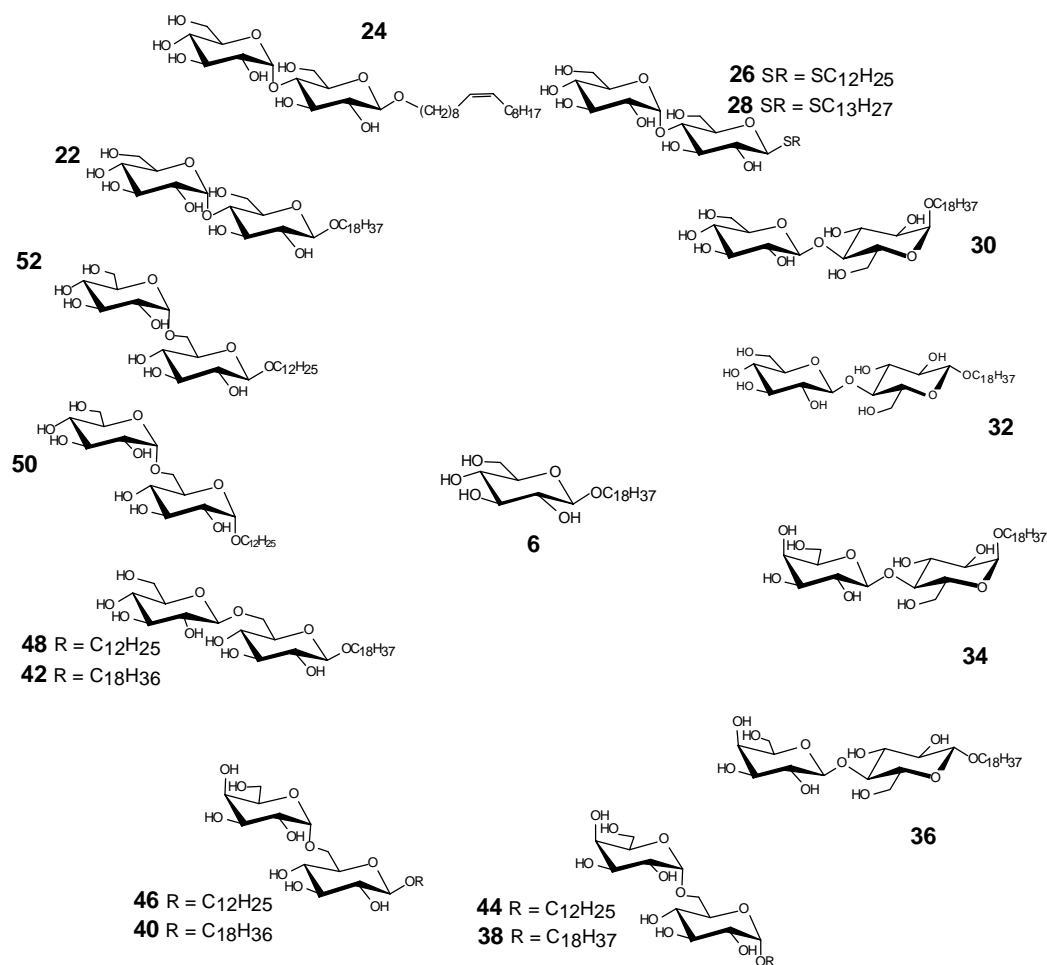
3.3.2 Long-chain alkyl glycopyranosides with disaccharide headgroups

Thermotropic properties

Figure 3.12 depicts a systematic structure variation of octadecyl- β -D-glycopyranoside **6**. If the glucose headgroup of compound **6** is replaced by the α 1 \rightarrow 4 linked disaccharide unit of maltobiose (compound **22**), the clearing temperature increases dramatically by 127 K due to increased hydrogen bonding in the headgroup region attributable to the increased number of hydroxyl groups. Furthermore, a better ratio between the polar and unpolar moieties is obtained by exchanging the glucose headgroup of **6** for a disaccharide unit. The optimal hydrophilic hydrophobic balance and therefore the highest clearing temperature is reached in the case of monosaccharide headgroups with a chain of 14 to 16 carbon atoms (Prade et al.,

1995). However, the optimal balance is reached in case of disaccharide headgroups at longer chain lengths.

The introduction of an unsaturation in compound **24** again lowered the clearing temperature, but with only 7 K less than in the case of the monosaccharide derivatives described in section 3.3.1. The reason for the lower clearing temperatures of the unsaturated derivatives in general can be seen in the disturbance introduced into the alkyl chain region by the double bond, preventing a close packing of the alkyl chains and therefore lowering the van der Waals interactions. The stronger effect of the unsaturation on the monosaccharide derivatives with an already imbalanced ratio between the polar and unpolar molecular moieties might be explained by the broadening of the alkyl chains introduced through the unsaturation, increasing the hydrophobic volume and hence the imbalance even further, but there is still a more general explanation: it seems that the effect of structural changes in the aliphatic chain on the clearing temperature is always stronger in the case of monosaccharide headgroups than in the case of disaccharide headgroups. An interesting observation which further supports this hypothesis is that of the effect on the clearing temperature, if the oxygen is replaced by sulphur as linking atom between the hydrophilic and hydrophobic moieties of a maltobioside. In the case of α -D-thioglycosides (van Dooren et al., 1989) [unfortunately no sufficient data are available about the β -D-thioglycosides] and also in the case of many other sulphur compounds with a monosaccharide headgroup – e.g. the 1-thioglycerides (van Doren et al., 1990), 1-alkylthio-1-deoxy-D-glucitols (Dahloff, 1990), thioesters of galacturonic acid (C. Vogel et al., 1992) and dialkyl thioacetals of D-glucose (Tietze et al., 1994; Dahloff, 1987; van Doren et al., 1988; Eckert et al., 1987) – the sulphur derivatives always exhibit distinctly higher clearing temperatures than the oxygen linked derivatives. Nevertheless the dodecyl thiomaltobioside **26** exhibits nearly the same clearing temperature as the oxygen-linked maltobioside (compound **53**, Figure 3.13) and proves therefore the above-mentioned hypothesis. For other reasons the tridecyl thiomaltobioside **28** with a clearing temperature of 260.0 °C was synthesised. Unfortunately no literature data are available about the clearing temperature of the analogous oxygen linked compound, but using the LiqCryst database (Vill, 1999) a value of 254.5 °C was calculated. This value seems reasonable, since the maltobiosides do not show an odd-even effect and the calculated temperature should thus lie in the middle of the clearing temperatures of the dodecyl and tetradecyl maltobioside (Figure 3.13, compounds **53** and **54**). This temperature is again only slightly lower than the clearing temperature of the sulphur derivative **28**.



6	Cr ₂	87.0	Cr ₁	93.3		S _A	146.8	I			
22			Cr	106.0		S _A	274.0	I			
24			g	?		S _A	267.0	I ^a			
26			Cr	135.7		S _A	246.2	I			
28			Cr	139.0		S _A	260.0	I			
30			Cr	130.0	cub	127.4	S _A	263.0	I		
32			Cr	151.7			S _A	283.5	I ^b		
34			Cr	181.4	cub	178.0	S _A	260.2	I		
36			Cr	183.0	cub	181.5	S _A	284.0	I		
38			Cr	129.8			S _A	252.0	I		
40			Cr	152.0			S _A	262.0	I		
42			Cr	169.2	cub	163.0	S _A	268.0	I		
44			Cr	90.5	cub	151.0	S _A	160.5	I		
46			Cr	155.0	cub	137.0	S _A	171.0	I		
48			Cr	152.0	cub	157.0	S _A	168.0	I		
50			Cr	?	non mesogenic						
52			Cr	120.0	X	96.0	cub	138.0	S _A	154.0	I ^c

Figure 3.12: Thermotropic behaviour of the synthesised amphiphilic liquid crystals

- a The compound formed a glass and thus no melting point could be determined.
- b The synthesis and the rough transition temperatures of this compound were first reported without an identification of the phase type by Hori (1958).
- c An additional (probably columnar) metastable mesophase was formed on cooling.

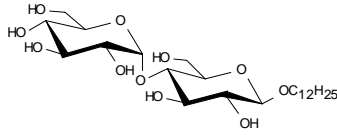
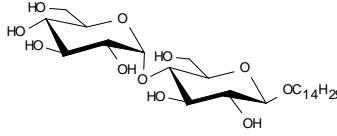
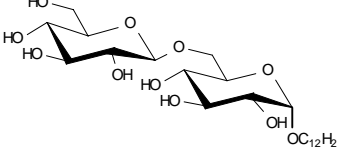
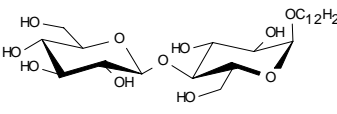
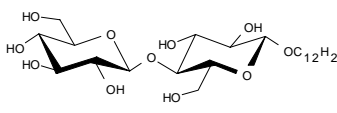
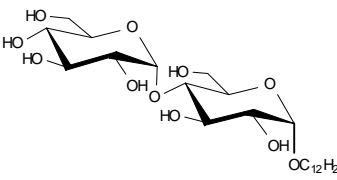
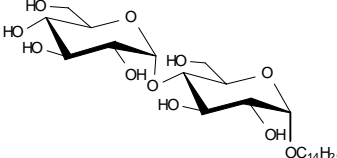
	Mal-β-OC ₁₂ H ₂₅ (53) Cr	102.0	S _A	245.0	I
	Mal-β-OC ₁₄ H ₂₉ (54) Cr	107.0	S _A	264.0	I
	Gen-α-C ₁₂ H ₂₅ (55) Cr	? ^a	cub	158.0	I
	Cel-α-C ₁₂ H ₂₅ (56) Cr	? ^a	S _A	224.0	I
	Cel-β-C ₁₂ H ₂₅ (57) Cr	? ^a	S _A	259.4	I
	Mal-α-C ₁₂ H ₂₅ (58) Cr	? ^a	S _A	205.0	I
	Mal-α-OC ₁₄ H ₂₉ (59) Cr	? ^a	S _A	231.0I	

Figure 3.13: Literature data for the transition temperatures of some amphiphilic liquid crystals for comparison

a In the literature no exact melting point was given, since the compounds formed non-crystalline solids after lyophilisation.

In the next step the type of the interglycosidic linkage (α vs. β), the position of linkage (1→4 vs. 1→6) and the configuration of the second sugar residue (glucopyranosyl vs. galactopyranosyl) was changed systematically. The clearing temperatures of these compounds varied over a range of 33 K owing to the various kinds of configurations and in several cases cubic phases were found.

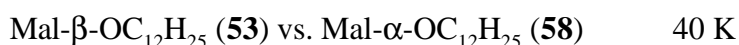
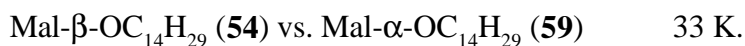
Influence of the type of linkage (α vs. β) between chain and headgroup

In all cases the compounds with the aliphatic chain linked by a β -glycosidic bond (compounds **32**, **36**, **40**, **46**, **48** and **52**) to the disaccharide moiety displayed a higher clearing temperature (and also the higher melting point) and hence the more stable smectic A phase than the corresponding α -anomer (**30**, **34**, **38**, **44**, **55** and **50**). This difference in stability between the anomers was in the case of compounds with headgroups with a interglycosidic 1 \rightarrow 6 linkage (Mel- β -OC₁₈H₃₇ **40**, Mel- β -OC₁₂H₂₅ **46** and Gen- β -OC₁₂H₂₅ **48** vs. Mel- α -OC₁₈H₃₇ **38**, Mel- α -OC₁₂H₂₅ **44** and Gen- α -OC₁₂H₂₅ **55**) with about 10 K smaller than in the case of compounds with the two glycosyl units connected by a 1 \rightarrow 4 linkage (about 20 K, compounds Cel- β -OC₁₈H₃₇ **32** and Lac- β -OC₁₈H₃₇ **36** vs. Cel- α -OC₁₈H₃₇ **30** and Lac- α -OC₁₈H₃₇ **34**). The reason for the greater stability of the compounds with a β -anomerically linked aliphatic chain might be seen in their somewhat more rod-like shape. This effect is not so strong in the case of compounds with a 1 \rightarrow 6 linked disaccharide unit, since the sugar moiety is angular and causes the molecule already to be banana-shaped. This deviation from a rod-like structure is much stronger than the one introduced by an α -linkage of the aliphatic chain to the sugar moiety and a further deviation from a rod-like structure due to the latter therefore decreases the stability of the S_A phase only slightly.

While this difference in stability between the two anomers is more or less chain length independent in case of a 1 \rightarrow 6 linked headgroup (α -melibiosides **40** and **46** vs. β -melibiosides **38** and **44**) it is strongly dependent on the chain length in case of compounds with a 1 \rightarrow 4 linked disaccharide headgroup. The difference in stability between the two anomers is in case of the cellobiosides (β 1 \rightarrow 4) e.g.:



and similar results are found for the maltobiosides (α 1 \rightarrow 4):

*Influence of the type of linkage between the two sugar residues (α vs. β)*

If the α 1 \rightarrow 4 linked second glucopyranosyl residue of the maltoside **22** is replaced by a

β 1 \rightarrow 4 linked glucopyranosyl residue (cellobioside **32**), the clearing temperature increases by 9.5 K due to the stiffer and more rod-like structure of the cellobiose headgroup. This difference in stability also increases again with decreasing chain length as can be seen easily from the data in Figure 3.13.

Whereas the maltobiosides displayed only smectic phases, the α -cellobioside **30** displays a monotropic cubic phase, which could not be found in the case of the β -cellobioside **32**, since on cooling of the S_A phase crystallisation occurred already some degrees below the melting point. These results will be discussed together with the lactosides in the following section.

Influence of the configuration of the hydroxyl groups of the second sugar residue (gluco vs. galacto)

If the second, β 1 \rightarrow 4 linked glucopyranosyl residue of the cellobiosides **30** and **32** is replaced by a β 1 \rightarrow 4 linked galactopyranosyl residue, the stability of the S_A is more or less not effected; the clearing temperature of the α -lactoside **34** is 2.8 K lower than the clearing temperature of the corresponding α -cellobioside while the clearing temperature of the β -lactoside **36** is 0.5 K higher than in the case of the β -cellobioside. The configuration at C-4 of the second sugar moiety seems to have therefore more or less no influence on the stability of the S_A phase in the case of 1 \rightarrow 4 linked disaccharide headgroups, but this is not true in the case of 1 \rightarrow 6 linked disaccharide headgroups (see below).

The α -lactoside **34** as well as the β -lactoside **36** displayed, as did the α -cellobioside **30**, a monotropic cubic phase. The introduction of the galactopyranosyl residue improved in case of the β -lactoside compared to the β -cellobioside the „supercoolebility“ and circumvented the crystallisation, which prevented the occurrence of a monotropic cubic phase of the β -cellobioside **32**. So far only a few sugar derivatives are known to show a thermotropic cubic phase (e.g.: Praefcke et al., 1990; Fischer et al., 1994; Borisch et al., 1996 and 1997; Beginn et al., 1997) and one of them is the dodecyl- α -D-gentiobioside **57** (Fischer et al., 1994), some homologous compounds of which have been synthesised in this work and will be discussed below. The occurrence of cubic phases might be attributable in these cases to their banana-shaped molecular structures, whereas the occurrence of thermotropic cubic phases in the case of cello- and lactobiosides is rather unexpected and hard to explain, since compounds of this type are so far only known to form S_A phases (Jeffrey and Wingert, 1992; Prade et al.,

1995). Because of their rod-like molecular shape they are indeed something like the prototype of S_A phase forming amphiphilic glycosides.

The exact structure of the headgroup seems to have an influence on the occurrence of this monotropic cubic phase (even if it cannot be understood yet), since the α -cellobioside **28**, the α - and β -lactobiosides **34** and **36** and the β -gentiobioside **42** exhibited a monotropic cubic phase while it was not found in the case of the β -maltobiosides **22** and **24** and the α - and β -melibiosides **38** and **40**. At present only two very general structural requirements can be derived:

- a disaccharide headgroup seems to be necessary, since the similar stearyl gluco- and galactopyranosides (see section 3.3.1) did not show this unusual mesogenic behaviour
- a chain of sufficient length is also necessary, since e.g. the homologous dodecyl cellobiosides or tetradecyl lactosides (Vill et al., 1989) only displayed a S_A phase.

Rod-like amphiphilic molecules are known to display a smectic A phase, the stability of which increases the more balanced the ratio between the polar and unpolar moieties becomes and decreases afterwards again. If this imbalance between the hydrophilic and hydrophobic moieties is increased sufficiently, a cubic phase might be observed instead of the S_A phase usually found. These findings are similar to the results obtained earlier with some glucamine derivatives (sodium salts of N-alkyl-N-carboxymethyl-D-glucamine, Vill et al., 1992), but it is still impossible to explain the above-mentioned influence of the sugar headgroup.

Influence of the position of linkage between the two sugar moieties in the disaccharide headgroup (1→6 vs. 1→4)

While the 1→4 linked disaccharides are always more or less linear, the 1→6 linked disaccharides are generally angular, yielding a banana-shaped structure of the glycosides made thereof, which influences their mesogenic behaviour strongly. The stability of the S_A phase is reduced due to the deviation from a rod-like shape as can be seen from a comparison with the transition temperatures of the analogous 1→4 linked derivatives. The extent to which the stability of the S_A phase is reduced depends strongly on the length of the alkyl chain e.g.:

Gen- β -OC₁₈H₃₇ (**42**) vs. Cel- β -OC₁₈H₃₇ (**32**): 15.5 K

Mel- β -OOC₁₈H₃₇ (**40**) vs. Mal- β -OC₁₈H₃₇ (**22**): 12.0 K

(note – because an exchange of the second glucopyranosyl residue in the cellobioside for a galactopyranosyl residue did not effect the clearing temperatures, it seems possible to compare the melibiosides with the maltobiosides instead of comparing with the proper compounds with a disaccharide headgroup of a galactopyranosyl residue linked by an α 1 \rightarrow 4 bond to a glucopyranosyl residue)

Gen- β -OC₁₂H₂₅ (**48**) vs. Cel- β -OC₁₂H₂₅ (**57**) : 91.4 K

Mel- β -OC₁₂H₂₅ (**46**) vs. Mal- β -OC₁₂H₂₅ (**53**): 74.0 K

Isomal- β -OC₁₂H₂₅ (**52**) vs. Mal- β -OC₁₂H₂₅ (**53**): 91.0 K

The most obvious difference between the glycosides with a 1 \rightarrow 6 and a 1 \rightarrow 4 linked disaccharide headgroup is the more or less abundant occurrence of cubic phases in the former case. Except for the dodecyl- α -isomaltoside **50** all of the dodecyl glycosides (**44**, **46**, **48**, **52** and **55**) with a 1 \rightarrow 6 linked disaccharide headgroup exhibit a cubic mesophase. Since the α -melibioside **44** showed a cubic mesophase while the α -isomaltoside **50** did not, this difference in the mesogenic behaviour must be attributed to the changed configuration at C-4 of the second sugar residue due to the exchange of a galactopyranosyl for a glucopyranosyl residue.

The occurrence of a cubic mesophase might be explained in these cases by the broad structure of the 1 \rightarrow 6 linked disaccharide headgroups, giving the molecules a banana shaped structure [this term has been used before by Takezoe (Niori et al., 1996) to describe the molecular shape of a completely different class of symmetric non-carbohydrate liquid crystals with different properties than the compounds discussed here].

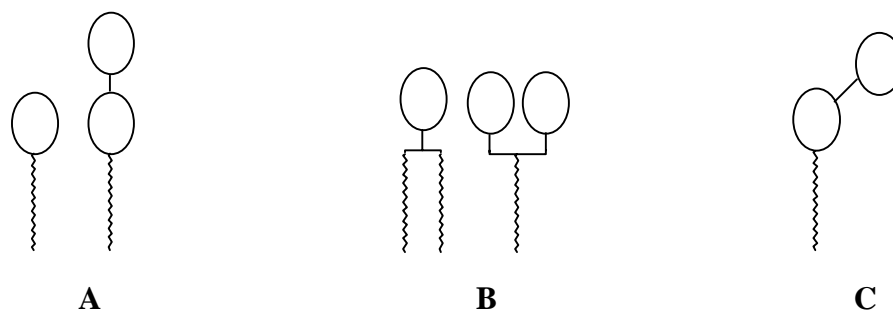


Figure 3.14: Types of amphiphiles

Compounds of the general structure **A** (Figure 3.14) have so far only been reported to display smectic phases (Jeffrey and Wingert, 1992; Prade et al., 1995) and compounds of type **B** show

columnar phases with the interfacial area being curved around the minor component (Mannock et al., 1987 and 1990; Jeffrey and Wingert, 1992; Prade et al., 1995). In the case of compounds of type **C**, the headgroup prefers a columnar structure while the aliphatic tail favours a smectic structure, but each is destabilised by the other moiety. The discussed glycosides with a 1→6 linked disaccharide headgroup belong to this last group, which as a result of frustration forms cubic mesophases as a compromise. The cubic to S_A transition may be attributed to the increasing thermal motion in the alkyl chains, leading to a greater effective volume of the hydrophobic chain. This causes the molecule to be rod-like at elevated temperatures and hence a cubic to S_A transition is found.

If the dodecyl chain is extended, as in the case of the stearyl melibiosides (**38**, **40**), only an S_A phase is observed whereas the stearyl gentiobioside **42** displays a monotropic cubic phase. This difference in behaviour might be explained by the difference in size of the sugar headgroups. With the melibiose headgroup, the stearyl glycosides apparently have a rod-like shape at all temperatures whereas in the case of the gentiobioside it becomes rod-like at elevated temperatures only.

These two cubic phases (the one observed with banana shaped short-chain molecules and the one observed with long-chain glycosides) belong probably to two different groups as might be concluded from the contact preparations with water (see below): the former to the normal type of bicontinuous cubic phases and the latter to the inverted type. These terms are normally only used to describe the structure of lyotropic cubic mesophases, but it seems likely that they can be extended to describe these structures. X-ray investigations and model simulations performed earlier to investigate the structure of the cubic mesophase of dodecyl- α -D-gentiobioside **57** (Fischer et al., 1994) point towards a cubic phase of the space group No. 230, Ia-3d, made up by a network of cylinders like in the lyotropic case.

At the end of this section it seems useful to summarise the results of the discussion of the thermotropic properties of the disaccharide derivatives:

- *The disaccharide derivatives show generally higher melting and clearing points than the monosaccharide derivatives due to the increased hydrogen bonding in the headgroup region.*
- *The influence of structural changes to the aglycon is diminished in the case of disaccharide derivatives compared with the monosaccharide compounds.*

- The stability of the S_A phase increases, the more rod-like the sugar headgroup becomes, favouring generally the β -linkage of the saccharide moiety to the aliphatic chain as well as the β -linkage between the two glycosyl residues. For the same reason the stability of the S_A phase of compounds with a 1 \rightarrow 6 linked disaccharide moiety is decreased compared to their counterparts with a 1 \rightarrow 4 linked disaccharide headgroup.
- The above-mentioned difference in stability between the anomers decreases with increasing length of the aliphatic chain.

There are two different structural features which support the occurrence of thermotropic cubic mesophases:

- linear structures with an imbalanced ratio between the hydrophilic and hydrophobic moieties may form monotropic cubic mesophases.
- bent molecular structures, as they are found in glycosides with a 1 \rightarrow 6 linked disaccharide moieties, form cubic mesophases in the case of an appropriate length of the aliphatic chain.

Lyotropic phase behaviour

The stearyl- β -D-glucopyranoside **6** displayed in a contact preparation with water only myelin figures as did other long-chain alkyl glycosides with a monosaccharide headgroup (see section 3.3.1). Myelins are mobile tubular structures which are considered to consist of cylindrical or helical arrangements of many (300-5000) of the bilayers that constitute the lamellar phase (Jeffrey and Wingert, 1992; Bouligand, 1998).

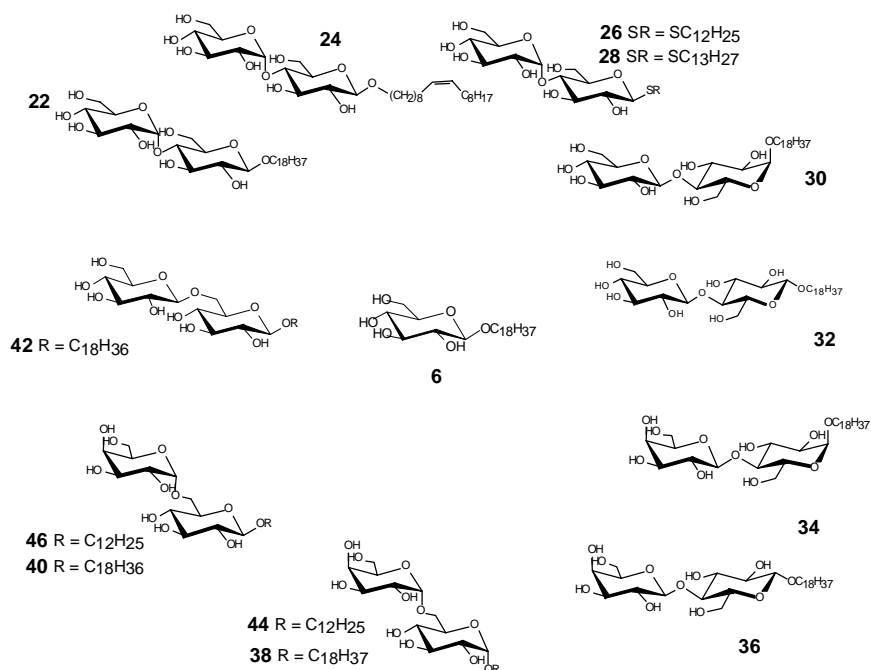
If the monosaccharide headgroup of **6** is replaced by the disaccharide maltobiose (compound **22**), three phases are formed (Figure 3.15) with increasing water concentration: a lamellar L_α phase, a columnar H_1 phase and a further, only weakly anisotropic phase. Replacing the stearyl chain by an oleyl chain (**24**) leads to the appearance of an additional broad bicontinuous cubic V_1 phase and this phase sequence, i.e. L_α , V_1 , H_1 and a weakly anisotropic phase, is also found in the case of the dodecyl- and tridecyl thiomaltosides **26** and **28**. The already mentioned weakly anisotropic phase, which appeared as a more or less thin band at the edge of the H_1 phase towards the water region, was also found with all other compounds except for the dodecyl α - and β -melibiosides **44** and **46** (Figure 3.15). Since a micellar cubic I_1 phase can be

ruled out as explanation because of its isotropic structure, a lyotropic cholesteric phase might be supposed as explanation. This phase is expected to appear at higher water concentration than the columnar H_1 phase and to be anisotropic. Both of these criteria are fulfilled by the phase that has been found. Whereas quite a lot is known about thermotropic cholesteric phases, their lyotropic counterparts are still seldom observed and not well understood. The mesophase of lyotropic cholesteric phases is build up by anisotropic micelles and therefore it should be possible to prove the occurrence of this phase by determining the size and shape of the micelles.

To verify or disprove the existence of a lyotropic cholesteric phase small-angle neutron scattering (SANS) measurements were performed using samples of dodecyl- and tridecyl- β -D-thiomaltobioside **26** and **28** to determine the size and shape of the micelles.

The shape of the distribution function (Figure 3.16) calculated from the scattering data using the program GNOM (by D. Svergun, EMBL, Hamburg) suggests that some non-spherical aggregates are formed, since in the case of spherical micelles a gaussian shaped distribution function would have been found. These results supported our hypothesis that the found phase might be a lyotropic cholesteric phase and in the next step model calculations (for details: see methods section) have been performed to simulate the SANS pattern of the two possible kinds of anisotropic micelles: disc like micelles and cylindrical micelles. In Figure 3.17 the experimental SANS data are shown, together with the model fits for the two different kinds of micelles. It can easily be seen that the experimental data match very well with the model fits for cylindrical micelles and with this information the size of the micelles forming the lyotropic cholesteric phase of compounds **26** and **28** was calculated from the SANS data:

- Compound **26** (Mal- β -SC₁₂H₂₅): Radius of cylinder 19.5/0.1 Å, Length 290/1 Å.
- Compound **28** (Mal- β -SC₁₃H₂₇): Radius of cylinder 20.0/0.1 Å, Length 290/1 Å



6		L_α (Myeline figures)					
22		L_α		H_1		ch	
24		L_α	V_1	H_1		ch	
26		L_α	V_1	H_1		ch	
28		L_α	V_1	H_1		ch	
30	V_2	L_α	V_1	H_1		ch	
32		L_α		H_1		ch	
34			glass ^a	V_1	H_1	(ch? ^b)	
36			glass ^a	V_1	H_1	(ch? ^b),	
38		L_α	Cr	V_1	H_1	ch	
40		L_α	Cr		H_1	ch	
42			glass ^a	V_1	H_1	ch	
44				V_1	H_1	I_1 I_{1*}	
46				V_1	H_1	I_1	

Figure 3.15: Phase sequences observed in the contact preparation of the synthesised amphiphilic liquid crystals with a disaccharide headgroup with water.

- a A cubic glass was formed on cooling of the melted sample, which was used for the contact preparation.
- b The boundary of the H_1 phase towards the water region was somewhat diffuse. Thus the existence of a lyotropic cholesteric phase could not be proved conclusively.

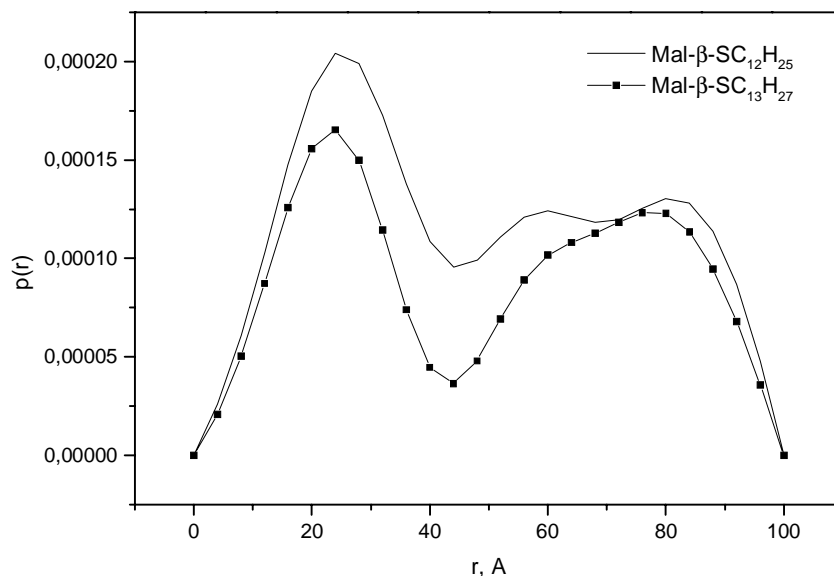


Figure 3.16: Distance distribution function $p(r)$ calculated from the experimental SANS data. The experimental solutions were prepared by dissolving the maltobiosides **26** and **28** in heavy water at a concentration of 90 mmol and 100 mmol respectively.

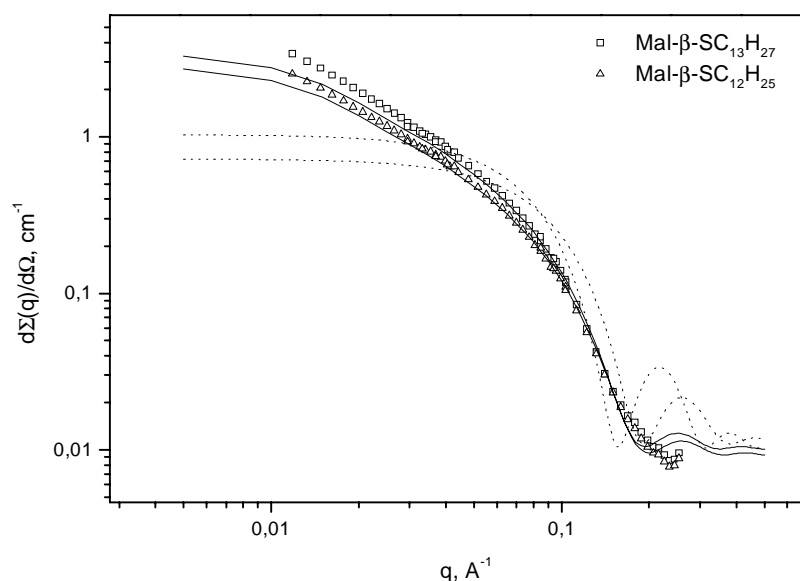


Figure 3.17: SANS data for compounds **26** and **28** together with the model fits; solid lines: model fits for cylindrical micelles, dashed lines: model fits for disc-like micelles.

Since this phase was found more less abundantly in the case of stearyl glycosides with a disaccharide headgroup, the question arose as to whether or not its occurrence is restricted to this long-chain compounds. To answer this question contact preparations using maltobiosides with a shorter alkyl chain were performed. In the case of the tetradecyl- β -D-maltobioside **54**, a

lyotropic cholesteric phase was still found by polarising microscopy. This phase disappeared if the tetradecyl chain was shortened by two CH_2 groups (dodecyl- β -D-maltobioside **53**).

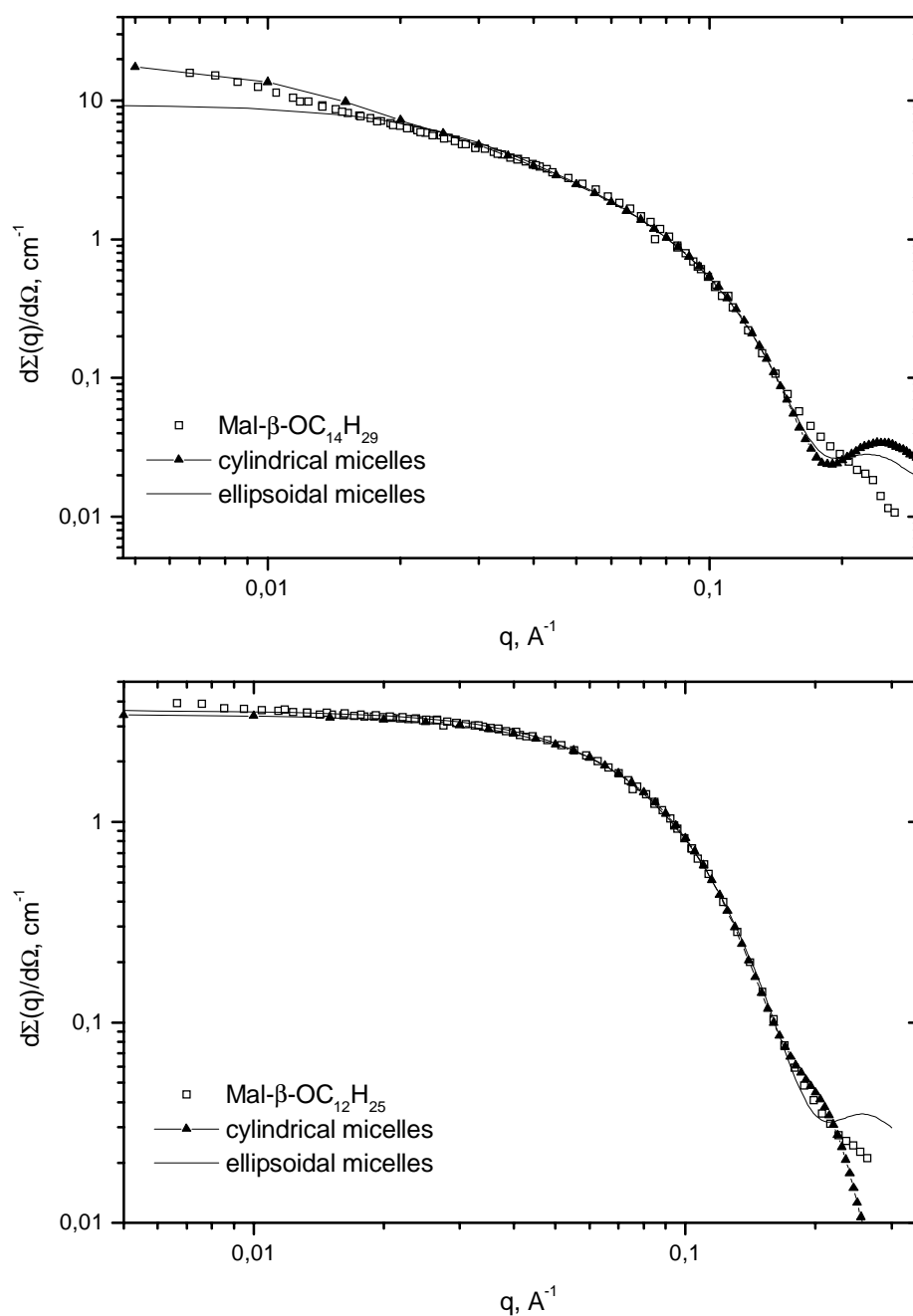


Figure 3.18: SANS data and model fits for:

- SANS data for Mal- β -OC₁₄H₂₉ (**54**) together with model fits for cylindrical and ellipsoidal micelles.
- SANS data for Mal- β -OC₁₂H₂₅ (**53**) together with model fits for cylindrical and ellipsoidal micelles.

These compounds have also been analysed by small-angle neutron diffraction (SANS). The SANS data of the tetradecyl- β -D-maltobioside **54** (Figure 3.18) again matched well with the model fits for cylindrical micelles (the size of the micelles was calculated as above from the SANS data; length of the cylinders: 200 Å, radius: 20 Å), while the SANS data of dodecyl- β -D-maltobioside **53** do not (Figure 3.18). These data match instead well with the model fit calculated for ellipsoidal micelles (again the size of the micelles was calculated from the SANS data; minor radius 20 Å, axis ratio 1.8). This result, together with the outcome of the contact preparations, can be interpreted in terms of a chain length dependence of the occurrence of a lyotropic cholesteric phase. This phase can only be found beyond a minimum chain length, which in the case of the alkyl- β -D-maltobiosides proved to be a tetradecyloxy chain. Below this chain length, only slightly unisotropic ellipsoidal micelles are formed which do not form a lyotropic cholesteric phase. The reason for this chain length dependence might be seen in constraints to the formation of unisotropic micelles, due to problems filling the hydrophobic volume of the anisotropic micelles in the case of short alkyl chains.

The α -cellobioside **30** formed on cooling of the melted sample the already described monotropic cubic phase, which was brought into contact with water. With increasing water concentration a lamellar phase formed, followed by another cubic phase, a columnar phase and a lyotropic cholesteric phase at the highest water concentration and the phase sequence is therefore: V_2 , L_α , V_1 , H_1 , ch (Figure 3.15). From this contact preparation it can be concluded that the thermotropic cubic phase of the cellobioside **30** should also be of the inverted type of bicontinuous cubic phases (see also thermotropic discussion above) and the same holds true for the monotropic cubic phases of the lactobiosides **34** and **36**, since the reason for the formation of this monotropic cubic phase –i.e. a linear structures with an extremely imbalanced ratio between the hydrophilic and hydrophobic moieties– is the same. After penetration with water, the lactobiosides **34** and **36** formed with increasing water concentration only a cubic, a columnar and probably also a lyotropic cholesteric phase, i.e. the phase sequence was V_1 , H_1 , ch. Within the cubic phase a sharp boundary could be seen, separating two isotropic regions. Since no lamellar phase was formed like in the case of the cellobioside **30** it is impossible to decide whether the inner isotropic region is of the inverted cubic V_2 type or a cubic glass, which has formed out of the cubic phase on cooling. The formation of a cubic glass on cooling could also account for the disappearance of the additional lamellar L_α phase.

Since the boundary of the H_1 phase towards the water region was somewhat diffuse in the case

of the lactobiosides, the existence of a lyotropic cholesteric phase, normally forming a thin weakly anisotropic band besides the columnar phase could not be proved unambiguously by polarising microscopy. However this seems very likely.

The β -cellobioside **32**, which crystallised much better than the α -cellobioside **30**, formed only an L_α phase, a H_1 phase and a lyotropic cholesteric phase with water.

The stearyl- α -melibioside **38** formed with increasing water concentration a lamellar L_α phase, followed by a region where crystallisation occurred, followed by a cubic V_1 phase, a columnar H_1 phase and a lyotropic cholesteric phase at the highest water concentration. For the β -anomer **40**, the same phase sequence was observed except for the bicontinuous V_1 phase, which disappeared completely while the region where crystallisation occurred broadened. The explanation for this behaviour might be again the already mentioned greater tendency of the compounds with a β -linked aliphatic chain to crystallise.

On penetration with water, the cubic phase of dodecyl- α -melibioside **44** developed a columnar phase followed by two isotropic regions separated from each other by a sharp border. These isotropic phases in the contact preparation beyond the H_1 phase towards higher water concentration are, according to the general phase behaviour of amphiphiles, supposed to be micellar cubic phases, i.e. the phase sequence is V_1, H_1, I_1, I_{1*} , but it is rather unusual that two of them are found and in the case of the β -anomer **46** the second discontinuous cubic phase disappeared. This different behaviour must be attributed to the different linkage of the aliphatic chain to the melibiose headgroup, yielding in the case of the α -anomer an even broader banana-shaped structure than in the case of the β -anomer.

These results can be summarised as follows:

- *Stearyl glycosides with a disaccharide headgroup display in the contact preparation with water a broad polymorphism while the alkyl monoglycosides exhibit only myelin figures.*
- *Regardless of the chemical structure, the stearyl glycosides with a disaccharide headgroup form a lyotropic cholesteric phase.*
- *The occurrence of a lyotropic cholesteric phase is chain length-dependent, as could be shown for the maltobiosides.*
- *In the case of very broad headgroups (e.g. melibiosides) and short chains, micellar cubic phases can be found.*
- *The bicontinuous cubic phase of type I occurs more or less abundantly in the contact*

preparation of the stearyl glycosides bearing disaccharide headgroups with water, except for the case of the maltobioside 22, the cellobioside 32 and the melibioside 40, in the latter two cases only because of crystallisation. Due to the disaccharide headgroup the size of the headgroup increases strongly on the addition of water because of hydration, causing the molecule not to be rod-like any more. With increasing hydration they become finally wedge-shaped and a hexagonal phase of type 1 is formed. At a medium water concentration the molecules are not rod-like any more and cannot be incorporated into a lamellar phase, but they are not really wedge-shaped to be incorporated into a hexagonal phase and thus a bicontinuous cubic phase is formed.

Fourier-transform infrared spectroscopy

The $L_{\beta} \longleftrightarrow L_{\alpha}$ alkyl chain melting was determined IR-spectroscopically via the $\nu_s(\text{CH}_2)$ -vibration. The phase transition temperatures of the melibiosides and thiomaltobiosides **26**, **28**, **44** and **46** with short lipid chains (C12 and C13) lie in the range <0 to 7 °C, i.e., there are only slight differences between the O- and S-containing samples (Figure 3.19a). The different wavenumber values corresponding to different states of order in the respective phase states are noteworthy: This relates in particular for the melibiosides, which are in the α -linkage more fluid (higher wavenumbers) than in the β -linkage. As should be expected, the T_c -values of the C18-containing samples are much larger than those with shorter alkyl chains (Figure 3.19b). However, the kind of disaccharide and the nature of the linkage strongly influences the T_c -value. For example, regarding the stereoisomeric stearyl melibiosides and lactosides, the T_c -value of the latter as well as their state of order is much higher than that of the former (Figure 3.19b). For the melibiosides, the T_c -values are 38 and 67.5 °C in α - and β -linkage (**38** and **40**), respectively.

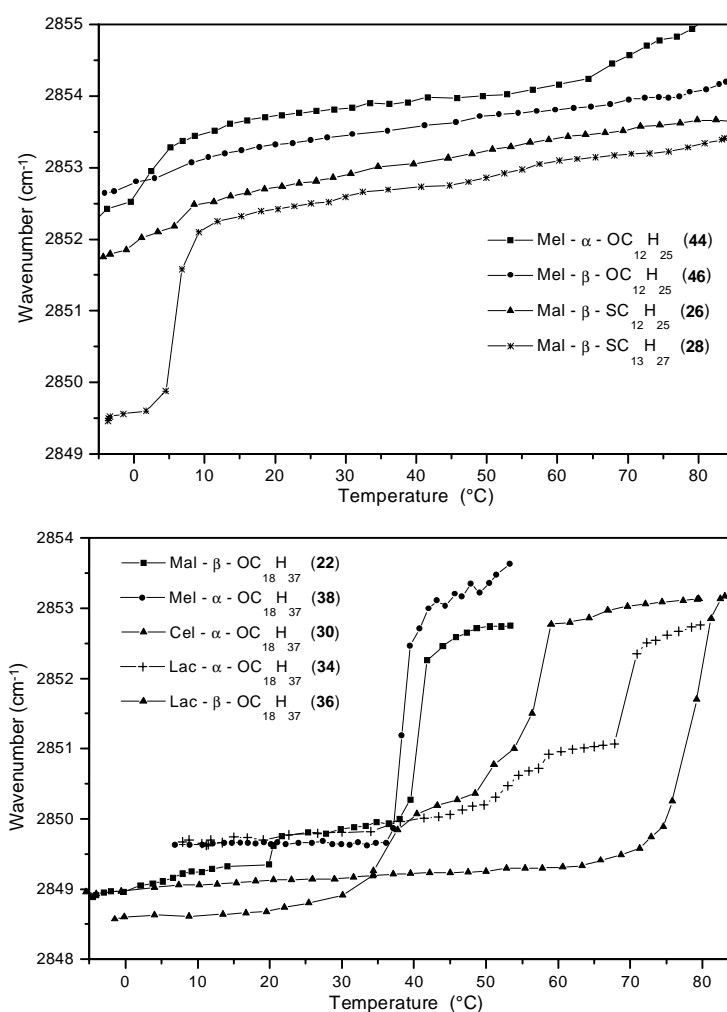


Figure 3.19: Peak position of the symmetric stretching vibration of the methylene groups $\nu_s(\text{CH}_2)$ versus temperature for various (a) short-chain disaccharide glycosides and (b) stearyl disaccharide glycosides.

Synchrotron radiation X-ray diffraction

The three-dimensional aggregate structures are also strongly dependent on the sugar- and linkage-types. The results for the dodecyl melibiosides (**44** and **46**) and the dodecyl and tridecyl thiomaltosides (**26** and **28**) with short alkyl chains are presented in Figure 3.20. The scattering curves basically consist of two broad intensity maxima around 0.1/nm and 0.25 to 0.30/nm, which might be interpreted as typical for unilamellar structures (Worthington and Khare, 1978; Bouwstra et al., 1993). For the maltosides, above 40 °C sharp reflections occur, which could be typical for multilamellar aggregation. However, the ‘normal’ bilayer L phase can be excluded, because in that case the periodicities should be much higher (for a maltose-containing ether-linked C14-dialkylglycolipid). Hinz et al. (1991) found values above 6 nm. Therefore, an interdigitation of the alkyl chains may be assumed similarly as found

recently for stearyl monosaccharides (Vill et al., in press), for these, however, only in the gel phase.

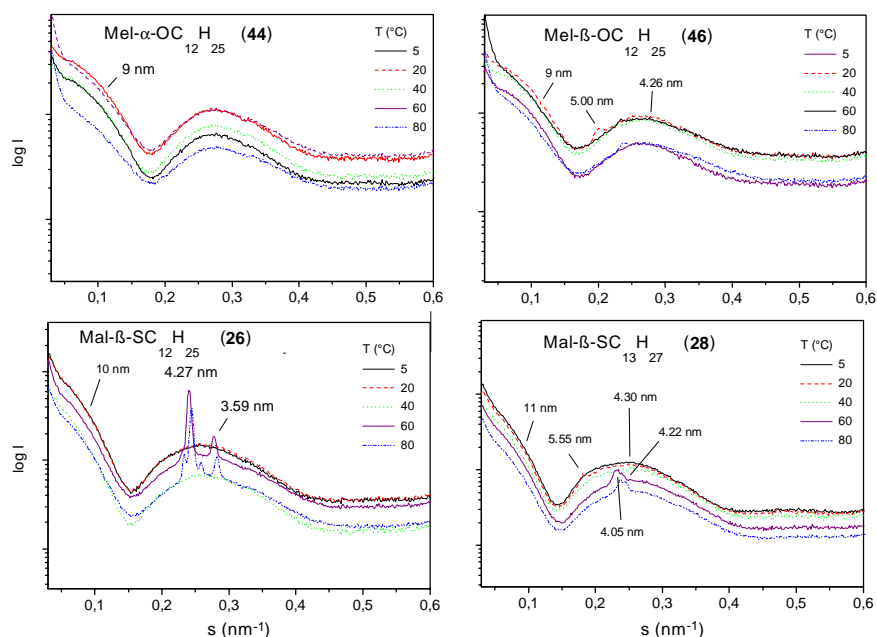


Figure 3.20: Small-angle X-ray diffraction patterns for various short-chain disaccharide glycolipids in the temperature range 5 °C – 80 °C. Water content: 90 %.

The samples with a C-18 chain and the different disaccharides maltose, melibiose, cellobiose and lactose as headgroup exhibit a much more complex structural polymorphism. The broad diffraction maxima indicate the existence of unilamellar structures, except for the β -linked maltobioside **22**. The latter undergoes two phase changes (Figure 3.21). At 5 °C, the two reflections at 6.22 and 3.58 nm are in a ratio of $\sqrt{3}$, indicating the absence of a lamellar phase, but rather the presence of the micellar H_1 phase. Above 20 °C, i.e., above the temperature of the ‘pre-transition’ (see Figure 3.19), clearly a multilamellar structure can be observed. Another structural change occurs above 60 °C, the diffraction patterns at 80 °C expressing a strong increase of the main peak to 5.59 nm and an occurrence of two new reflections at 4.55 and 2.75 nm. These numbers, however, are not interconnected by a particular numerical relation as found in lamellar or cubic structures possibly indicating the superposition of different structures. From Figure 3.21 it becomes clear that the stereoisomeric maltoside and cellobioside behave quite differently, emphasising the importance of the kind of anomeric linkage.

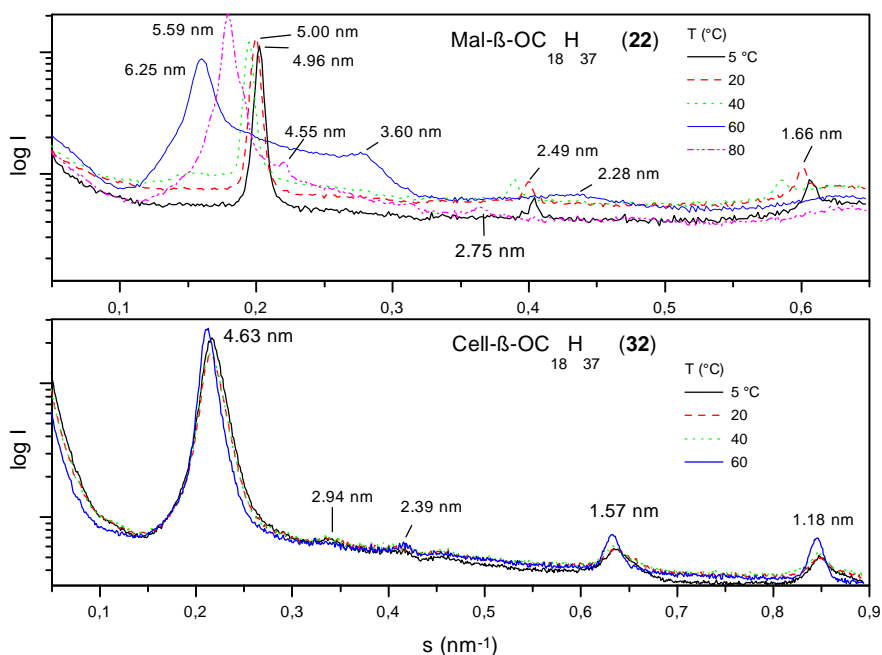


Figure 3.21: Small-angle X-ray diffraction patterns in the temperature range 5 °C – 80 °C for the stereoisomers stearyl- β -maltoside (22) and stearyl- β -cellobioside (32). Water content: 90 %.

The melibiose-containing α -linked sample exhibits complex diffraction patterns between 5 and 40 °C (Figure 3.22), which may be due to a cubic structure (e.g., the relations hold $3.59 \text{ nm} = 12.5 \text{ nm} / \sqrt{12}$ and $2.77 \text{ nm} = 12.5 \text{ nm} / \sqrt{20}$). Above $T_c = 40 \text{ }^\circ\text{C}$, the structure converts into a different, possibly unilamellar one. The shape of the broad diffraction maxima indicates, however, that another unresolvable structure may be superimposed. A similar polymorphism like that of the latter sample is expressed by the cellobiose-containing compound, the only difference is the higher temperature at which the change into a mainly unilamellar phase occurs - corresponding to the higher value of $T_c = 55 \text{ }^\circ\text{C}$.

The two lactosides exhibit a very similar behaviour over the entire temperature range (data not shown). The patterns might be interpreted as resulting from lamellar structures - the broadness of the peaks indicates a low number of lamellae. However, a jump of the peak maximum to higher values (4.76 and 4.65 nm, respectively) at $T_c = 70 \text{ }^\circ\text{C}$ is observed, which does not indicate a pure $L_\beta \leftrightarrow L_\alpha$ transition, because this should be accompanied by a decrease rather than an increase of the periodicity. The latter observation could be consistent with a transition

from a lamellar into a non-lamellar phase as previously found for lipid A from *Salmonella minnesota* for the $L \longleftrightarrow H_2$ transition (Brandenburg et al., 1998).

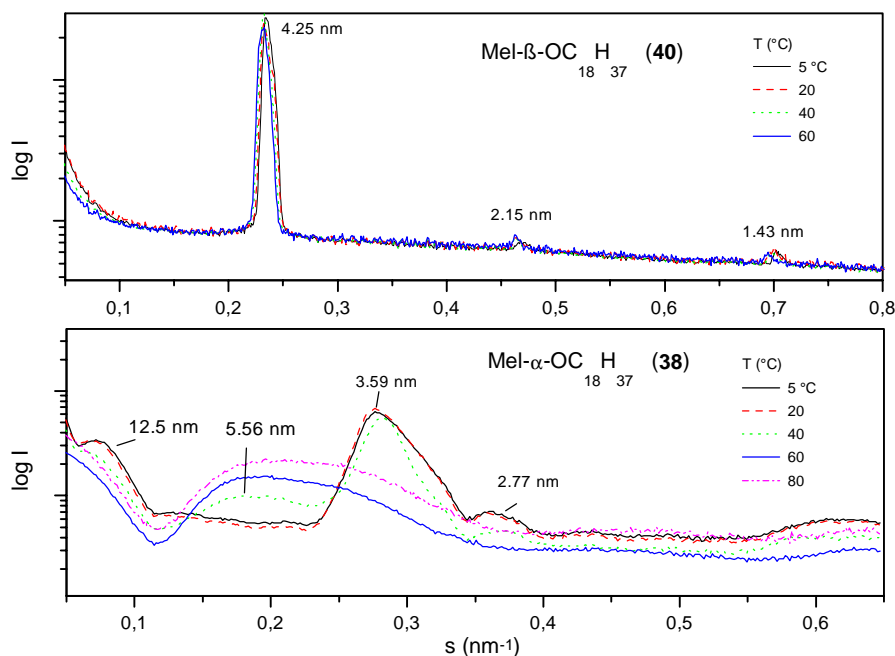


Figure 3.22: Small-angle X-ray diffraction patterns in the temperature range 5 °C – 80 °C for the two melibioside anomers **38** and **40**. Water content: 90 %.

For some of these glycosides, also wide-angle X-ray diffraction experiments were performed to determine the short range order, i.e., the packing of the alkyl chains, in particular in their gel phase. It was found that, for example, for the two melibiosides the α -anomer has a reflection at 0.451 nm, whereas that of the β -anomer is centred at 0.420 to 0.424 nm, indicating, in accordance to the infrared data, a higher order of the latter anomeric configuration. Table 1 summarises the results of the infrared spectroscopic and the X-ray diffraction experiments. In accordance with the microscopic contact preparations, $Cel\text{-}\alpha\text{-OC}_{18}\text{H}_{37}$ forms a cubic phase, whereas for the lactosides only lamellar phases are observed in contrast to the contact preparation. For an understanding, it should be considered that the X-ray data were obtained at a much higher (90 %) water content than in the microscopic preparations (see lyotropism). The reduction of the water concentration in X-ray diffraction experiments to 55% gave results very similar to those obtained at 90 % buffer content, i.e., a lyotropic phase behaviour as described above should play a role only at water

concentrations below 50 %.

Glycolipid	T_c (°C)	Aggregate Structures	Wide-angle reflection (nm)
Mel- α -OC ₁₂ H ₂₅ (44)		L	no reflection
Mel- β -OC ₁₂ H ₂₅ (46)	<0	L	no reflection
Mel- α -OC ₁₈ H ₃₇ (38)	38	Q(5-40 °C) L/unknown (60-80 °C)	0.451, unsharp
Mel- β -OC ₁₈ H ₃₇ (40)	67.5	L	n.m.
Mal- β -SC ₁₂ H ₂₅ (26)	<0	L (5-40 °C) L/L' interdigitated (60-80 °C)	no reflection
Mal- β -SC ₁₃ H ₂₇ (28)	6	L	0.441 and 0.256
Mal- β -OC ₁₈ H ₃₇ (22)	40	H ₁ > L > Q	0.424 (5°C), 0.420 (20-40 °C)
Mal- β -OC _{18:1} ^{Δ^9} H ₃₇ (24)	<0	L	no reflection
Cel- α -OC ₁₈ H ₃₇ (30)	36 (T _{pre}) 56	Q (5-60 °C), L (80°C)	0.466 and 0.390
Cel- β -OC ₁₈ H ₃₇ (32)	70	L	n.m.
Lac- α -OC ₁₈ H ₃₇ (34)	53(T _{pre}) 70	L	0.442
Lac- β -OC ₁₈ H ₃₇ (36)	78	L	0.453, unsharp
Gen- β -OC ₁₈ H ₃₇ (42)	54	L(5-60 °C), H ₂ (80°C)	n.m.

Table 3.1: Gel to liquid crystalline phase transition T_c , type of supramolecular aggregate structures (L lamellar, Q cubic and H hexagonal) and position of wide-angle X-ray diffraction for various „Glc-Glc“ and „Glc-Gal“ glycolipids. n.m. = not measured.

Although the investigated disaccharide headgroups exclusively consist of a „Glc-Glc“ or „Glc-Gal“ compound, an enormous diversity of structural polymorphism (alkyl chain melting and order, types of aggregate structures) are observed dependent of the kind of sugars and of the anomeric linkage to the acyl chain and within the two sugars. These observations might give an insight into the complex biological functions of such glycolipids in nature.

4. Synthesis and mesogenic properties of glycosyl diacylglycerols

4.1 Introduction

Glycosyl diacylglycerols are known to be important constituents of many cell membranes. These lipids (e.g. β -glucosyl glycerols, Figure 4.1) consist of a carbohydrate polar headgroup (containing 1-8 sugar moieties) attached to a 1,2-di-*O*-acyl-*sn*-glycerol via an α - or β -glycosidic linkage (Ishizuka and Yamakawa, 1985). Glycosyl diacylglycerols with a sugar headgroup of one to three glycosyl residues are major structural components of the cell membrane while the more complex examples with bigger carbohydrate headgroups are involved in cell surface recognition processes (Curatolo, 1987).

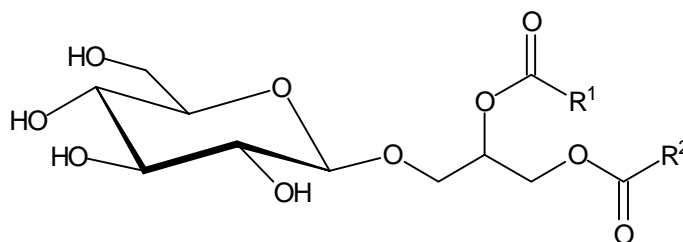


Figure 4.1: 1,2-di-*O*-acyl-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol

Despite the great importance of this class of glycolipids, very little data is available in the literature concerning their physical properties, which hampers a clear understanding of the way in which their structure is related to their unique role in biomembranes. In a review article about the mesogenic properties of glycosyl diacylglycerols published in 1994 by Caffrey (Koyanova and Caffrey, 1994) most of the entries refer only to glucosyl diacylglycerols and their ether analogues followed by a less comprehensive group of galactosyl diacyl- and dialkylglycerols. Besides these „bigger“ compilations only a few other entries can be found concerning glycolipids with disaccharide or larger headgroups, and all of them belong to the dialkylglycerol type with the aliphatic chains bound by ether instead of ester bonds to the glycerol moiety.

The reason for the aforementioned lack of information might be the difficulty obtaining sufficient amounts of glycosyl diacylglycerols necessary for a thorough physical characterisation. Traditionally the lipids have mostly been isolated from natural sources. For example, monogalactosyl and digalactosyl diacylglycerols with polyunsaturated fatty acid

chains have been extracted from plants and algae where they account for more than 80 % of the polar lipids in the photosynthetic membranes (Quinn and Williams, 1983). The investigation of the mesogenic properties of these extracted lipids also improved the understanding of their role in the structure and function of photosynthetic membranes (review: Quinn and Williams, 1983), e. g. that the activity of enzymes of the photosynthetic process strongly depends on the presence of these lipids (Pick et al., 1987).

Unfortunately it is impossible to obtain glycolipids with a homogeneous fatty acid composition by extraction from natural sources. After purification and separation, the extracted glycolipids have a common sugar headgroup but always a heterogeneous fatty acid composition, with a statistical mix of different chain lengths and degree of unsaturation dependent on the source, environmental/growing conditions and the exact extracting procedure. Hence it was impossible to analyse the mesogenic properties of well-defined compounds and thus to understand the properties of a given membrane on the basis of its constituting components.

To circumvent these problems, chemical synthesis was used to obtain pure compounds, but this was hampered by difficulties encountered in synthesising optically active compounds of high anomeric purity. Several strategies have been used to solve this problem:

- glycolipids that have been extracted from natural sources have been used as starting materials and by means of classical synthesis semisynthetic compounds with a defined acyl chain structure were obtained (Heinz 1971; Heinz et al., 1979). Since sources of large quantities of natural glycolipids with a wide range of headgroup structures are scarce, this approach is still rather limited and not helpful for this work, i.e. performing a systematic structure variation to elucidate structure-property relationships.
- another solution to the problem of glycolipid synthesis was to avoid some of the difficulties inherent in the synthesis of glycosyl diacylglycerols by preparing the corresponding dialkyl analogues. Based on this approach, the synthesis of glucosyl (Six et al., 1983; Hinz et al., 1991 and 1996), glucuronosyl (Koynova et al., 1993), galactosyl (Kuttenreich et al., 1988; Hinz et al., 1991 and 1996), mannosyl (Hinz et al., 1991 and 1996), maltosyl (Six et al., 1983; Hinz et al., 1991) and maltotriosyl (Hinz et al., 1996) dialkylglycerols was described and except for the glucosyl compounds (Six et al., 1983), mesogenic properties were also investigated. However, the properties of the dialkyl compounds differ from the properties of the diacyl compounds. The former are therefore of limited value as model compounds for the naturally occurring glycosyl diacylglycerols (Lewis et al., 1990 and references cited therein).

Finally Mannock et al. (Mannock et al., 1987 and 1990) presented a convenient synthetic pathway to saturated α - and β -glucosyl diacylglycerols and determined their mesogenic properties in detail but hitherto neither the synthesis nor the mesogenic properties of similar compounds with other carbohydrate headgroups have been described and no data on synthesised glycosyl diacylglycerols with unsaturated chains are available.

Whereas Chapter 3 dealt with the synthesis and mesogenic properties of alkyl glycosides the synthesis and mesogenic properties of glycosyl diacylglycerols will be described here. Because of the aim of this work to derive structure-property relationships, a systematic variation of the carbohydrate headgroup will be presented. Whereas alkylglycosides are the simpler model compounds, glycosyl glycerols are more complex and closer to nature. Because of the experiences made before while analysing the mesogenic properties of the alkyl glycosides, glycosyl diacylglycerols with unsaturated *cis*-9-octadecanoyl chain were chosen as model systems to prevent crystallisation, as these compounds were intended for use in binary mixtures (see Chapter 5) where crystallisation may cause problems because of inhomogeneities in the mixture.

4.2 Synthesis of glycosyl diacylglycerols

The well-elaborated procedure from Mannock et al. (Mannock et al., 1987) for the synthesis of glucosyl diacylglycerols had to be modified for glycosyl diacylglycerols bearing unsaturated fatty acid chains. The synthetic strategy used by Mannock et al. is sketched in Figure 4.2. The first step is a condensation of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide **60** with 1,2-di-*O*-benzyl-*sn*-glycerol **71** under well-established Koenigs-Knorr conditions to obtain the β -glucoside **61**. The optically pure aglycon **71** is prepared in a 6-step procedure (Figure 4.3) starting with D-mannitol **65** (van Boeckel et al., 1985; Mannock et al., 1987). In this respect it is noteworthy that the easily accessible and optically pure 1,2-*O*-isopropylidene-*sn*-glycerol racemises during the Koenigs-Knorr condensation procedure (Wickberg, B., 1958; Wehrli and Pomeranz, 1969), due to intramolecular migration of the isopropylidene group and cannot be used thus. After hydrogenolytic removal of the benzyl protective groups of compound **61**, the glycerol **62** is afforded which yields after esterification and subsequent reductive deacetylation the glucosyl diacylglycerol **64**.

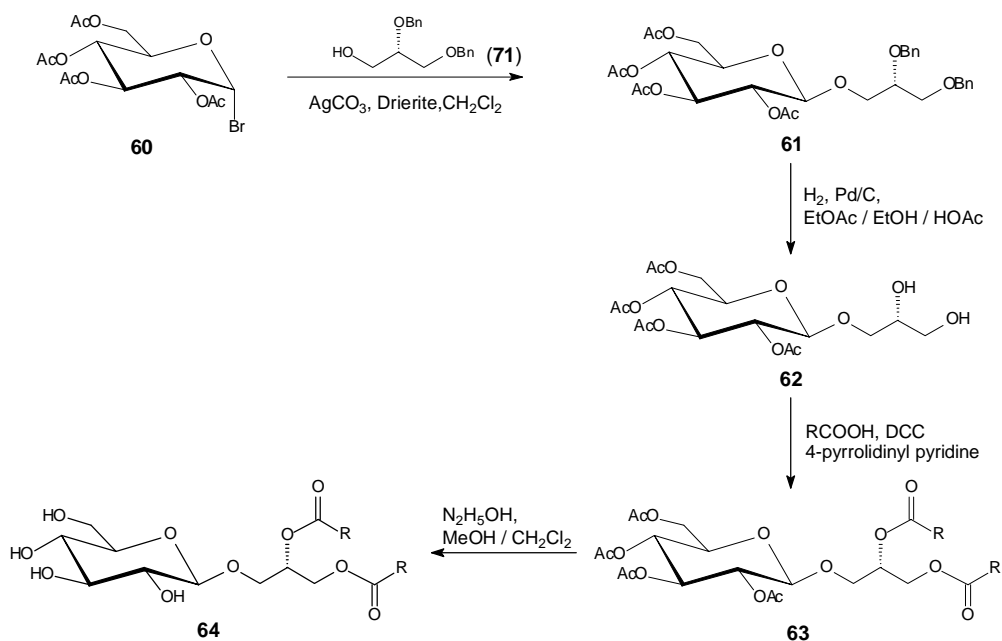


Figure 4.2: Synthesis of glycosyl diacylglycerols according to Mannock et al. (Mannock et al., 1987).

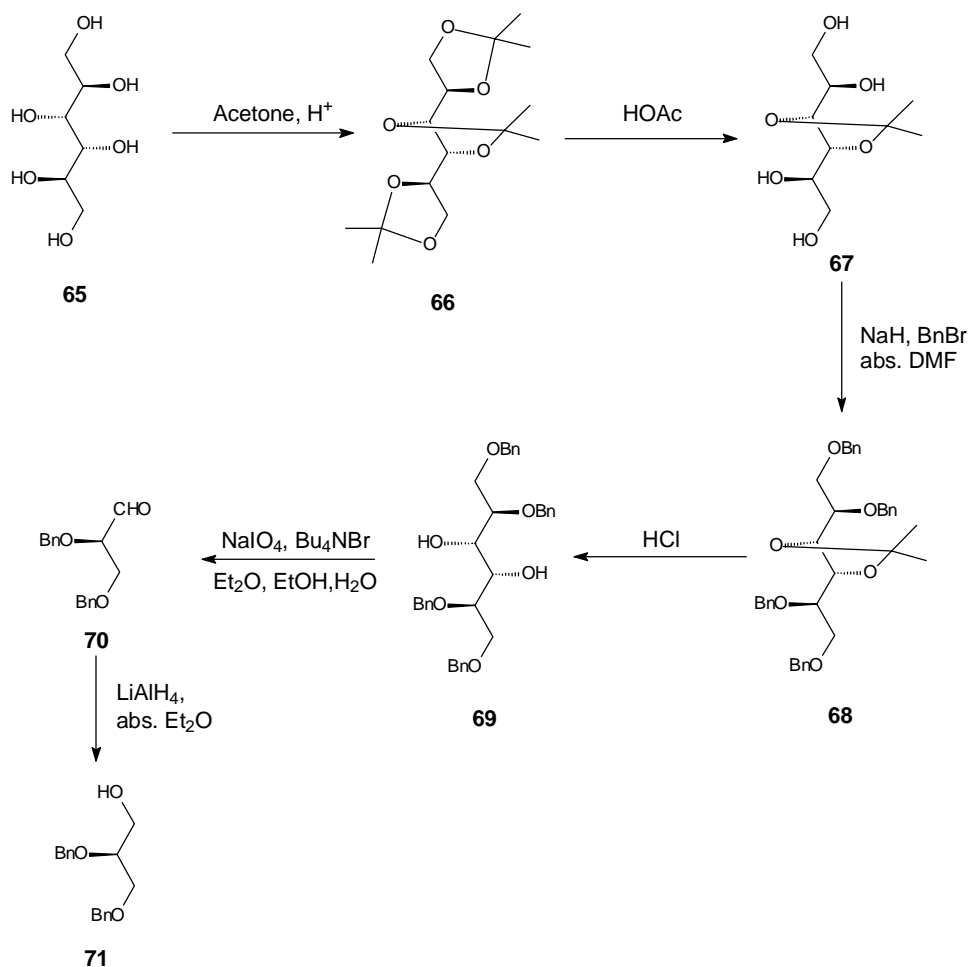


Figure 4.3: Synthesis of 1,2-di-*O*-benzyl-*sn*-glycerol

The final selective removal of the acetyl protecting groups of **63** in the presence of the fatty acyl groups esterified to the glycerol moiety is only possible under reductive conditions using hydrazine hydrate, and it is this final step which is troublesome in the case of unsaturated fatty acids (Nagatsu et al., 1994). For example, on treating 1,2-di-*O*-linoleoyl-3-*O*-(β -D-galactopyranosyl)-*sn*-glycerol with hydrazine hydrate Nagatsu observed only a low yield of the desired product, because linoleoyl groups were reduced to oleoyl groups, other monounsaturated and/or saturated acyl groups. Thus Nagatsu later exchanged the acetyl groups, which are necessary as neighbouring groups in the glycosylation step, for 4-methoxybenzyl groups which can easily be cleaved under mild conditions.

In the literature only a few cases of the synthesis of glycosyl diacylglycerols with unsaturated fatty acids can be found (Nagatsu et al., 1994; Chupin et al., 1994; van Boeckel et al., 1985). Nagatsu et al. described the synthesis of some galactosyl diacylglycerols with unsaturated acyl chains and the investigation of their anti-tumor-promoting activity. The inhibitory activity of the synthesised compounds on Epstein-Barr virus early antigen activation was evaluated as anti-tumor-promoting activity, with 1,2-di-*O*-oleoyl-3-*O*-(β -D-galactopyranosyl)-*sn*-glycerol showing the strongest activity. Unfortunately, no attempts have been made in the course of these investigations to characterise the liquid crystalline properties of the synthesised compounds, and the same holds true for the work of van Boeckel et al. (van Boeckel et al., 1985), who reported the synthesis of 1,2-di-*O*-oleoyl-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol used as a building block for the synthesis of a complex phospholipid. These efforts have been made by Chupin et al. (Chupin et al., 1994), who also synthesised 1,2-di-*O*-oleoyl-3-*O*-(β -D-galactopyranosyl)-glycerol, using however a synthetic strategy which only led to the formation of a product with a racemic glycerol moiety. Since the naturally occurring glycerol derivatives are never racemic, it seems unwise to use this strategy to synthesise model compounds.

In a first approach, the route and reaction conditions outlined in Figure 4.4 and 4.5 have been used in this work, and are a combination of the works from Nagatsu and van Boeckel. For example, glucose **1** was peracetylated and transformed into the sugar bromide **60** by the action of hydrogen bromide in glacial acetic acid. The bromide **60** was condensed with optically pure 1,2-Di-*O*-benzyl-*sn*-glycerol **71** under well-established Helferich conditions (Helferich and Olst, 1962) giving the glucosylglycerol **61** in excellent yield. Hydrogenolytic removal of the benzyl groups afforded the diol **62**, which was protected as isopropylidene ketal **72** by treatment with 2,2-dimethoxypropane in the presence of a catalytic amount of

4-toluenesulfonic acid. Deprotection of the acetylated sugar moiety using the Zemplen procedure yielded the glucoside **73**.

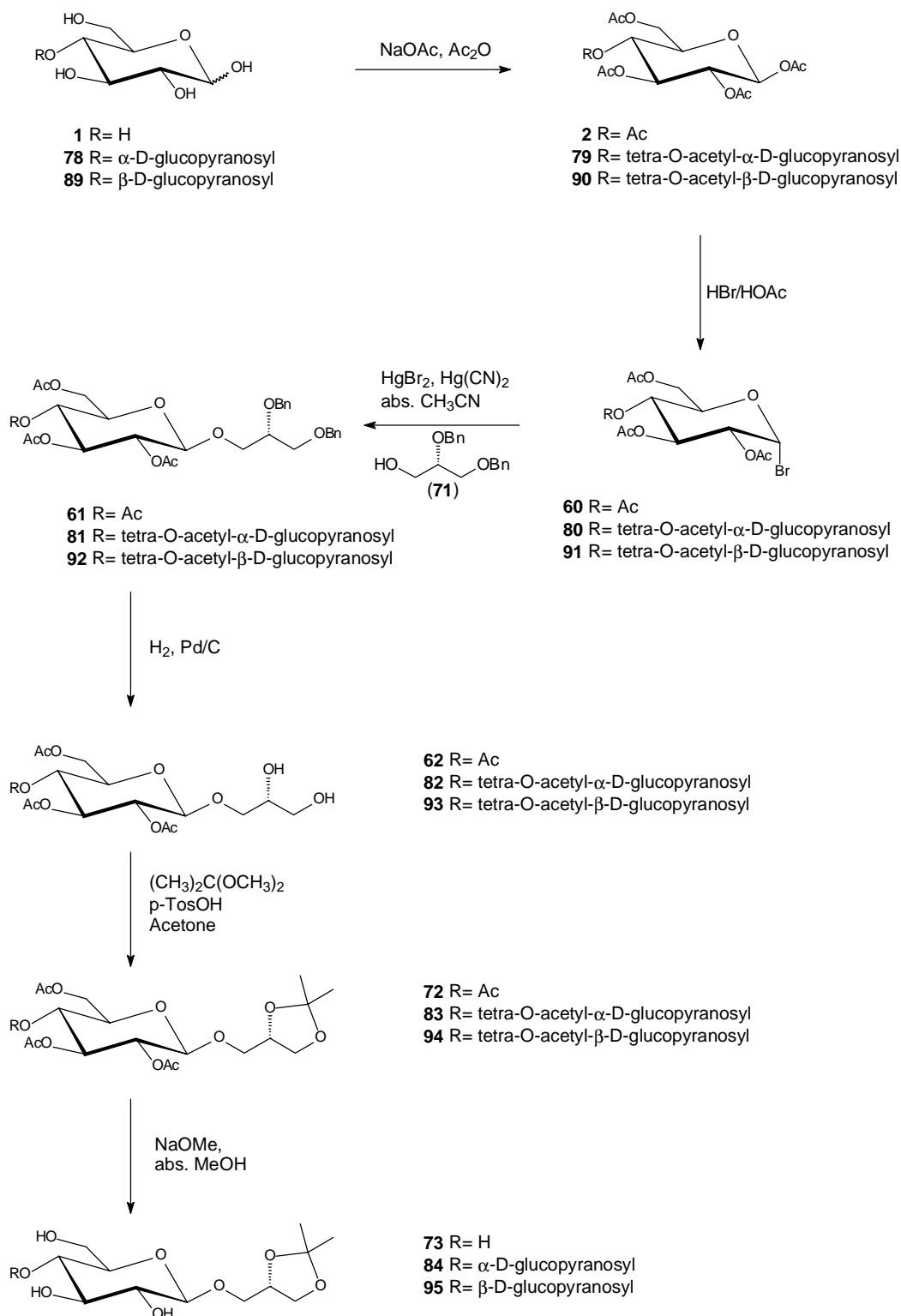


Figure 4.4: Synthesis of the intermediates **73**, **84** and **95**

The free hydroxyl groups of compound **73** were protected with *p*-methoxybenzyl groups (Classon et al., 1984; Johansson and Samuelsson, 1984; Oikawa et al., 1982), which can easily be cleaved in the final step under mild conditions, avoiding any interference with the double bonds. In the following synthetic steps the glycerol moiety was deprotected by treatment with aqueous acetic acid, giving the diol **75**. This was esterified with oleic acid using the DCC method (Hassner and Alexanian, 1978) and DMAP, yielding the ester **76** which upon removal of the 4-methoxybenzyl groups with ceric ammonium nitrate (Classon et al., 1984; Johansson and Samuelsson, 1984; Oikawa et al., 1982) gave the desired glyco lipid 1,2-di-*O*-oleoyl-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol **77** as a waxy solid.

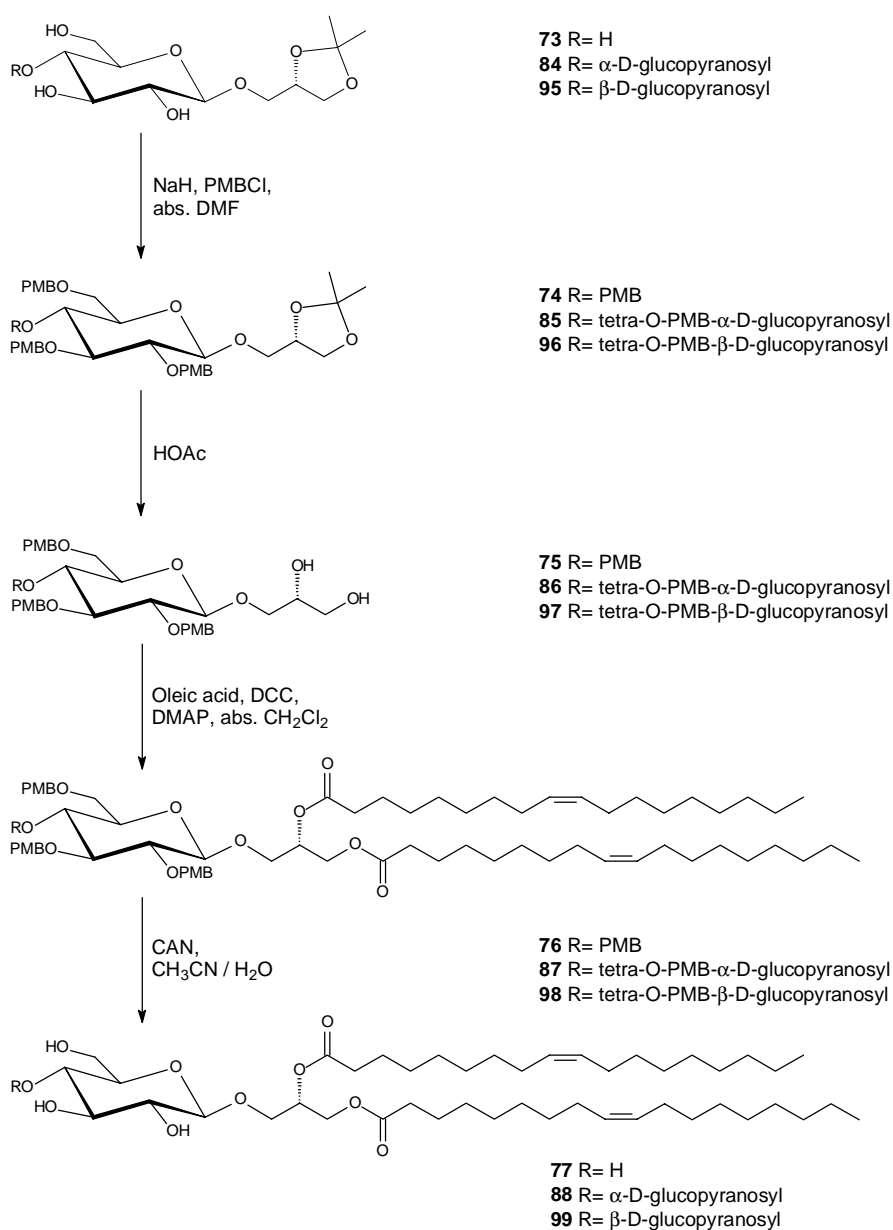


Figure 4.5: Synthesis of the glycosyl diacylglycerols **77**, **88** and **99**

Due to its liquid crystallinity at ambient temperature, the glycolipid **77** could not be recrystallised as additional purification after silica gel chromatography. To ensure the high purity which is necessary for the exact determination of the liquid crystalline transition temperatures, **77** was purified by means of an additional gel filtration. The same procedure as described above for the synthesis of the glucosyl compound **77** was also applied to the synthesis of the maltobiosyl and cellobiosyl compounds **88** and **99**. In the case of the disaccharide derivatives, the final deprotection step turned out to be troublesome since the end product was more or less insoluble in the solvent system and precipitated together with small amounts of partially deprotected intermediates, rendering the purification more difficult. For this reason, as well as to shorten the lengthy procedure by two steps, the chloroacetate protecting group was subsequently used instead of the 4-methoxybenzyl group. The chloroacetate group can be cleaved under very mild conditions using thio urea as reagent in ethanolic solution (T. Ziegler, 1990; van Boeckel and Beetz, 1983; Bertolini and Glaudemans, 1970). This new route is depicted in Figures 4.6 and 4.7. It was decided not to take advantage of the even shorter synthetic route starting with the perchloroacetylated sugar as the glycosyl donor precursor, because of the well known low stability of perchloroacetylated sugars as well as because of the significantly lower anomeric selectivity using this glycosyl donor in the glycosylation step (Ziegler, 1990). It was believed that the reactivity of the chloro acetates could easily have caused problems in a multistep synthesis.

Acetobromo galactose **102** was prepared as outlined in Figure 4.6 using standard procedures, and condensed with 1,2-di-*O*-benzylglycerol **71** affording the β -galactoside **103**, which was deacetylated using the Zemplen procedure to obtain compound **104**. The free hydroxyl groups of **104** were chloroacetylated with chloroacetic acid anhydride in the presence of sodium hydrogen carbonate in absol. dimethylformamide (Ziegler, 1990; Chittenden and Regeling, 1987). The hydrogenolytic removal of the benzyl protecting groups of derivative **105** in ethanol afforded compound **106**, which on evaporation of the solvent at 40 °C decomposed completely and even at 20 °C to some extent. This decomposition can be prevented by using ethyl acetate as solvent, and demonstrates the aforementioned and sometimes troublesome reactivity of the chloroacetate protecting group. The diol **106** was esterified with oleic acid using the procedure developed by Hassner and Alexanian (Hassner and Alexanian, 1978), and the ester **107** was dechloroacetylated in the final step by treatment with thio urea (T. Ziegler, 1990; van Boeckel and Beetz, 1983; Bertolini and Glaudemans, 1970).

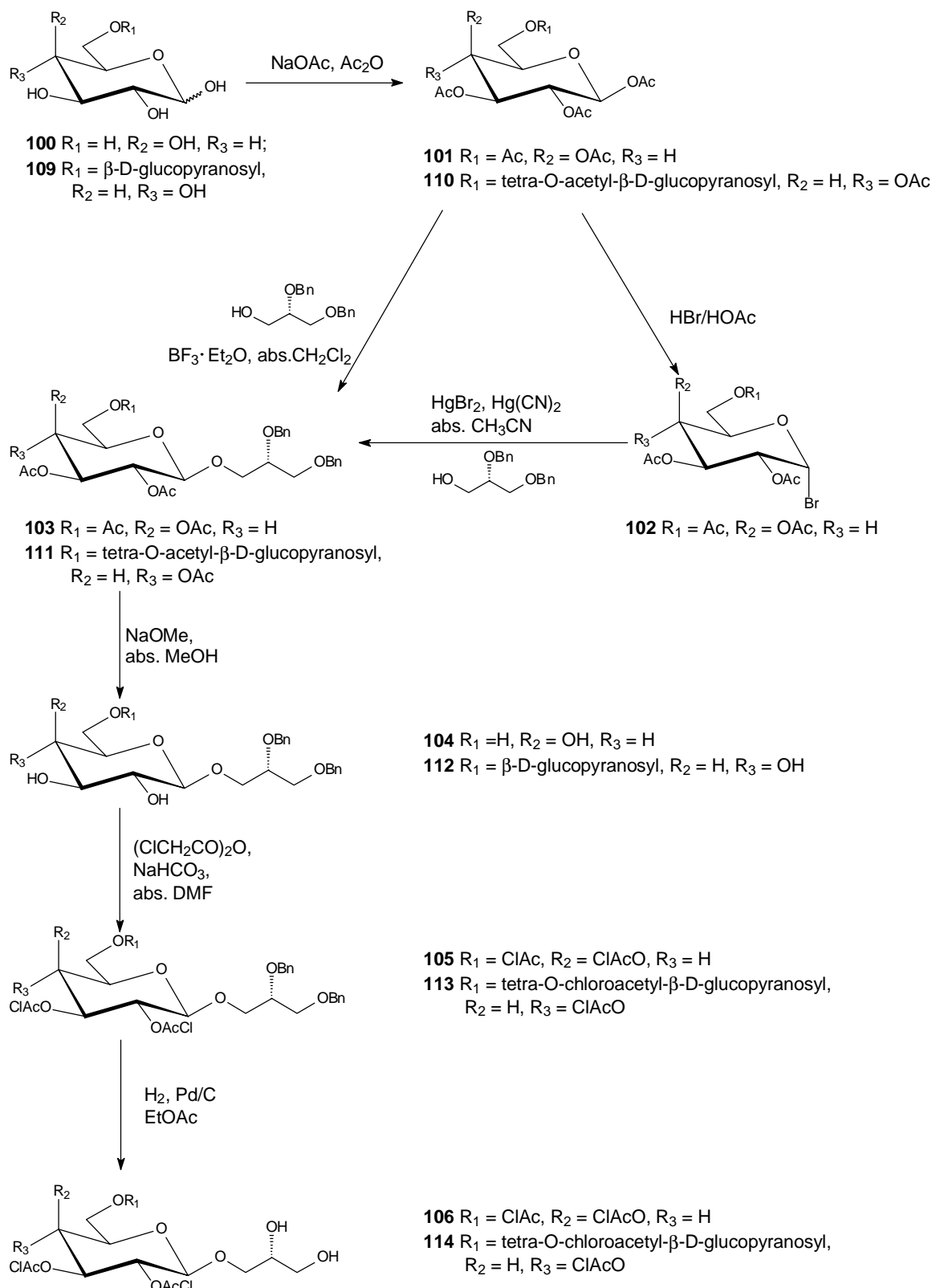


Figure 4.6: Synthesis of the intermediates **106** and **114**

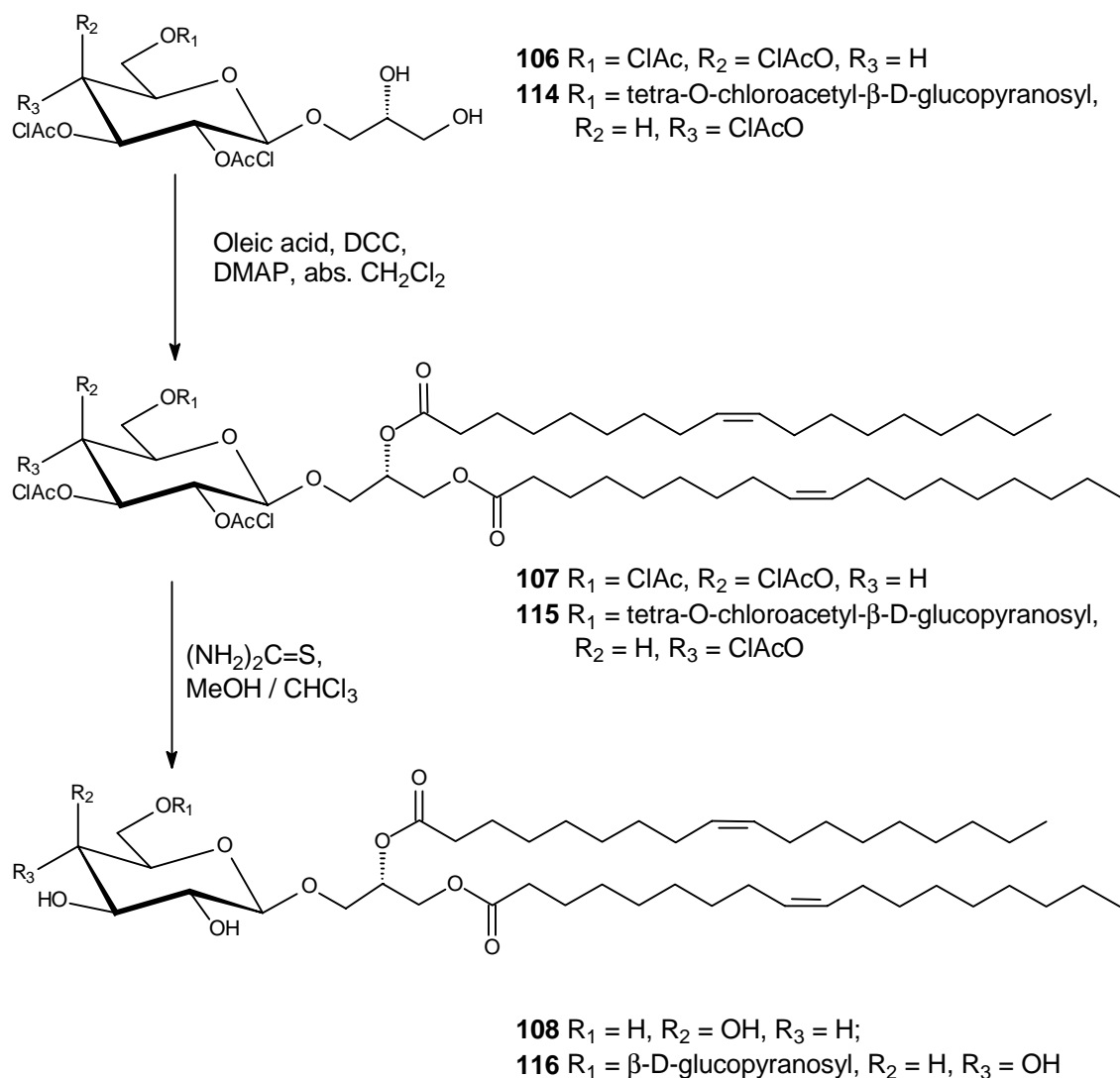


Figure 4.7: Synthesis of the glycosyl diacylglycerols **108** and **116**

The same procedure was also used for the synthesis of 1,3-di-*O*-(β -D-glucopyranosyl)-2-*O*-oleoyl-*sn*-glycerol **122** (Figure 4.8) using commercially available 2-benzyloxy-1,3-propanediol as aglycon.

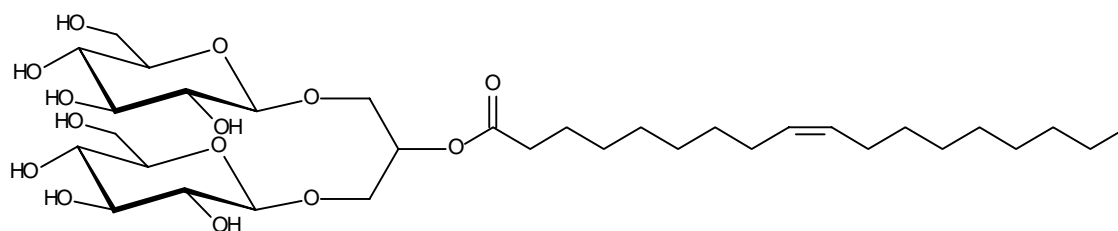


Figure 4.8: 1,3-di-*O*-(β -D-glucopyranosyl)-2-*O*-oleoyl-*sn*-glycerol **122**

In a further attempt to shorten the lengthy procedure, the peracetylated saccharide **110** was treated directly with the protected glycerol **71** in abs. dichloromethane in the presence of boron trifluoride ethyl etherate. Using these conditions the glycoside **111** was achieved in an excellent yield of 71 %, especially in comparison with an overall yield of 52 % for the synthesis of the analogous maltoside **81** starting from the peracetylated sugar, using the Koenigs-Knorr procedure requiring the intermediate synthesis of the aceto bromo sugar. Compared to the initial strategy (Figure 4.4, 4.5) this last strategy, with only 6 steps starting from the peracetylated sugar, is shorter by 3 steps.

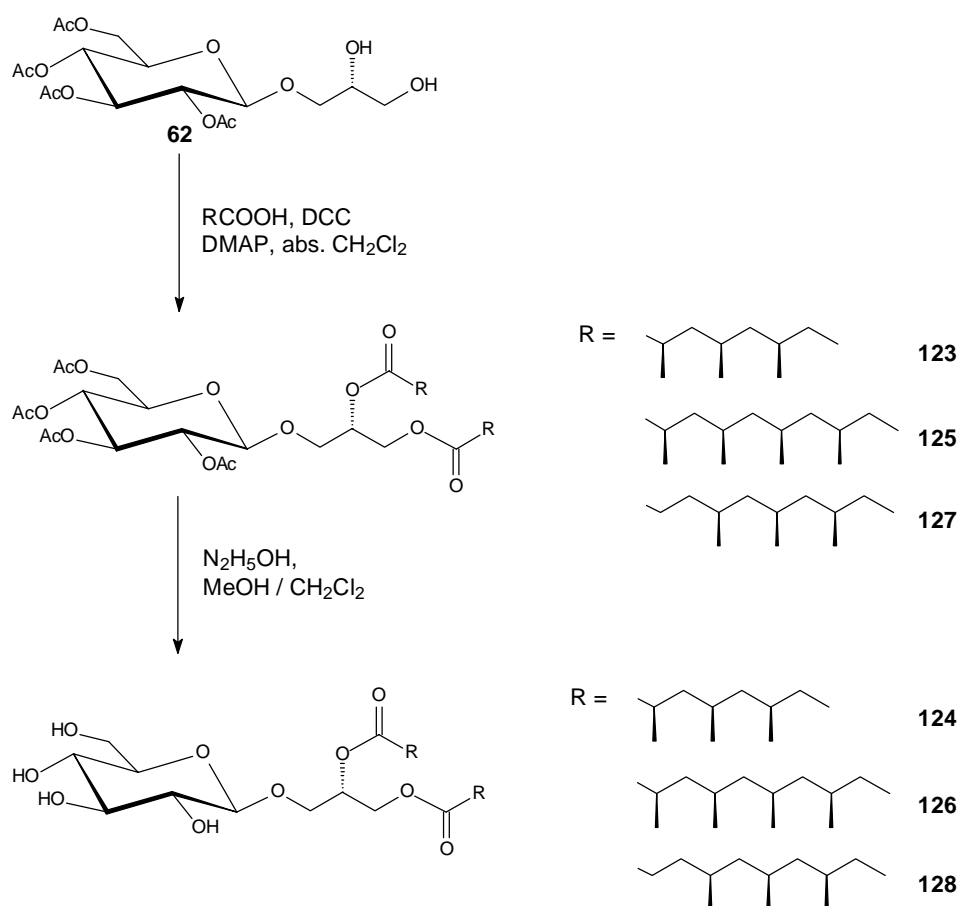


Figure 4.9: Synthesis of glucosyl diacylglycerols with chiral methyl branched fatty acids

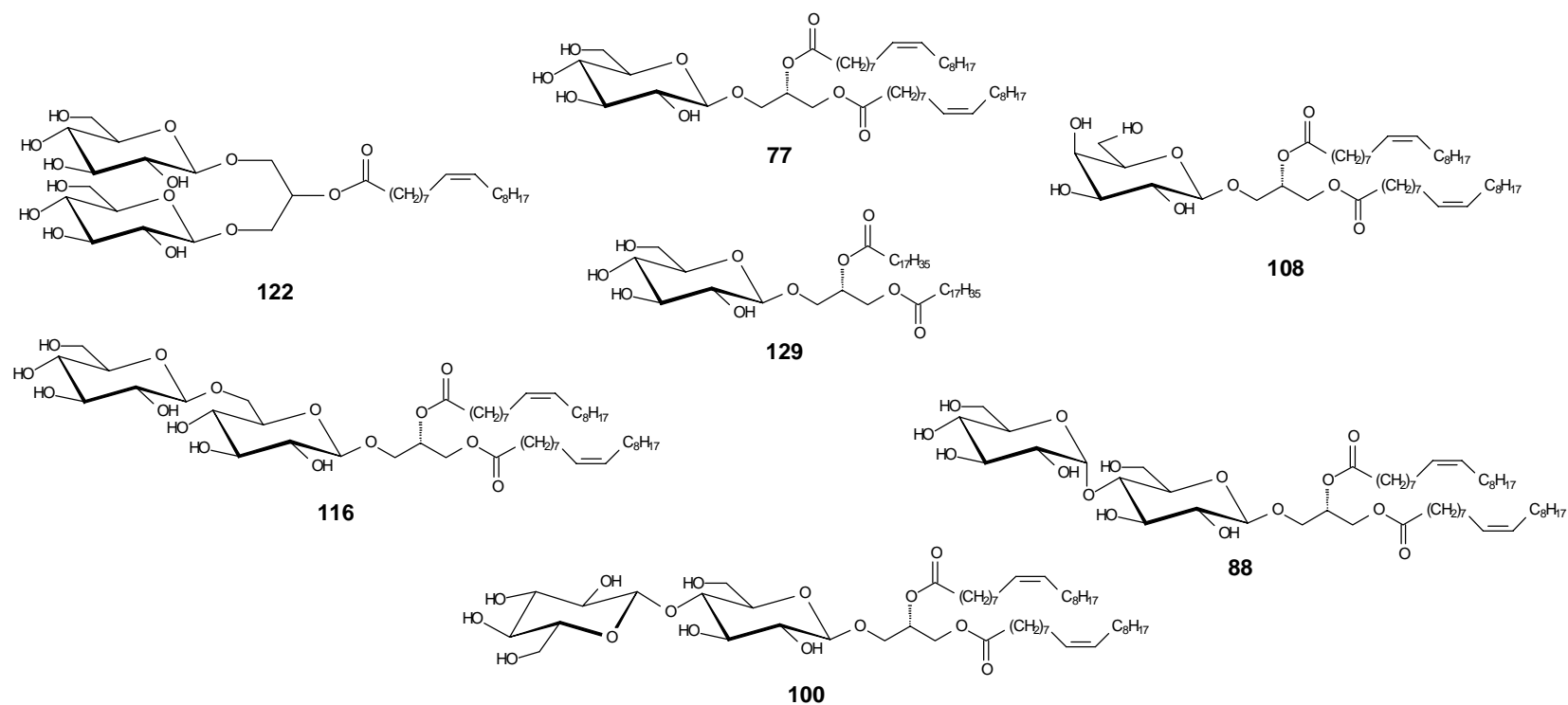
The decision to synthesise glycolipids with unsaturated chains was initially made to prevent crystallisation, which might have rendered the use of the compounds in binary mixtures difficult. Another aspect was that an easy procedure for the synthesis of these interesting compounds was missing, and therefore little was known about their physical properties. With the synthetic route outlined in Figures 4.6 and 4.7 this problem has been solved. Another well known possibility in liquid crystal chemistry to prevent crystallisation is to disturb the

molecular packing by branching of the aliphatic chains. To date only a few phospholipids with branched fatty acid chains have been synthesised (Morr et al., 1997 and references cited therein) besides some ferro- and antiferro-electric thermotropic liquid crystals (Heppke et al., 1997), and nothing is known about glycolipids with methyl branched fatty acid chains. Hence some glucosyl diacylglycerols of this kind have been synthesised here to investigate the exact influence of the highly methyl-substituted chiral fatty acid chains on the mesophase behaviour in comparison to the analogous, non-methyl-substituted compounds. The chiral methyl branched fatty acids used for this synthesis have been isolated from rump glands of *Cairina moschata* (Fortkamp, 1994) and *Anser a. f. domesticus* (Morr et al., 1992), and for the preparation of these compounds the above-mentioned procedure developed by Mannock et al. (Mannock et al., 1987) (Figure 4.9) was utilised.

4.3 Mesogenic properties of glycosyl diacylglycerols

Thermotropic properties

Figure 4.10 depicts a systematic structure variation of a well known glycosyl diacylglycerol, 1,2-di-*O*-stearoyl-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol **129**, the mesogenic properties of which were reported first by Mannock et al (1987). Due to its wedge-shaped structure compound **129** and similar glycosyl diacylglycerols form columnar mesophases of type 2 with the hydrophilic/hydrophobic interface being curved towards the sugar component (the minor component), while the mono-tailed alkyl glycosides described in Chapter 3 mostly formed S_A phases due to their rod-like molecular shape. The introduction of unsaturation into the fatty acid chains (compound **77**) lowered the clearing temperature of the columnar phase by 21 K. It is interesting to compare this result with the structure-property relationships derived in Chapter 3, since the same value (20.8 K) was found for the lowering of the clearing temperature of the S_A phase in the case of the stearyl monoglucoside (compound **6**, Chapter 3), upon introduction of a double bond into the alkyl chain. The effect of the introduction of an unsaturation can be attributed – as already explained in Chapter 3 – to the disturbance in the alkyl chain packing. The size of this disturbance seems to be the same regardless if the sugar bears one chain (alkyl glucosides) or two chains (glucosyl diacylglycerols), since in both cases the clearing temperature was depressed by 21 K. Due to the unsaturation of the fatty acid chains in compound **77** the melting point is also lowered relative to compound **129**, causing the former to be liquid crystalline even at ambient temperature. Hence, the melting



129	Cr	94								col	153	I
77	Cr	< 20								col	132.0	I
88	Cr	< 20								col	239.2	I
100	Cr	< 20								col	238.6	I
108	Cr	< 20								col	136.8	I
116	Cr	< 20				S _A	82	cub	149	col	200	I
122	Cr	< 20	col	72	cub	156	S _A				217	I

Figure 4.10: Systematic structure variation of glycosyl diacylglycerols

point is depressed by more than 70 K due to the disturbed packing of the alkyl chains and as in the case of the alkyl glucoside **8**, the effect of the unsaturation on the melting point is also much stronger than the effect on the clearing point (Figure 4.10).

Influence of the configuration of the hydroxyl groups of the sugar residue (gluco vs. galacto)

If the β -D-glucopyranosyl residue of compound **77** is replaced by a β -D-galactopyranosyl residue (compound **108**), the clearing point increases by about 5 K. Therefore, it can be concluded that the configuration of the hydroxyl groups in the headgroup has a small effect on the mesophase stability, but this effect is much smaller for glycosyl diacylglycerols than for the mono-tailed alkylglycosides. For example, in the case of alkyl glycosides the exchange of a gluco- (compound **8**) for a galactopyranosyl moiety (compound **18**) increased the stability of the S_A phase by 19 K (figure 3.4).

Influence of the type of linkage between the two sugar residues (α vs. β)

In the next step, the glucose headgroup of compound **77** was replaced by the disaccharides maltobiose (compound **88**) and cellobiose (compound **100**). In both cases the clearing temperature was raised by about 107 K due to increased hydrogen bonding in the headgroup region, attributable to the increased number of hydroxyl groups. However, there is more or less no difference in stability between compound **88** and compound **100**. Hence, the kind of interglycosidic linkage - α 1 \rightarrow 4 in the former and β 1 \rightarrow 4 in the latter - seems to have no significant influence on the stability of the columnar mesophase.

Influence of the position of linkage between the two sugar moieties in the disaccharide headgroup (1 \rightarrow 6 vs. 1 \rightarrow 4)

If the position of the linkage between the two sugar moieties in the disaccharide headgroup was changed (1 \rightarrow 4 to 1 \rightarrow 6), a complex polymorphism was found. Compound **116** with a β 1 \rightarrow 6 linked diglucoside headgroup displayed a S_A phase up to 82 °C, followed by a broad cubic phase, which transformed at 149 °C into a columnar mesophase and cleared at 200 °C. The reason for this complex behaviour is the broad structure of the 1 \rightarrow 6 linked disaccharide headgroup, giving compound **116** at low temperatures a rod-like shape and hence a S_A phase is found as the low temperature phase. With increasing temperature the molecule becomes more

and more wedge-shaped due to an increased motion of the aliphatic chains and thus at 149 °C a columnar phase is found. In the temperature range between 82 and 149 °C a cubic phase is formed as a compromise, since both other phases are destabilised by the other molecular moiety. This result proves again the interesting and important influence of 1→6 linked disaccharide headgroups on the mesogenic properties of glycolipids as already proposed in Chapter 2. A similar mesogenic behaviour was found in the case of a glycosyl diacylglycerol with a 1→6 linked digalactoside headgroup that has been extracted from Heinz (unpublished results) from natural sources. After hydrogenation to reduce at least the heterogeneity of the sample due to a statistical degree of unsaturation of the various fatty acids linked to the glycerol, the following mesogenic behaviour was found by means of polarising microscopy:

Cr 85 S_A 130 cub 180 col 233 I

Hence, it seems very likely that broad 1→6 linked carbohydrate headgroups as a general structural principle lead to the formation of a broad polymorphism in glycosyl diacylglycerols and that nature possibly uses the demanding stereochemistry of carbohydrates to control biological processes as outlined in Chapter 1 and 2.

To investigate the effect of very broad hydrophilic headgroups, the neoglycolipid **122** with two β-D-glycopyranosyl moieties linked to position 1 and 3 of the glycerol and only one oleic acid chain linked to position 2 was synthesised. This compound exhibited as low temperature phase a columnar phase up to 72 °C, followed by a very broad cubic phase up to a temperature of 156 °C. The high temperature phase was a S_A phase with a clearing temperature of 217 °C (Figure 4.10). This phase sequence is exactly of the opposite order to that found for compound **116**. Because of the very broad structure of the hydrophilic headgroup compared to that of the single fatty acid chain, compound **122** forms a columnar phase of type 1, i.e. the hydrophilic/hydrophobic interface curves towards the fluid hydrocarbon chain region (the minor component). With increasing temperature, the spacial demand of the hydrophobic region increases again due to an increased motion of the fatty acid chain, and the molecule becomes finally rod-shaped and forms as high temperature phase a S_A phase. In the temperature range between 72 °C and 156 °C a cubic phase (also type 1) is formed as a fact of frustration from compound **122**, since the columnar phase is already destabilised due to the increased volume of the fluid hydrocarbon chain region. However, a S_A phase cannot yet accommodate the

hydrophilic headgroup, which is too broad compared to the hydrocarbon chain and hence a cubic phase is formed. To obtain further structural information and to prove the phase type, X-ray experiments were also performed. In good accordance with the results of the polarising microscopy, the columnar to cubic transition at 72 °C turned out to be a transition from a 2-d hexagonal phase with a lattice parameter of 51 Å to a cubic phase of the space group Ia3d with a lattice parameter of 99 Å. This space group is frequently described in the literature for lyotropic cubic phases and was also found in at least one case for a thermotropic cubic phase, i.e. that of dodecyl- α -D-gentiobioside (Fischer et al., 1994).

Table 4.1 summarises the mesogenic properties of some glycosyl diacylglycerols and alkyl glycosides. Depending on the number of alkyl chains linked to the hydrophilic headgroup (1 vs. 2) and the position of linkage between the two sugar moieties in the disaccharide headgroup (1 \rightarrow 6 vs. 1 \rightarrow 4), all different phases (bicontinuous cubic, columnar and lamellar) and types of phases (normal and inverted) can be found on heating in this system as they can be found in lyotropic systems depending on concentration. Compound **122** forms a columnar phase of type 1, due to the very broad headgroup and the single chain. This phase transforms with increasing temperature, for the reasons discussed above, to a cubic phase and finally to a S_A phase. If the very broad headgroup of compound **122** is exchanged for a somewhat smaller 1 \rightarrow 6 linked diglucoside headgroup (compounds **42** and **48**), the columnar phase disappears. Moreover, depending on the chain length the bicontinuous cubic phase eventually becomes monotropic (compound **42**; C-18), while the dodecyl glycoside **48** displays a „ordinary“ enantiotropic cubic phase.

On the introduction of a stiff and linear β -cellobiose headgroup (compound **32**) the cubic phase disappears also and only the S_A phase remains. Compound **100** with the same carbohydrate headgroup displays a columnar phase of type 2, because of its wedge-shaped structure due to the introduction of a second chain. Finally, the exchange of the β 1 \rightarrow 4 linked cellobiose headgroup for a broader β 1 \rightarrow 6 linked gentiobiose headgroup (compound **116**) again introduces a broad polymorphism with a S_A phase, a bicontinuous cubic phase of type 2 and a columnar phase of type 2.

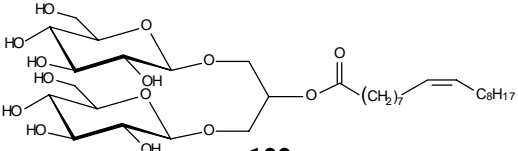
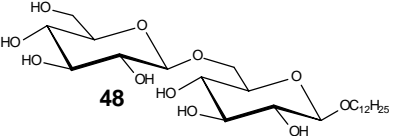
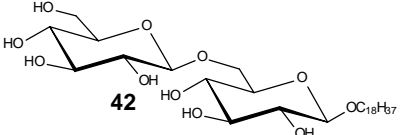
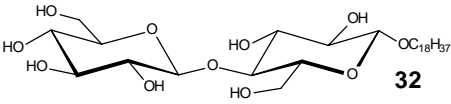
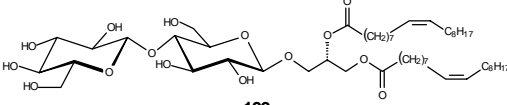
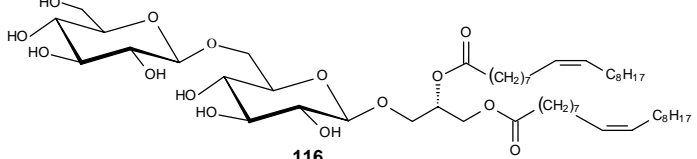
H_1	V_1	L_α	V_2	H_2
 <p style="text-align: center;">122</p>				
	 <p style="text-align: center;">48</p>			
	 <p style="text-align: center;">42</p>			
		 <p style="text-align: center;">32</p>		
				 <p style="text-align: center;">100</p>
			 <p style="text-align: center;">116</p>	

Table 4.1: Mesogenic properties of some carbohydrate amphiphiles depending on the number of alkyl chains and the position of linkage

No data can be found in the literature about the synthesis and mesogenic properties of glycoylglycerolipids with chiral fatty acid chains, while the synthesis of some phospholipids with chiral fatty acid chains has been described previously (M. Morr et al., 1997). In addition to the introduction of unsaturation, the introduction of lateral branches is a well known method in liquid crystal chemistry to prevent crystallisation.

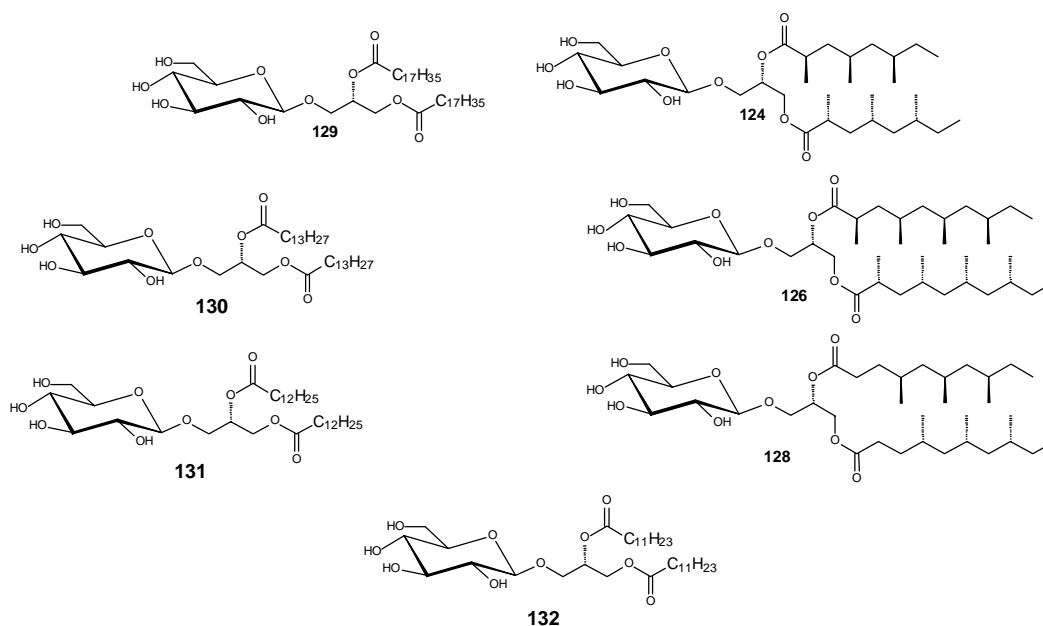
Compounds **124**, **126** and **128** with a glucose headgroup displayed as should be expected a columnar mesophase at ambient temperature. Unfortunately no data are available about the physical properties of the analogous compounds with the same chain length, but without the methyl branching. One reason might be that the glucosyl diacylglycerols with octanoyl and decanoyl chains are not liquid crystalline, because of the too short fatty acid chains. This idea is strongly supported by the changes in the transition temperatures of the liquid crystalline compounds **129**, **130**, **131** and **132** (Figure 4.11).

It is also interesting to compare the transition temperatures of the methyl branched compounds **126** and **128** (Figure 4.11) with those of compounds **130** and **131** with unbranched fatty acid chains having the same total number of carbon atoms. While the compounds **130** and **131** have a crystal to liquid crystal transition at 80 and 83 °C, the compounds **126** and **128** are already liquid crystalline at room temperature. The clearing point of compound **126** (4 methyl branches) is lowered in comparison to **130** by 73.8 K and in the case of compound **128** (3 methyl branches) in comparison to **131** by 56 K, yielding in both cases an average lowering of the clearing point of about 18 K per methyl branch, if the total number of carbon atoms is kept constant.

Compounds **124** and **126** differ in that the terminal methyl group of **124** has been replaced by a 1-methylpropyl group. Normally one should have expected in the case of these short-chain compounds an increase of the clearing point upon elongation of the acyl chain (e.g. **124** and **128**), but this effect is overcompensated by the effect of the additional methyl branch, giving a lowering of the clearing point of 4.9 K. If at a constant chain length one methyl group is removed (**126**, **128**) the clearing point rises up by 17.8 K.

It can be concluded that the methyl branching disturbs the interaction in the hydrophobic tail region and therefore destabilises the mesophase, but enlarges the mesophase range, since the crystal to liquid crystal interconversion is depressed much more strongly. Hence, the methyl branching has the same effect on the mesogenic properties as the introduction of double bonds into the fatty acid chains. Since these branched compounds are much more stable, e.g. they can not be degraded by β -oxidation, they might be interesting for future application in drug carriers

or the development of cubic-phase derived nano porous materials, since they could substitute unsaturated lipids while still maintaining favourable transition temperatures.



124	Cr	< 20	col	78.1	I
126	Cr	< 20	col	73.2	I
128	Cr	< 20	col	91.0	I
129	Cr	94	col	153	I
130	Cr	83	col	147	I
131	Cr	80	col	139	I
132	Cr	79	col	105	I

Figure 4.11: Mesogenic properties of some glycosyl diacylglycerols bearing chiral methyl branched fatty acids and literature data (Mannock et al., 1987) of unbranched compounds for comparison.

Lyotropic properties

The glycosyl diacylglycerols **77**, **124**, **126**, and **128** displayed in a contact preparation with water exclusively a columnar phase, as in the anhydrous state. The same holds true for compound **108** with a galactopyranosyl headgroup, and there seems therefore to be no difference between the glucoside **77** and the galactoside **108** despite the different configuration

of the hydroxyl group at C-4, influencing e. g. the ability to form hydrogen bonds.

If the glucose headgroup of compound **77** is replaced by the disaccharides maltobiose (compound **88**) or cellobiose (compound **100**) a much more complex polymorphism is found in the contact preparation with water. In both cases, three phases are formed with increasing water concentration: an H_2 phase, a bicontinuous cubic V_2 phase and an L_α phase. Furthermore, beyond the lamellar region towards higher water concentration myelin figures (Jeffrey and Wingert, 1992; Bouligand, 1998) can be found. These are very interesting results, since it was believed until now that the introduction of a second or third sugar moiety in the headgroup regions strongly simplifies the phase behaviour and suppresses the ability of these lipids to form non-lamellar structures (Hinz et al., 1996). However, the observed mesogenic behaviour seems to be reasonable, since the size of the headgroup should increase with increasing hydration, and hence the molecule should become less wedge-shaped and finally even rod-shaped. This corresponds exactly with the observation of a cubic and finally a lamellar phase (rod-like shape of the molecules) at the highest water concentration.

Compound **116** with a β 1 \rightarrow 6 linked diglucoside headgroup displayed, interestingly, only myelin figures besides the lamellar L_α phase. The next phase that might have been expected to be formed on hydration is in this case a V_1 phase with the polar/unpolar interface being curved towards the fluid hydrocarbon chain region. Since this phase cannot be found, the amount of hydration of the gentiobiose headgroup seems to be not sufficient to increase its size as much as necessary to become the major component and to force the polar/unpolar interface to curve towards the chain region. The opposite is true for compound **122**, with two glucopyranosyl moieties linked to the position 1 and 3 of the glycerol moiety and bearing only a single fatty acid chain at C-2. This compound forms, even without hydration, a columnar phase of type 1 and in the contact preparation with water two additional cubic phases, separated from one another by a sharp boundary, can be found. At present it is difficult to speculate about their exact structure, but two different micellar cubic phases of type 1 seem to be quite probable and only further X-ray experiments can help to unravel the exact structures.

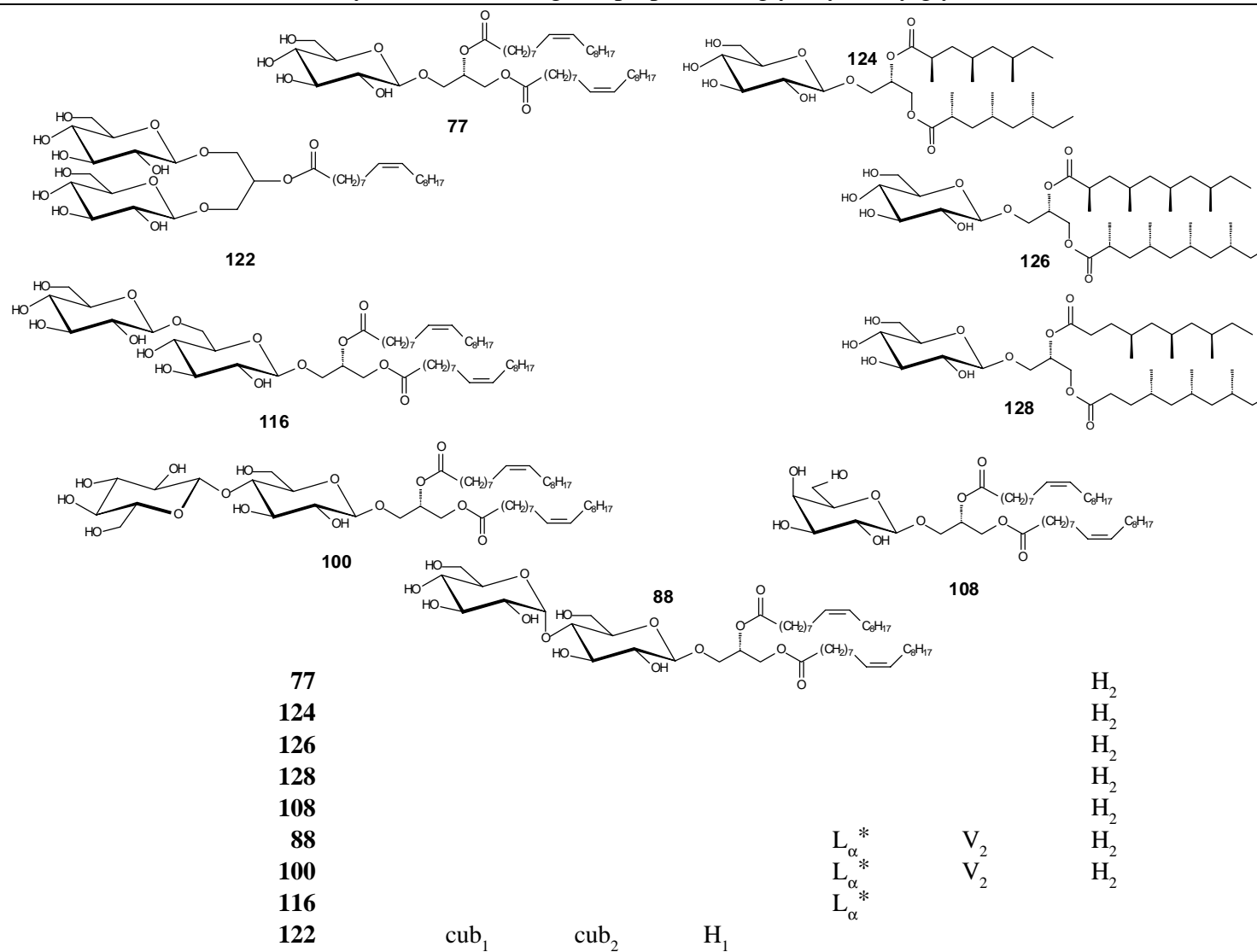


Figure 4.12: Lyotropic properties of the synthesised glycosyl diacylglycerols

*: Myelin figures beyond the S_A phase in the contact preparation with water

5. Mixture systems

5.1 Introduction

In Chapter 3 and 4 the synthesis of alkyl glycosides and glycosyl diacylglycerols was described and the mesogenic properties of the pure compounds were discussed in terms of chemical structure. Since the membranes occurring in nature are complex mixtures of various lipids, further components (e.g. proteins) and of course water, the next step was to prepare binary mixtures of the synthesised lipids to investigate the effects occurring in these mixtures.

For each mixture system of two different lipids the composition was changed systematically by increasing the concentration of the other component stepwise by 10 weight percent and the mesogenic behaviour was determined at each composition by polarising microscopy. Hence, the whole phase diagram was obtained by plotting the types of phases that have been observed and the transition temperatures against the composition of the mixture.

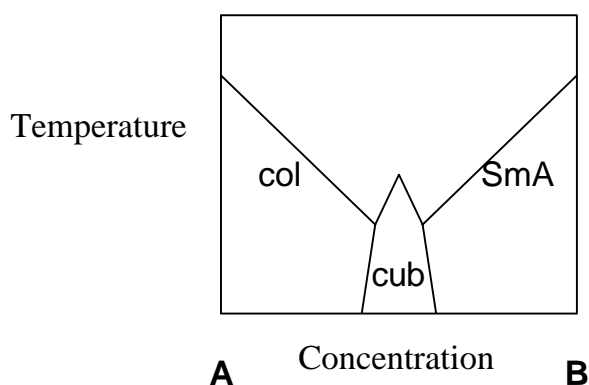


Figure 5.1: Binary mixture diagram

Figure 5.1 displays how one might have expected the phase diagram of a binary mixture of two compounds **A** and **B** to appear, if **A** forms a columnar mesophase and **B** forms a lamellar phase in their pure state:

the columnar and the lamellar phase are each destabilised in the mixture by the other component and at a medium concentration a cubic phase is induced. The stability of the

columnar and lamellar phases decreases linear with increasing concentration of the other component whereas the phase boundaries of the induced cubic phase are mainly concentration and not temperature dependent and therefore nearly vertical.

The subsequent discussion will show that the observed phase behaviour and the obtained phase diagrams deviate significantly from this classical pattern. Since the chemical structure of the components that have been used to prepare the different mixture systems has been changed systematically it is possible to derive structure-property relationships for mixture systems, i.e. how for example the stability range of the cubic phase is affected, if one component is exchanged.

5.2 Binary mixtures

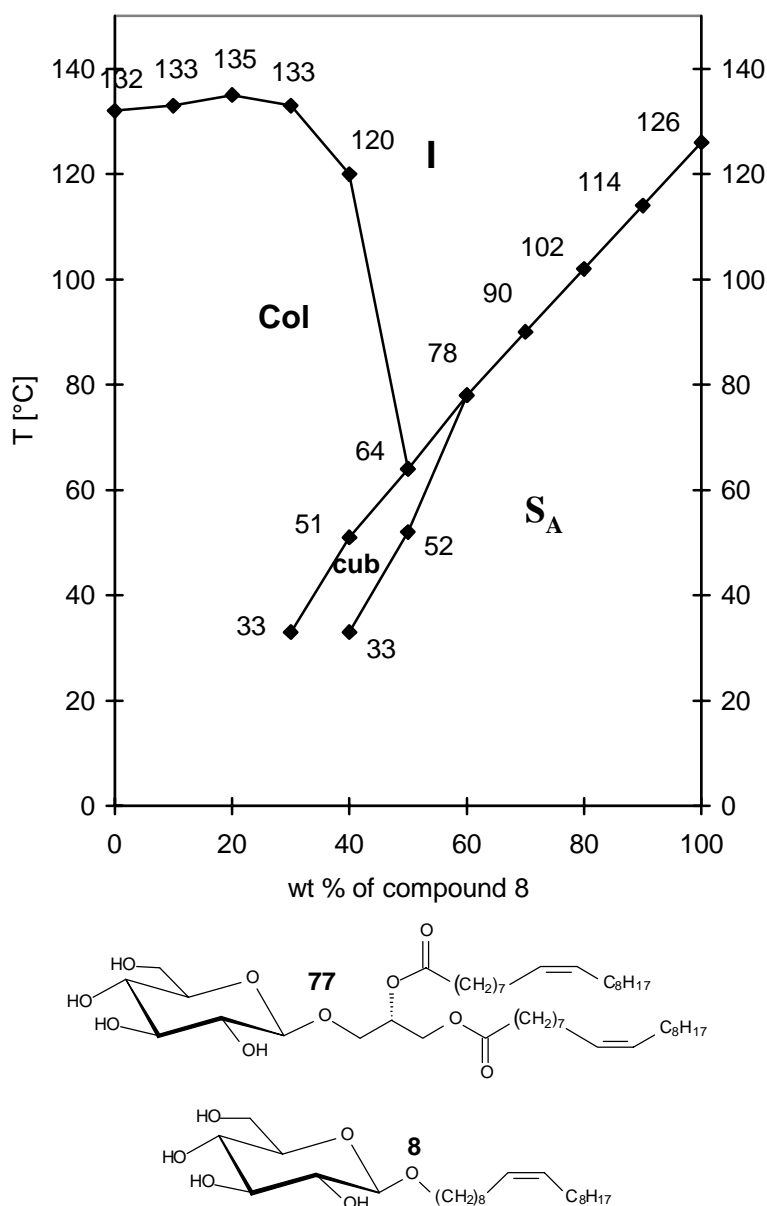
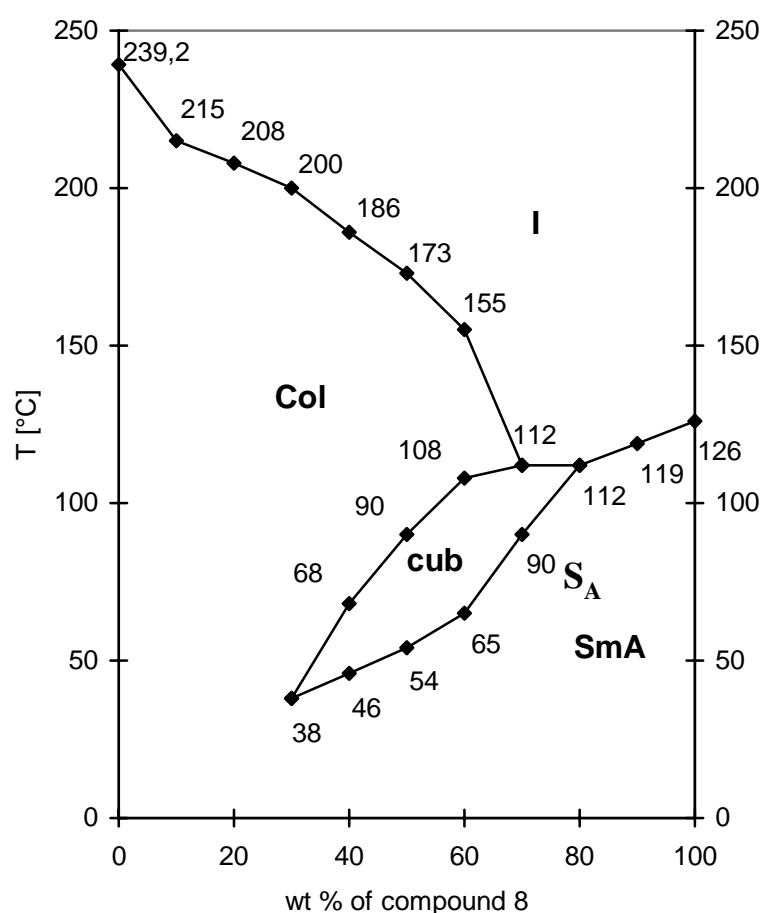


Figure 5.2: Phase diagram 1. Binary mixture of the glucosyl diacylglycerol **77** and the alkyl glucoside **8**.

Figure 5.2 displays the phase diagram of the binary mixture of the glucosyl diacylglycerol **77** and the alkyl glucoside **8**. The lamellar (S_A) phase demonstrates an almost linear dependence on concentration while the columnar phase displays a much more complex and unexpected behaviour: its stability increases slightly with increasing concentration of the lamellar phase forming alkyl glucoside **8** and reaches a maximal stability with a clearing temperature of 135 $^{\circ}\text{C}$ at a concentration of 20 wt % of compound **8**. If the concentration of the lamellar component is increased further a steep decrease of the stability of the columnar phase is observed which disappears completely at a concentration of 50 wt %. An induced cubic phase occurs in a wide concentration range from at least 30 up to 60 wt

% of the alkyl glucoside but only in a limited range of temperature. Hence, the phase boundaries of the induced cubic phase are, contrary to the above mentioned assumptions (Chapter 5.1), not vertical but instead diagonal, since its stability range is temperature as well as concentration dependent. The cubic phase seems to be a derivative of the lamellar phase which extends in the phase diagram just below the cubic phase continuously over the whole cubic existence range and can be transformed into the cubic phase by just small changes in concentration or temperature. This general observation was also made in all the other phase diagrams that have been recorded.

As another general observation the lamellar to cubic transition became towards lower temperatures (i.e. lower concentrations of the lamellar component) increasingly slow. The establishment of exact phase boundaries at the low temperature region of the cubic phase was therefore tedious and often even impossible. For example, in the case of the just discussed phase diagram the sample with a concentration of 30 wt % of the alkyl glucoside had to be stored at least one day at ambient temperature to allow the lamellar to cubic transition to occur, and on heating the cubic to columnar transition at 33 °C could still be determined. Nevertheless, beyond this concentration no transition could be determined anymore.



In the next step, the β -D-glucopyranosyl headgroup of the glycosyl diacylglycerol was replaced by the disaccharide maltobiose (compound **88**). Due to the increased size of the sugar headgroup of the columnar component the induced cubic phase is extended to an even broader concentration and temperature range (Figure 5.3). A cubic phase can now be found from 30 - 80 wt % of the lamellar component. Furthermore, the stability of the columnar mesophase decreases now with increasing concentration of compound **8** over the whole range of its existence without reaching a maximum in-between and disappears at 70 wt %. Again, the columnar phase is destabilised by the lamellar component and finally destroyed, while the lamellar phase is transformed through the presence of

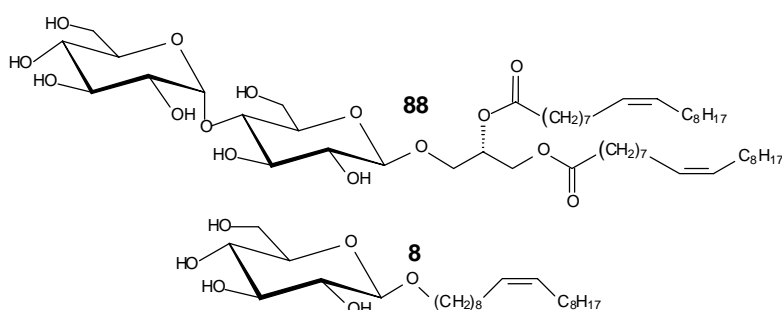


Figure 5.3: Phase diagram 2. Binary mixture of the maltosyl diacylglycerol **88** and the alkyl glucoside **8**.

the columnar component into a cubic phase. The effect of an exchange of the mono- for a

disaccharide headgroup in the glycerol component can be seen even better by superimposition of phase diagrams 1 and 2 (Figure 5.4A). As well as increasing in size, the cubic phase existence range is slightly shifted towards higher temperatures and higher concentrations of the lamellar component.

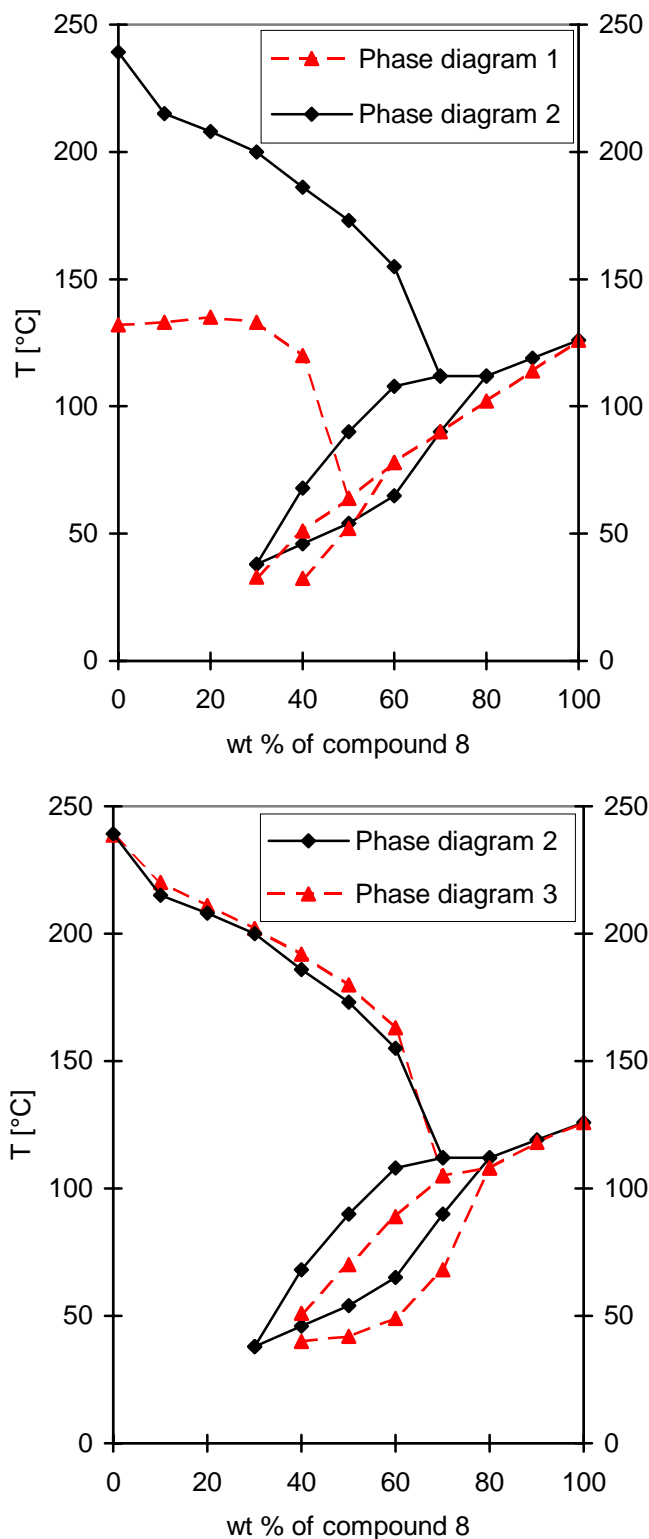


Figure 5.4: Superimposition of phase diagrams: A: diagrams 1 and 2; B: diagrams 2 and 3.

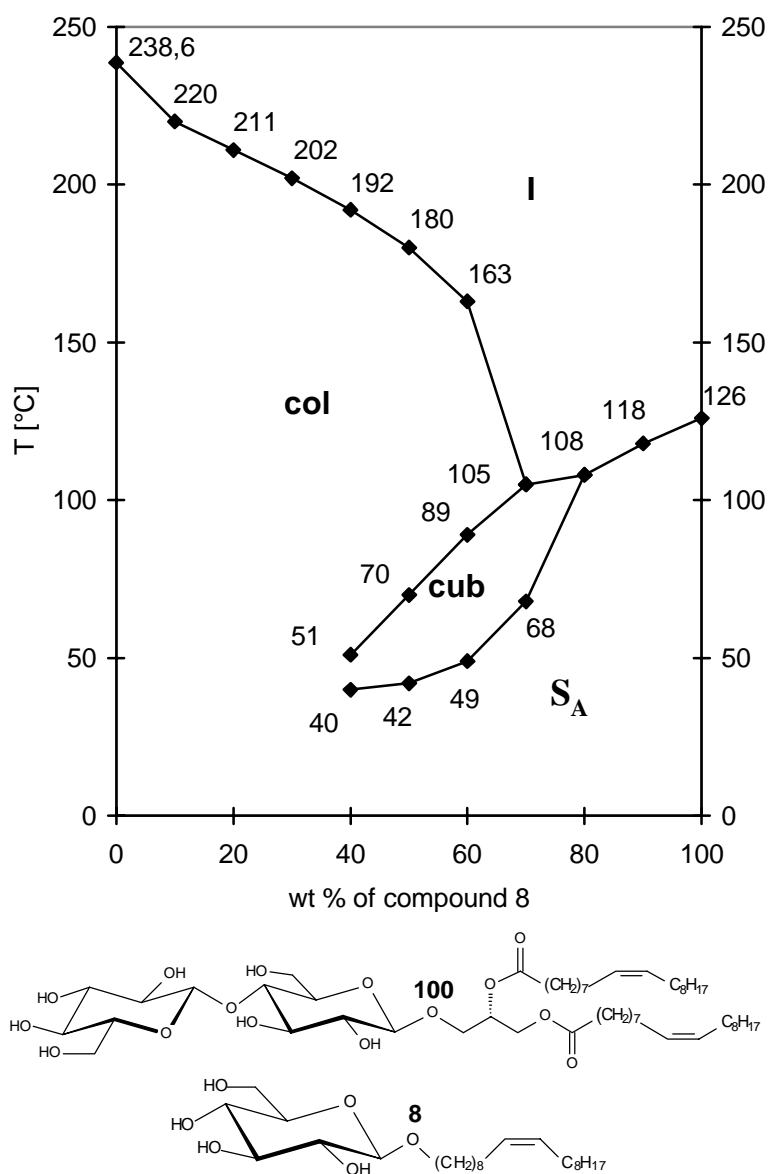


Figure 5.5: Phase diagram 3. Binary mixture of the cellobiosyl diacylglycerol **100** and the alkyl glucoside **8**.

To investigate the influence of the interglycosidic linkage, the α 1→4 linked headgroup of compound **88** was replaced by a β 1→4 linked cellobiose headgroup (compound **100**, Figure 5.5). At a first glance there seems to be no difference between phase diagrams 2 and 3 and this might be not so surprising, since the maltosyl diacylglycerol **88** and the cellobiosyl diacylglycerol **100** exhibited both in their pure state a columnar phase, the stability of which was not affected by the different type of interglycosidic linkage (Chapter 4). However, in the superimposition of both diagrams a remarkable influence of the type of interglycosidic linkage (α 1→4 vs. β 1→4) on the stability of the induced cubic phase in mixture systems becomes obvious (Figure 5.4B). In the case of a glycosyl diacylglycerol

bearing a β 1→4 linked disaccharide headgroup the cubic phase existence range is shifted in the mixture system distinctly towards lower temperatures, while the columnar phase is again not affected at all, as in the case of the pure compounds. From this point of view it is interesting to compare phase diagrams 2 and 3 with phase diagram 4 (Figure 5.6) of a mixture of two lipids each forming only a columnar phase in the pure state. As one might have expected, the mixture of the glucosyl diacylglycerol **77** and the maltosyl diacylglycerol **88** also exhibits only a columnar phase but the clearing temperature of this columnar phase does not change linearly with composition. Instead a completely unexpected sigmoidal-shaped dependence is observed which points towards a selective stabilisation of the columnar phase in the binary mixture.

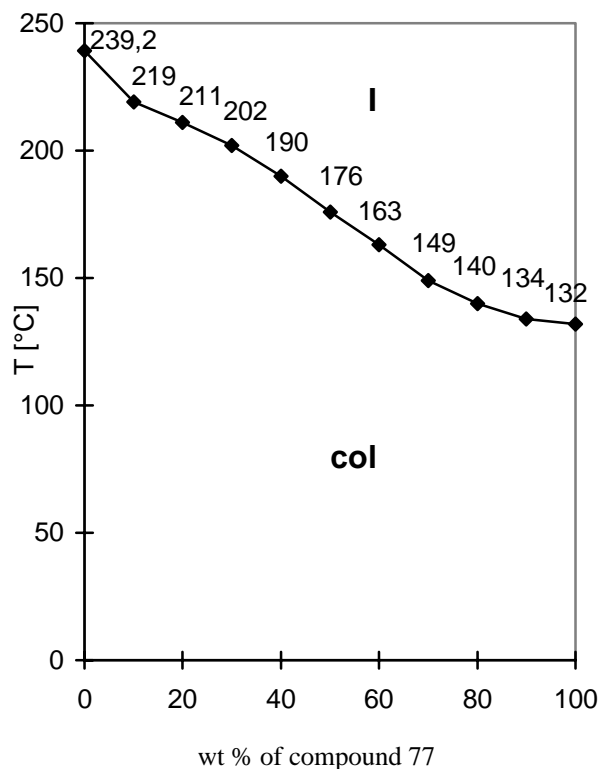


Figure 5.6: Phase diagram 4. Binary mixture of glucosyl diacylglycerol **77** and maltosyl diacylglycerol **88**.

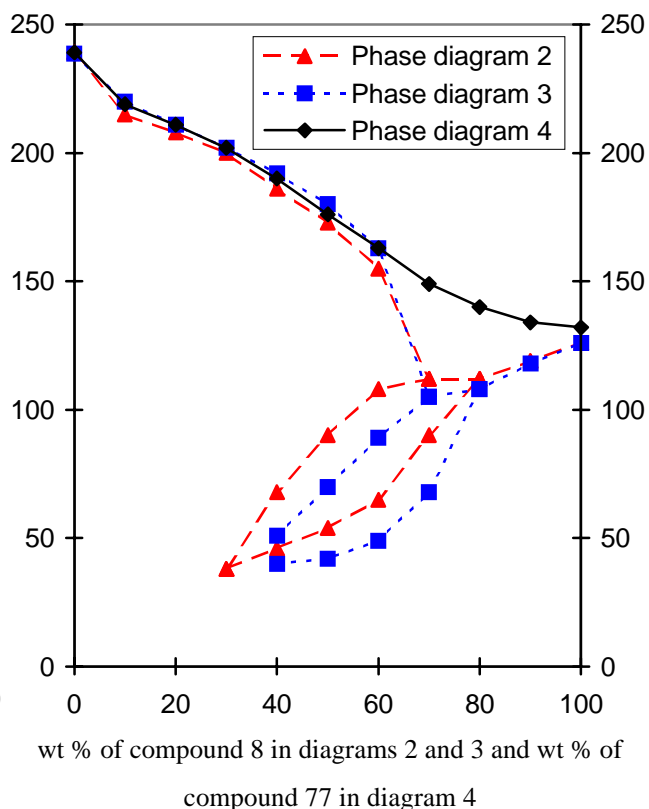


Figure 5.7: Superimposition of phase diagrams 2 (compounds **8** and **88**), 3 (compounds **8** and **100**) and 4 (compounds **77** and **88**).

In Figure 5.7 phase diagram 4 is superimposed with phase diagrams 2 and 3 for comparison, since some interesting insights into the effects governing the stability of columnar phases can be obtained thus. In a wide range of concentration (0-60 wt %), nearly the same clearing temperature is found in these three diagrams. Beyond a concentration of 60 wt % the columnar phase persists only in phase diagram 4 (the mixture of two columnar components), while it is quickly destabilised beyond this concentration in phase diagrams 2 and 3 (mixture of a columnar and a lamellar component) and disappears here at concentration of 70 wt %. It is still surprising that the columnar phase, which is formed by wedge-like molecules, tolerates the disturbance due to the presence of a rod-like and lamellar phase forming molecules in such a wide range.

The common feature of the „guest molecules“ introduced into the columnar phase of compound **88** is in the case of phase diagrams 2 and 4 the monosaccharide headgroup. The exchange of maltosyl diacylglycerol molecules with a disaccharide headgroup for alkyl glucoside or glucosyl diacylglycerol molecules with a monosaccharide headgroup reduces the amount of hydroxyl groups in the polar headgroup region. Hence, it can be concluded that the hydrogen bonding in

the headgroup region is crucial for the stabilisation of the columnar phase whereas the *Van der Waals* interactions in the fluid hydrocarbon chain region seem to play no important role, since in both cases the mono-tailed and the double-tailed monosaccharide derivatives destabilise the columnar phase at the same composition of the mixture to exactly the same extent. This idea is further supported by phase diagram 5.

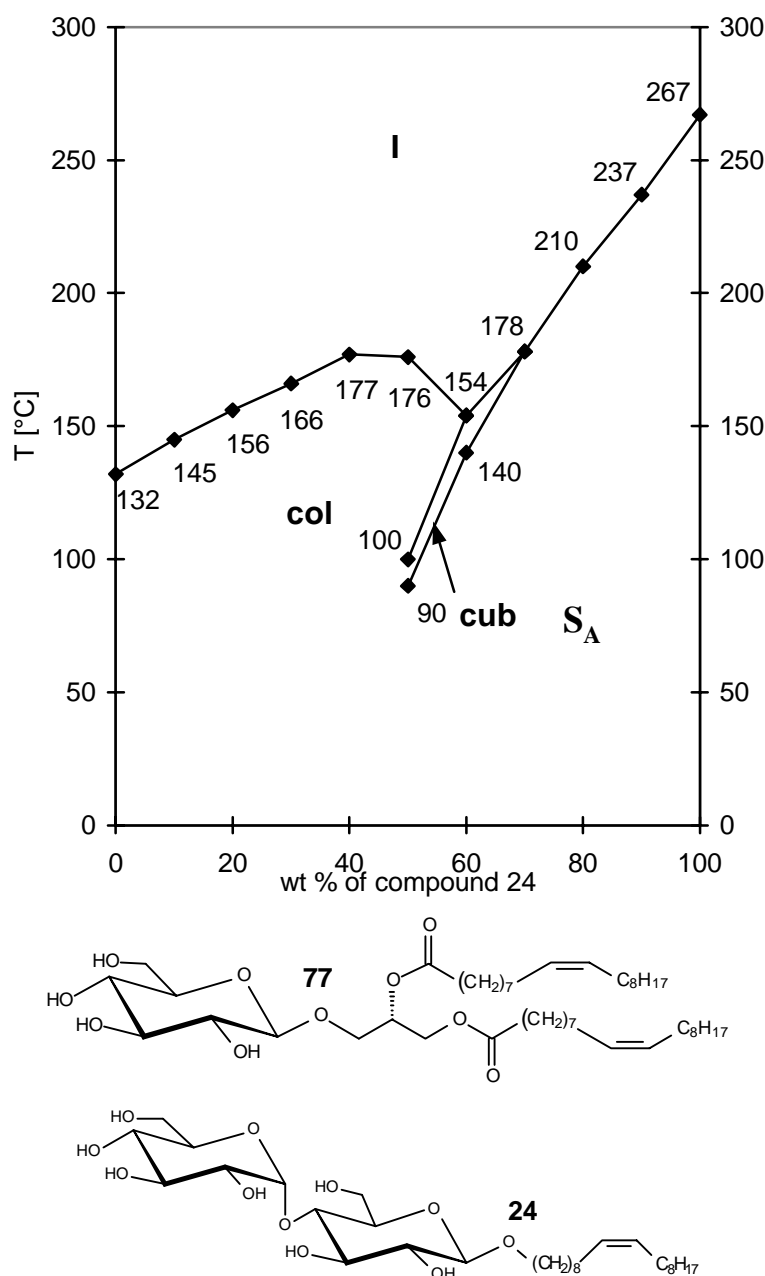


Figure 5.8: Phase diagram 5. Binary mixture of the glucosyl diacylglycerol **77** and the alkyl maltoside **24**.

Figure 5.8 displays the phase diagram of the binary mixture of the glucosyl diacylglycerol **77** and the alkyl maltobioside **24**. The stability of the columnar phase increases dramatically with increasing concentration of the alkyl maltobioside **24** and reaches its maximum with a clearing temperature of 177 °C – i.e. 45 °C above the clearing temperature of the columnar glycerol **77** in its pure state – at a concentration of 40 wt % of compound **24**. This observation proves the hypotheses given above about the effects governing the stability of columnar phases: the incorporation of the alkyl maltobioside with its disaccharide headgroup into the columnar phase of the monosaccharide derivative **77** increases the hydrogen bonding

in the headgroup region and stabilises therefore the columnar mesophase.

Besides this stabilising effect, the maltobioside also exerts a weak destabilising effect: the rod-like structure of the alkyl maltobioside **24** disturbs of course the packing of the wedge-shaped

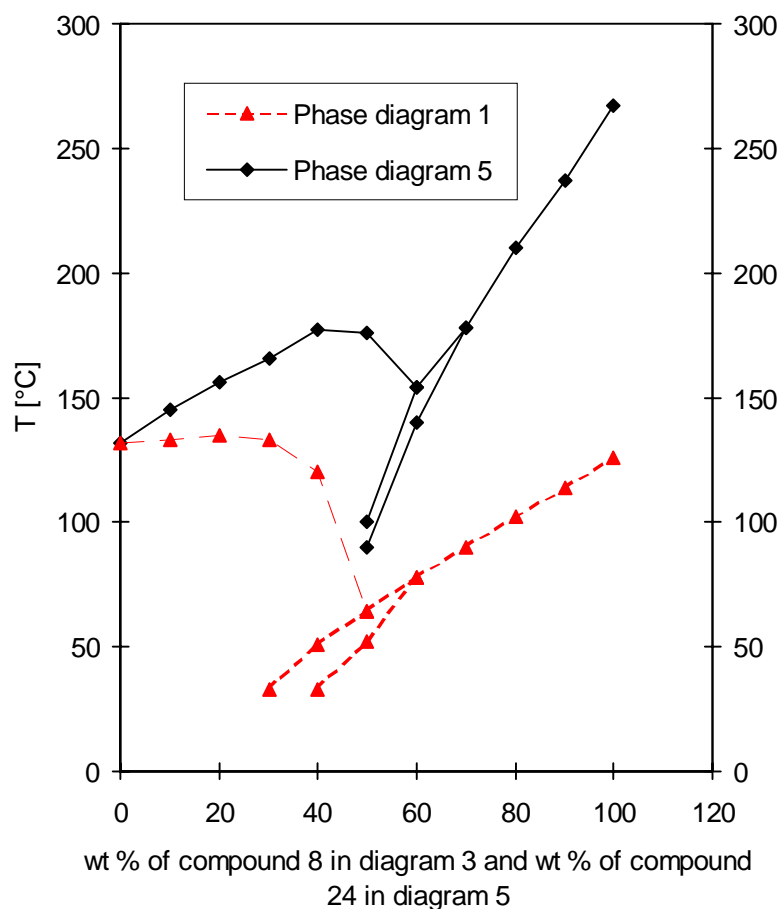


Figure 5.9: Superimposition of phase diagrams 1 and 5.

molecules of compound **77** into a columnar phase and hence the stability of the columnar phase decreases finally again at higher concentrations of the lamellar component.

The effect on the cubic phase, if the monosaccharide headgroup in the lamellar component is exchanged for a disaccharide, can better be seen by superimposition of phase diagrams 1 and 5 (Figure 5.9).

Besides a small decrease of the size of the cubic phase, its existence range is significantly shifted towards much higher temperatures.

The glucose headgroup of one of the glycolipids used in phase diagram 1 was exchanged in phase diagram 2 and 5 for the disaccharide maltobiose while the other component was kept constant. In Figure 5.10 the headgroup of both components was replaced by maltobiose. Compared to the other phase diagrams, the cubic phase existence range is enlarged and shifted significantly towards lower concentrations of the lamellar component, reducing the existence range of the columnar phase. From this phase diagram can roughly be extrapolated that a few wt % of the alkyl maltobioside should already be enough to induce a cubic phase in this mixture whereas the induced cubic phase was found in all the other phase diagrams more or less at medium concentrations, i.e. in the middle of the diagram.

The superimposition of the cubic phase existence ranges of phase diagrams 1, 2, 5, and 6 (Figure 5.11) clearly illustrates how the exchange of a mono- for a disaccharide headgroup in one or both components in this binary mixture affects the stability of the induced cubic phase.

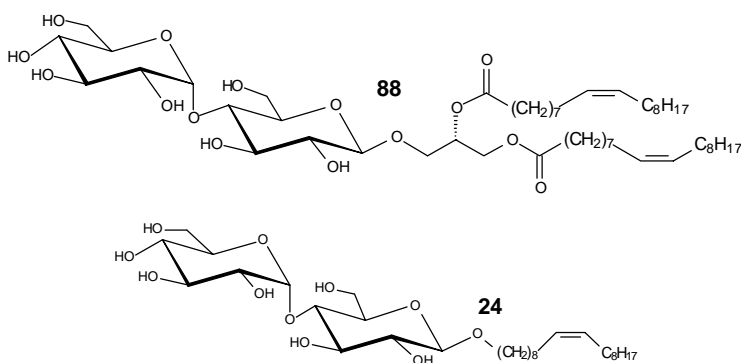
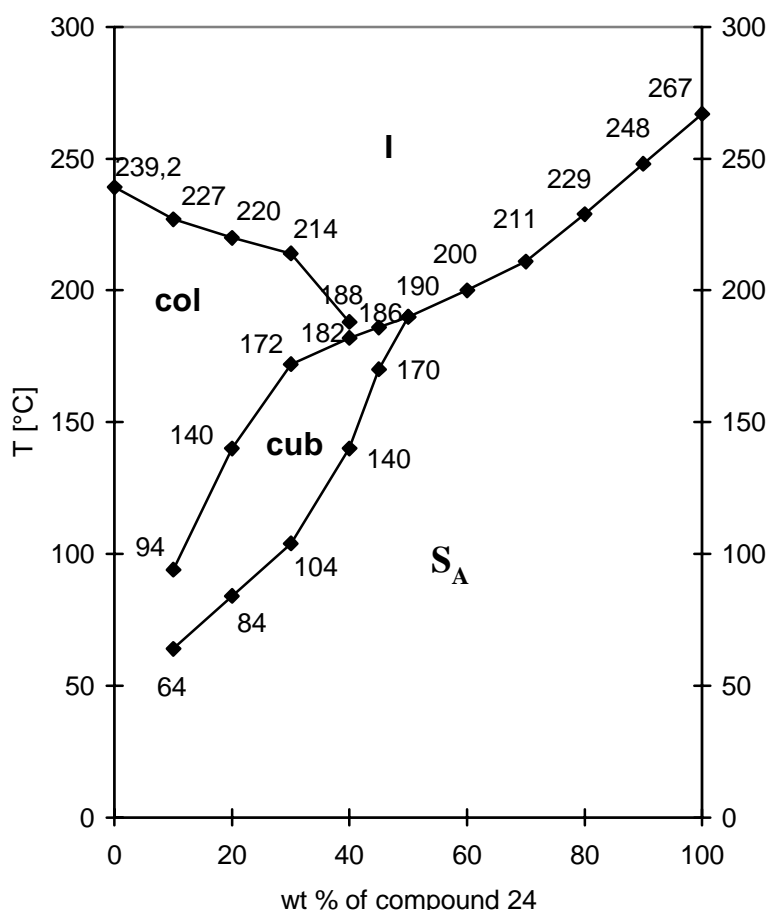


Figure 5.10: Phase diagram 6. Binary mixture of the maltosyl diacylglycerol **88** and the alkyl maltoside **24**.

increased. Furthermore, the phase boundaries of the cubic phase become much steeper, i.e. the temperature dependence of the cubic phase decreases whereas its concentration dependence increases. In phase diagram 6 the sugar headgroups of both components are replaced by the disaccharide maltobiose to investigate whether or not the effects described above operate in an additive manner. As one might have expected, the cubic phase existence range is enlarged as in diagram 2, and shifted towards higher temperatures as in diagram 5. Since the phase boundaries also became steeper as in diagram 5, it can be concluded that the observed effects indeed operate

If the monosaccharide headgroup of the glucosyl diacylglycerol in phase diagram 1 is replaced by the disaccharide maltobiose (phase diagram 2), the cubic phase existence range is significantly enlarged and slightly shifted within the diagram towards higher temperatures and higher concentrations of the lamellar component. A completely different effect is observed if the monosaccharide headgroup of the alkyl glucoside in phase diagram 1 is replaced by a maltobiose headgroup (phase diagram 5), stabilising the lamellar phase. The cubic phase existence range is slightly reduced in size and significantly shifted towards higher temperatures. Since the cubic phase - as already explained - seems to be a derivative of the lamellar phase, its existence range is also shifted towards higher temperatures, if the thermal stability of the lamellar component is

in an additive manner. However, the shift of the cubic phase towards lower concentrations of the lamellar component in this mixture is new.

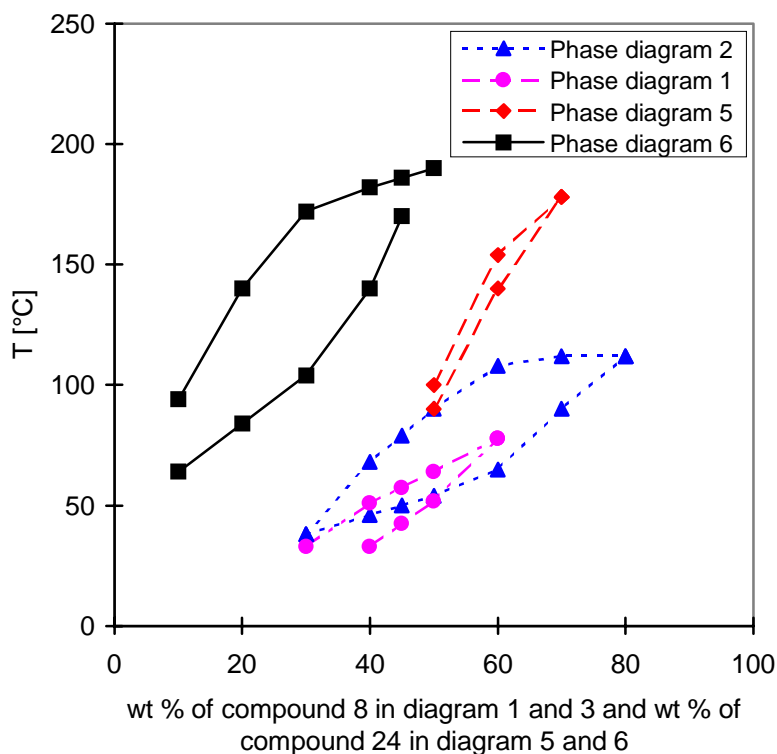


Diagram:

Components:

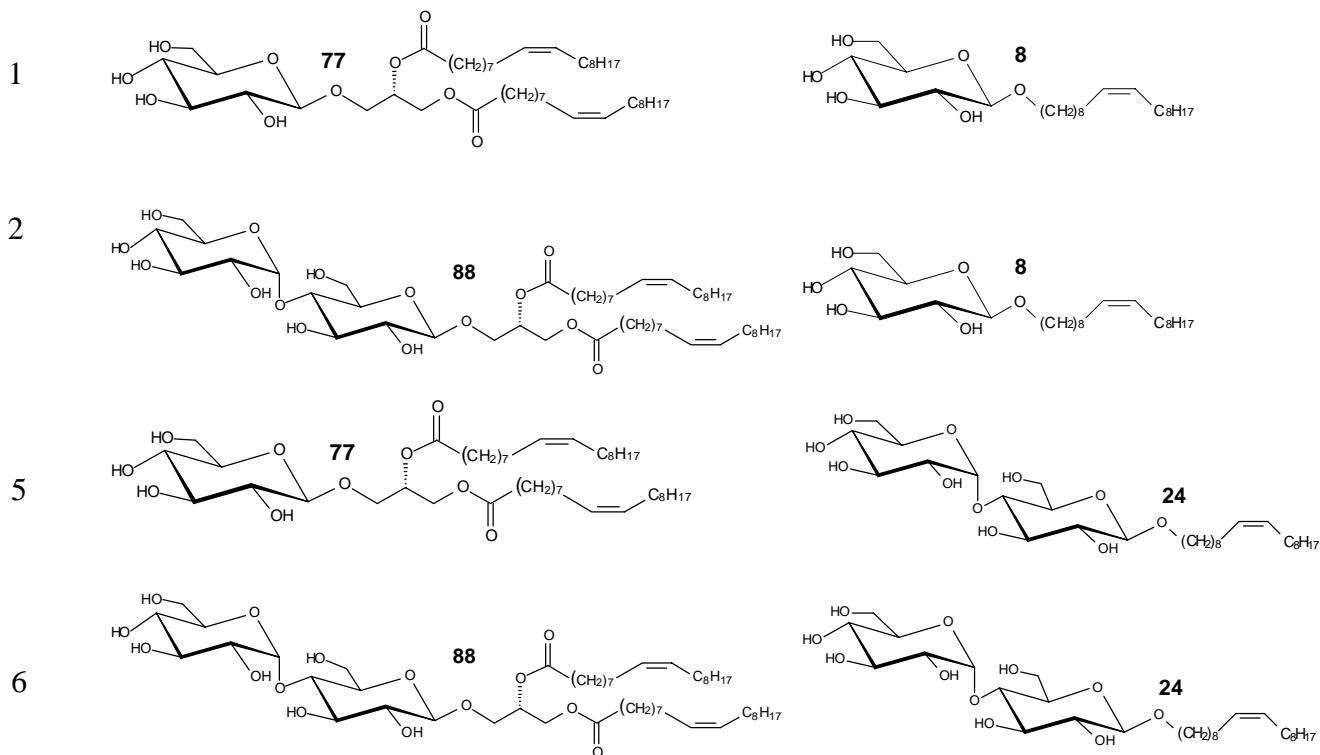
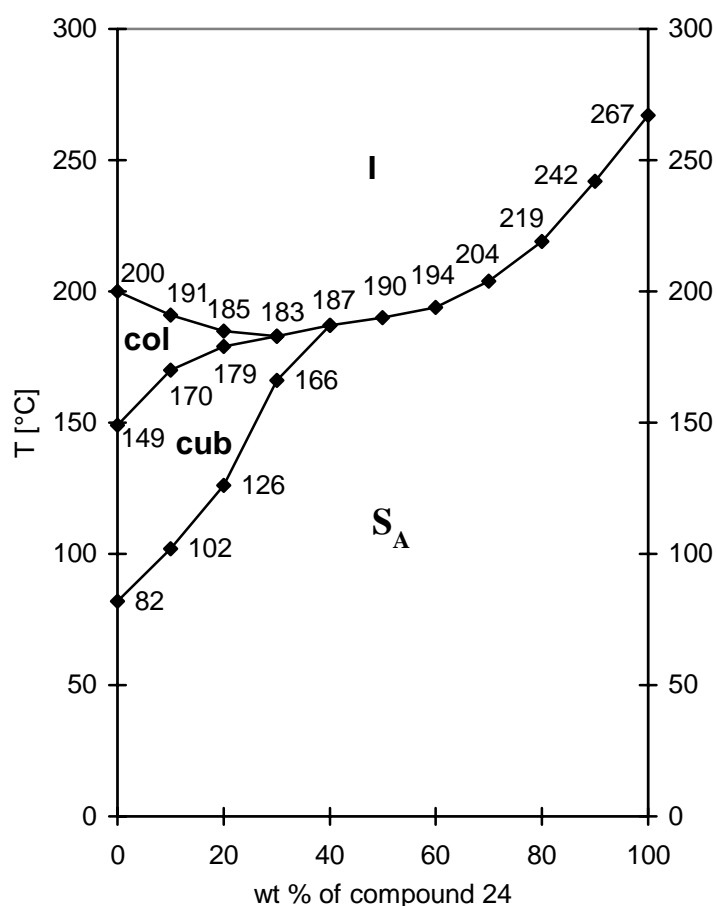


Figure 5.11: Superimposition of the cubic phase existence range of diagrams 1, 2, 5 and 6.



Phase diagram 7 (Figure 5.12) is helpful to understand the aforementioned shift of the induced cubic phase in phase diagram 6 towards lower concentration of the lamellar component. In phase diagram 7 the maltobiose headgroup of the glycosyl diacylglycerol was replaced by the β 1 \rightarrow 6 linked disaccharide gentiobiose (compound **116**). This glycosyl diacylglycerol forms due to the broad structure of the sugar headgroup – as already explained in chapter 4 – a broad polymorphism. The cubic phase existence area is shifted in phase diagram 7 towards very low concentrations of the lamellar component, and the size of the columnar phase is extremely small in comparison with all the other phase diagrams. If phase diagram 7 is superimposed with diagrams 5 and 6 (Figure 5.13, the lamellar component is in this case always the alkyl maltoside **24**), an effect of the shape of the columnar glycosyl diacylglycerol component on the position of the cubic

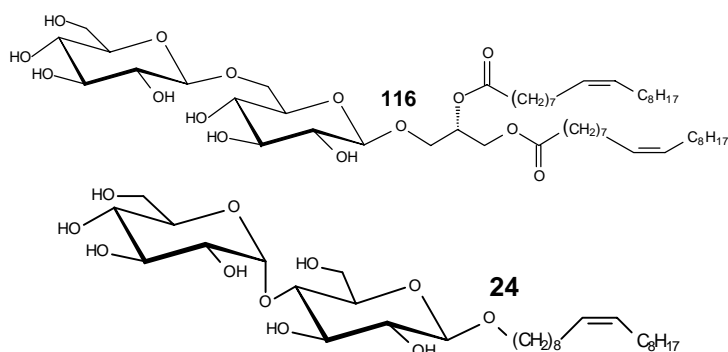


Figure 5.12: Phase diagram 7. Binary mixture of the gentiobiosyl diacylglycerol **116** and the alkyl maltoside **24**.

phase within the phase diagram becomes visible. The gentiobiosyl diacylglycerol **116** is at elevated temperatures only slightly wedge-shaped and rod-like at lower temperatures (see also chapter 4) while the maltosyl diacylglycerol **88** is wedge-shaped at all temperatures, but due to the disaccharide headgroup less so than the glucosyl diacylglycerol **77**. Thus it can be concluded, that the induced cubic phase is shifted within the phase diagram the more towards lower concentration of the lamellar component, the less wedge-shaped the columnar component becomes, since this destabilises the columnar phase for geometrical reasons and hence facilitates the induction of a

cubic phase. This destabilisation of the columnar phase can also be seen in Figure 5.13: The less wedge-shaped the columnar component becomes, the smaller the area of the columnar phase in the phase diagram becomes.

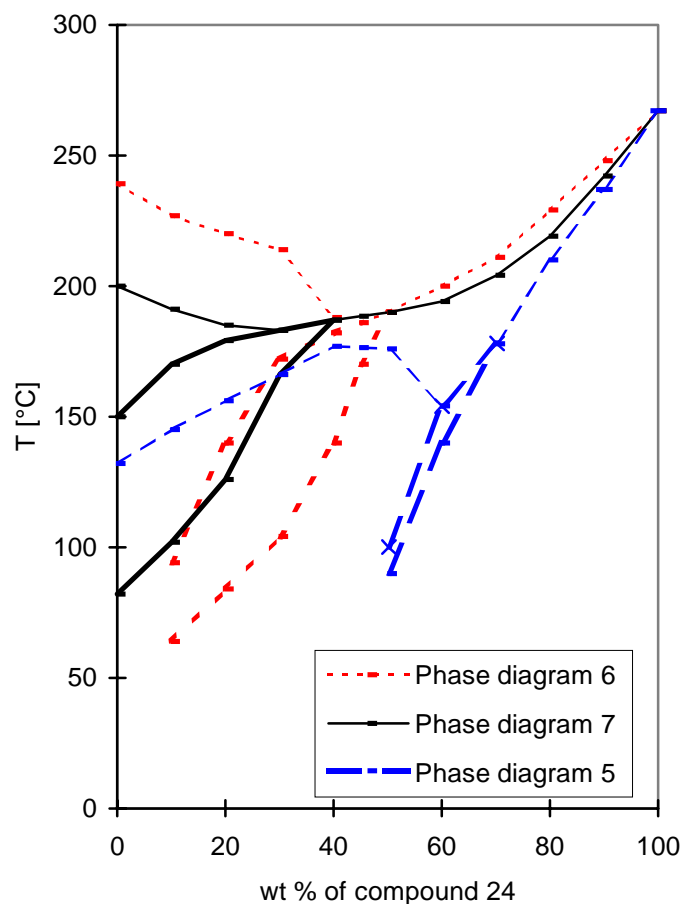


Diagram:

Components:

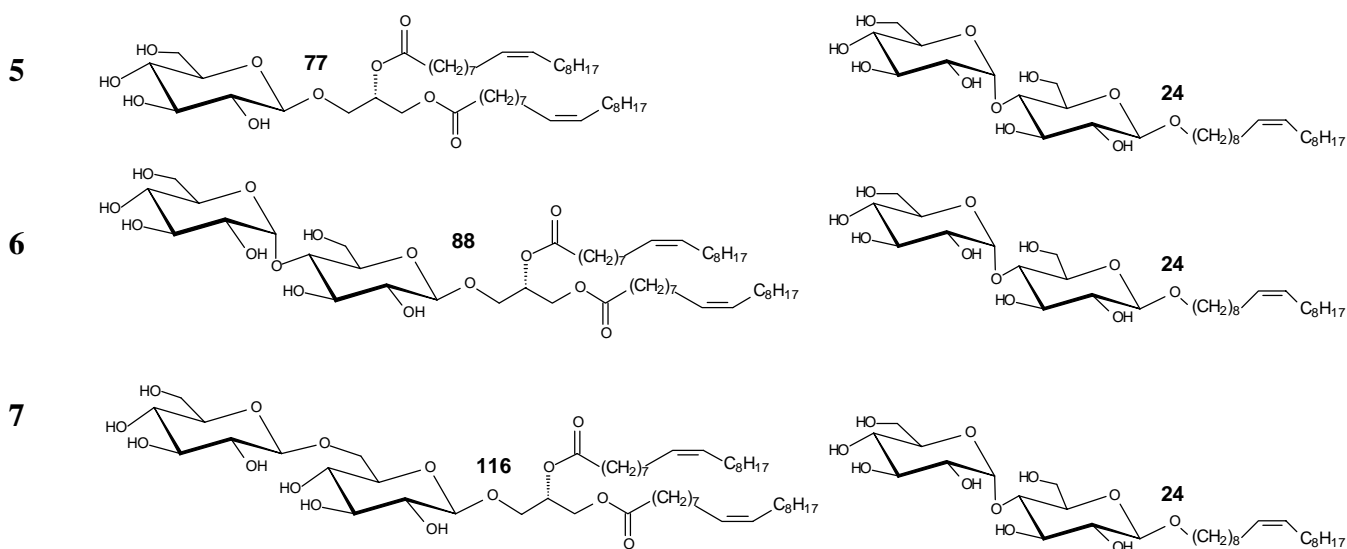


Figure 5.13: Superimposition of phase diagrams 5, 6 and 7.

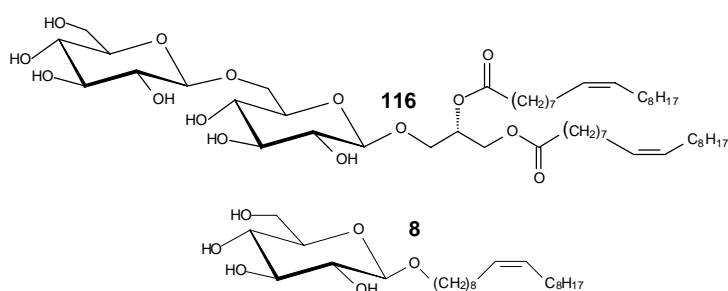
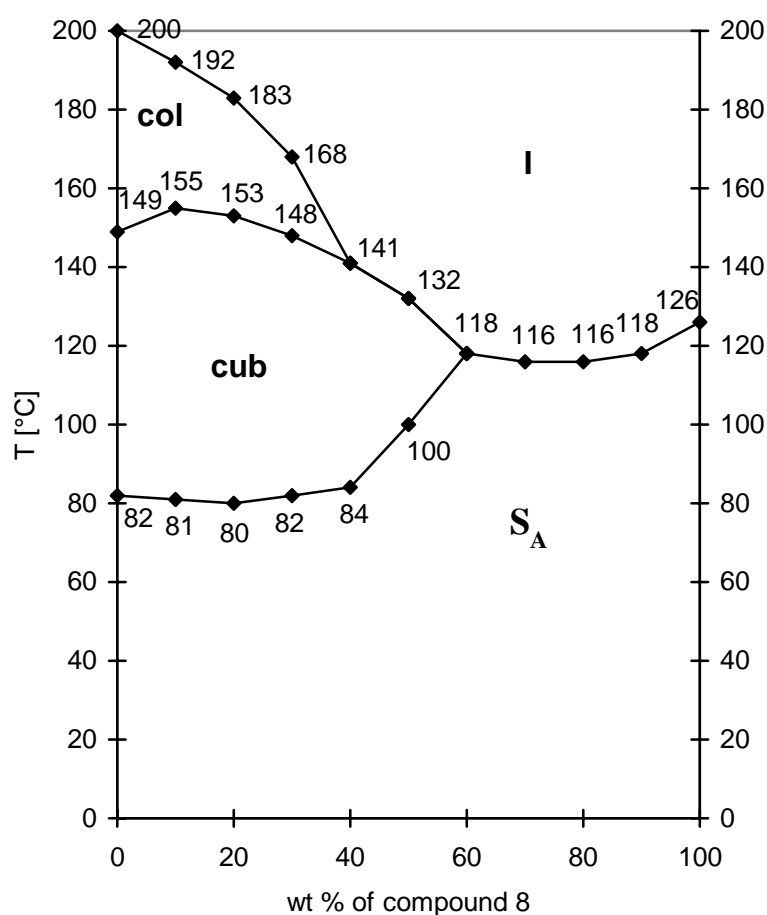


Figure 5.14: Phase diagram 8. Binary mixture of the gentiobiosyl diacylglycerol **116** and the alkyl glucoside **8**.

and higher concentrations of the lamellar component (in the case of phase diagram 8 the cubic phase existence range is extended and not shifted towards higher concentrations of the lamellar component as in the case of phase diagram 2, since the glycosyl diacylglycerol **116** exhibits a cubic phase even in its pure state). Comparing the cubic phase existence ranges of phase diagrams 1 and 5, the shift of the cubic phase towards lower temperatures if the disaccharide headgroup of the lamellar component is replaced by a monosaccharide has already been discussed before (Figure 5.8, 5.9 and 5.11). The concomitant shift of the cubic phase towards higher concentrations of the lamellar phase was not observed in this case, since the alkyl maltobioside stabilised in phase diagram 5 (Figure 5.8) the columnar phase of the glucosyl diacylglycerol due to

If the disaccharide headgroup of the alkyl maltobioside – the lamellar component – in phase diagram 7 is replaced by a monosaccharide (Phase diagram 8, Figure 5.14) the cubic phase existence range is shifted towards lower temperatures and extended towards higher concentrations of the lamellar component. Comparing (Figure 5.11) the cubic phase existence range of phase diagram 6 – the binary mixture of the maltosyl diacylglycerol **88** and the alkyl maltoside **24** – with the cubic phase of phase diagram 2 – the binary mixture of the maltosyl diacylglycerol **88** and the alkyl glucoside **8** – the same behaviour is found: The replacement of the disaccharide headgroup of the lamellar component by a monosaccharide shifts the cubic phase towards lower temperatures

its disaccharide headgroup (see discussion about the effects stabilising the columnar phase). Hence, a much higher concentration of the lamellar component was necessary to induce a cubic phase and therefore only the shift in temperature was found in the comparison of phase diagram 5 with phase diagram 1. This simple example already illustrates how complex the interactions in this binary mixtures are and thus how difficult it is to derive structure-property relationships. For the same reason, a systematic attempt to derive structure-property relationships governing the stability of cubic phases has not been made to date.

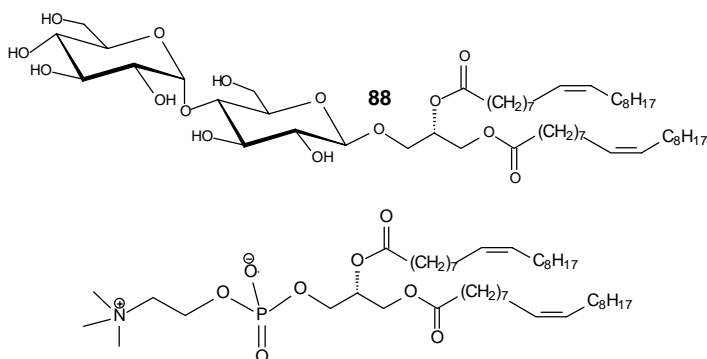
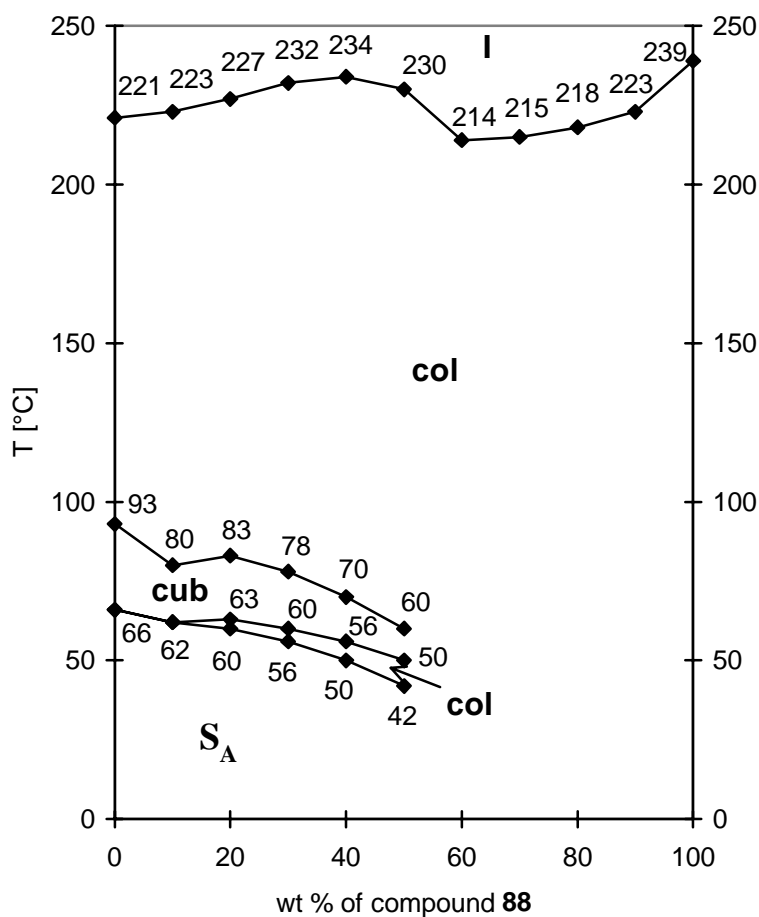


Figure 5.15: Phase diagram 9. Binary mixture of maltobiosyl diacylglycerol **88** and dioleoyl lecithin.

How complex the interactions and the observed phase behaviour can be is also illustrated by phase diagram 9 (Figure 5.15). The binary mixture of the maltobiosyl diacylglycerol **88** and dioleoyl lecithin displays a reentrant columnar phase, i.e. at a concentration of e.g. 40 wt % of the glycosyl diacylglycerol **88**, the mixture is lamellar at low temperatures and with increasing temperature a transition to a columnar phase, a cubic phase and again a columnar phase is observed. Furthermore, the clearing temperature of the columnar phase changes in a very unusual manner with concentration. It increases first with increasing concentration of the maltosyl diacylglycerol and after it has passed a maximum of stability it decreases again, reaching a minimum after which it increases again.

The maltosyl diacylglycerol forms a columnar phase of type 2 in its pure state, i.e. the polar/unpolar interface curves towards the hydrophilic headgroup region. Despite the repulsive electrostatic forces within the headgroup region because of the charged cholin moieties the columnar phase formed by the lecithin has to be of the same type since no intermediate lamellar or cubic phases were found by polarising microscopy, separating the columnar phases of different types on both sides of the phase diagram from each other. Instead a large columnar phase is found which extends across the whole phase diagram.

At least the increase in stability of the columnar phase („left hand side“ in the phase diagram) with increasing concentration of the maltosyl diacylglycerol can easily be explained: the maltosyl diacylglycerol dilutes the lecithin and due to the incorporation of the maltose headgroup into the polar region the distance between the charged cholin headgroups increases, reducing the repulsive electrostatic interactions. Due to these repulsive interactions the stability of the columnar phase („right hand side“ of the phase diagram) decreases with increasing concentration of the lecithin, since the charged cholin moiety has to be incorporated into the headgroup region. The electrostatic repulsion between the cholin moieties destabilises the headgroup region and hence the columnar phase.

In the case of the binary mixture of the gentiobiosyl diacylglycerol **116** and the maltosyl diacylglycerol **88** (phase diagram 10, Figure 5.16) an even more complex behaviour of the columnar phase is observed, showing one maximum of stability in the middle of the diagram. On each side of this maximum a minimum of stability is found. Contrary to phase diagram 9, a simple explanation for this complex behaviour cannot be found.

Furthermore, a reentrant columnar phase was again observed within this phase diagram towards higher concentrations of the maltobiosyl diacylglycerol, but an unambiguous determination of the phase boundaries by polarising microscopy was impossible. Hence, the phase diagram is incomplete.

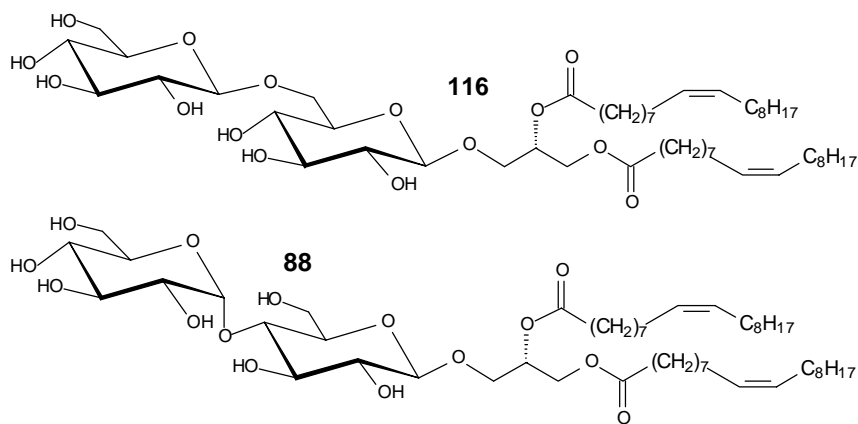
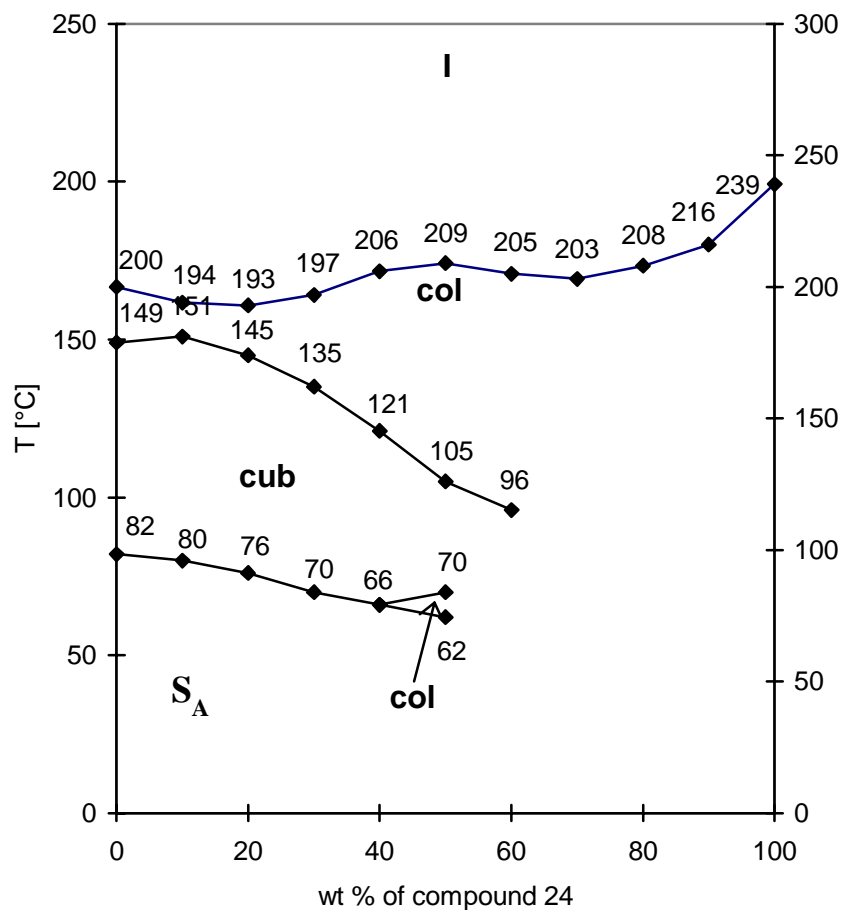


Figure 5.16: Phase diagram 10. Binary mixture of the gentiobiosyl diacylglycerol **116** and the maltosyl diacylglycerol **88**.

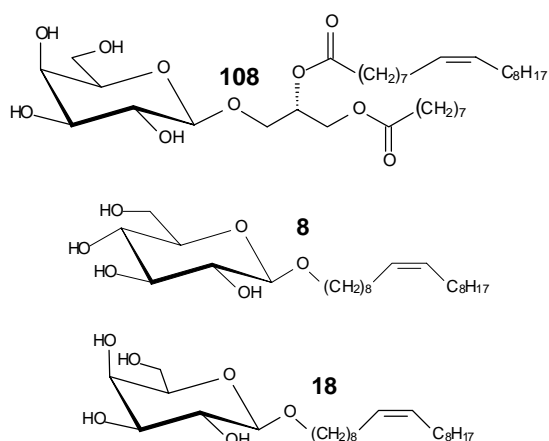
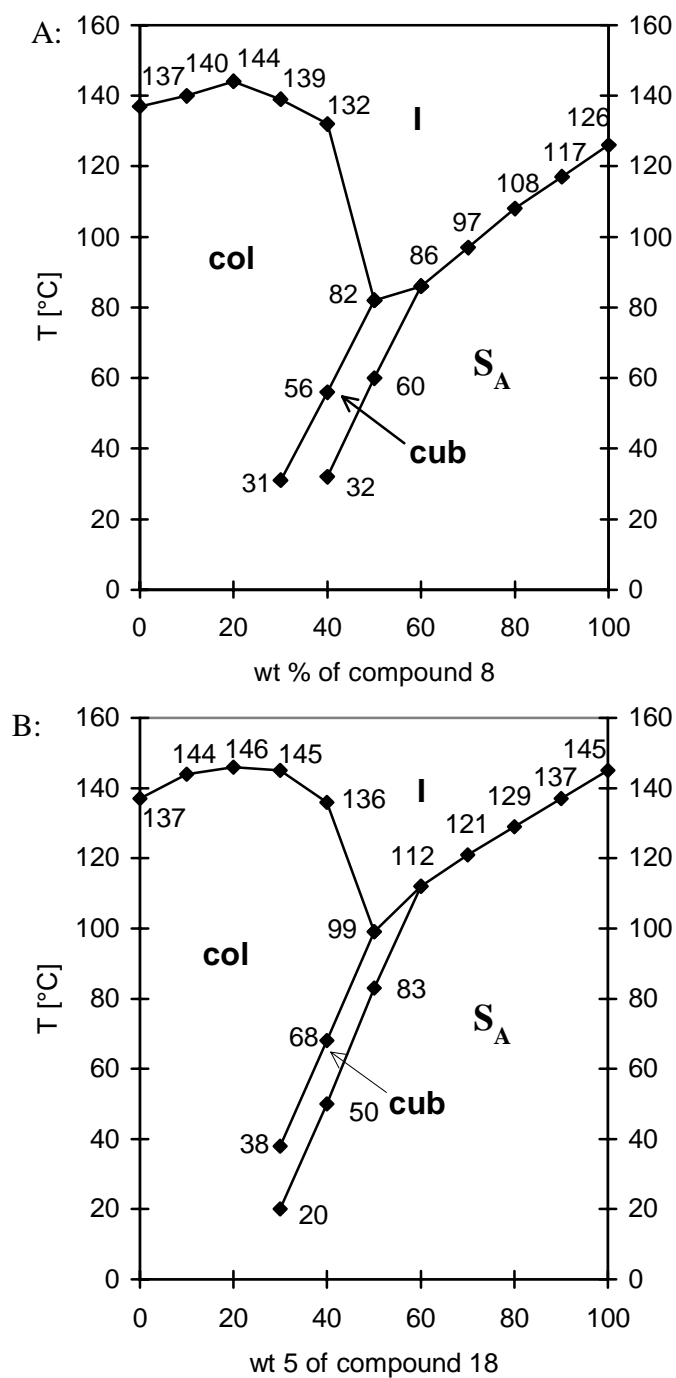


Figure 5.17: Phase diagrams of the binary mixtures of
 A: Compound **108** and compound **8** (diagram 11).
 B: Compound **108** and compound **18** (diagram 12).

In an effort to unravel the effect of the configuration of the hydroxyl groups of the sugar residue on the phase behaviour the glucose moiety in phase diagram 1 was replaced by galactose, having a different configuration at C-4.

Figure 5.17A shows the phase diagram of the binary mixture of the galactosyl diacylglycerol **108** and the alkyl glucoside **8** (phase diagram 11)

This diagram resembles at the first glance phase diagram 1 (binary mixture of the glucosyl diacylglycerol **77** and the alkyl glucoside **8**; Figure 5.2) as well as phase diagram 12 (binary mixture of the galactosyl diacylglycerol **108** and the alkyl galactoside **18**; Figure 5.17B). In all these diagrams the stability of the columnar phase increases slightly with increasing concentration of the lamellar component and passes a maximum of stability at 20 wt % of the lamellar component. Nevertheless, there is a remarkable difference which can again be seen best by superimposition of these three diagrams (Figure 5.18). Going from phase diagram 1 (mixture of two *gluco* compounds) over phase diagram 11 (one *gluco* and one

galacto compound) to phase diagram 12 (two *galacto* compounds), the boundaries of the cubic phase become steeper and steeper, i.e. the temperature dependence of the cubic phase decreases whereas its concentration dependence increases.

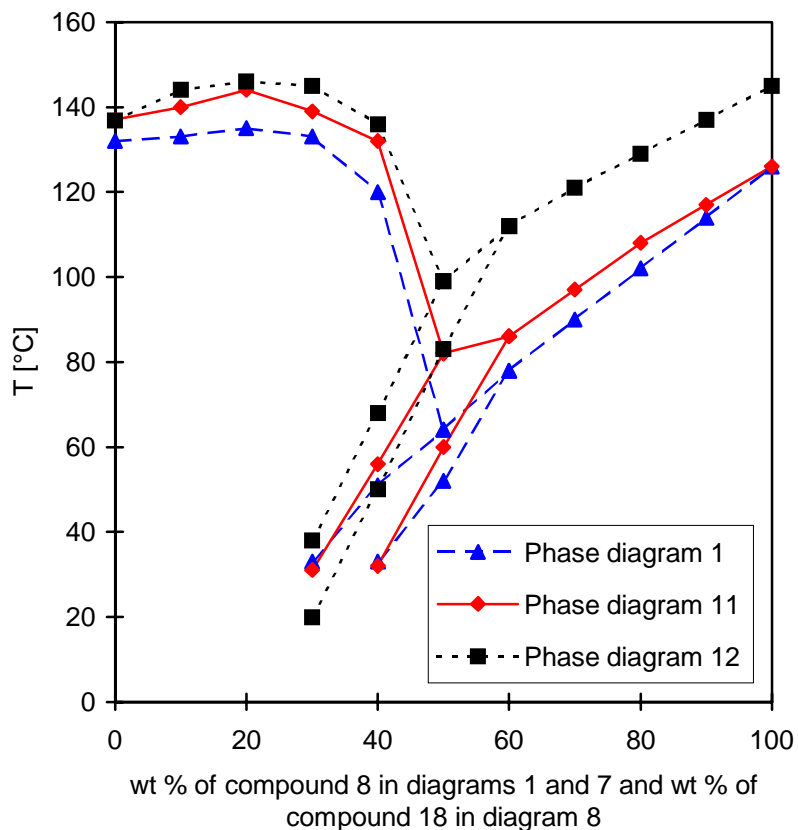


Diagram:

Components:

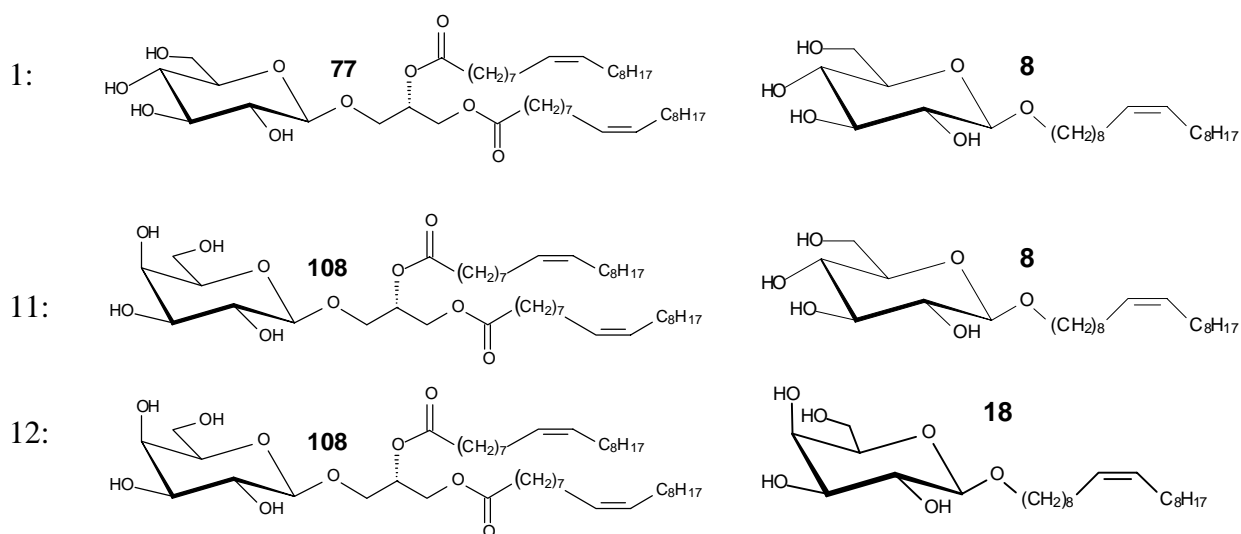


Figure 5.18: Superimposition of phase diagrams 1, 11, and 12.

Based on the results of this chapter the following structure-property relationships governing the stability of cubic phases can be summarised:

- *In mixtures of two components, one forming a columnar phase in its pure state and the other one a lamellar phase, an induced cubic phase can be found.*
- *The stability of the induced cubic phase is temperature as well as concentration dependent. Hence, the phase boundaries of the induced cubic phase are diagonal.*
- *The induced cubic phase is a derivative of the lamellar phase which extends in the phase diagram just below the cubic phase continuously over the whole cubic phase existence range and can be transformed into the cubic phase by just small changes in concentration or temperature.*
- *If a monosaccharide is replaced by a disaccharide as headgroup of the columnar glycosyl diacylglycerol component, the cubic phase existence range is enlarged and slightly shifted towards higher temperatures. This shift towards higher temperatures is larger in the case of a α 1 \rightarrow 4 linked disaccharide headgroup than in the case of a β 1 \rightarrow 4 linked disaccharide headgroup.*
- *If a monosaccharide is replaced by a disaccharide as headgroup of the lamellar component, the cubic phase is shifted towards much higher temperatures and lower concentrations of the lamellar component, i.e. smaller amounts of the lamellar component are necessary to induce a cubic phase in the mixture with the columnar component. This last effect is not seen in mixtures with glycosyl diacylglycerols with monosaccharide headgroups, since the lamellar component stabilises the columnar phase due to its disaccharide headgroup. Furthermore, the phase boundaries of the induced cubic phase become much steeper in the case of a lamellar component bearing a disaccharide headgroup, i.e. the temperature dependence of the cubic phase is decreased, while the concentration dependence is increased.*
- *The less wedge-shaped the columnar component is, the more the induced cubic phase is shifted towards lower concentrations of the lamellar component.*
- *If a glucopyranosyl moiety is replaced by a galactopyranosyl moiety as headgroup of the columnar component, the boundaries of the cubic phase become steeper and hence, the temperature dependence of the cubic phase decreases while its concentration dependence increases. The additional introduction of a galactopyranosyl moiety as headgroup of the*

lamellar component increases this effect further.

This last observation might be of great biological relevance, since galacto lipids are found in particular in plants, which must withstand a wide range of ambient temperatures during the different seasons and still maintain their membrane properties.

However, there is still an even more important general observation, which has been made whenever a cubic phase was found:

At elevated temperatures it took only a short time for the lamellar to cubic transition to occur throughout the whole sample, while at low temperatures this transition took several hours, if it happened at all. However, the formation of a seed of a cubic phase is expected to occur immediately. This seed of a cubic phase in a membrane is equivalent to a pore, which is necessary for a non-leaky fusion, whereas the transformation of the whole membrane into a cubic phase would destroy its barrier function. The quick formation of a seed of a cubic phase whilst the macroscopic phase transition is hindered for kinetical reasons – as it has been found here – might be the crucial key-step in processes such as cell fusion.

6. Summary

A wealth of experimental evidence points towards a great importance of the supramolecular structures – and in particular of cubic structures – of lipids for processes in membranes. However, very little was known about the prerequisites to chemical structure for cubic phases to occur and model-systems were lacking which would enable the correlation of chemical structures with mesogenic properties.

The aim of this work was to synthesise simple model compounds and to derive structure-property relationships in general as well as for cubic phases in particular. The working hypothesis was that sterically problematic sugar headgroups may destabilise the ordinary lamellar and columnar phases and thus stabilise cubic phases (Figure 2.1).

In the first step, alkyl glycosides were synthesised as the most simple model system and the sugar headgroup structure was changed systematically. The synthesis was accomplished using the peracetylated saccharides as glycosyl donors and the Lewis acid-catalysed displacement of the acetoxy group at C-1 for glycoside synthesis. This strategy simplifies the synthesis, since both anomers of a glycoside can be obtained from the same glycosyl donor, depending on the reaction conditions (Figure 3.3).

The alkyl glycosides with a monosaccharide headgroup displayed thermotropically a S_A phase and in the contact preparation with water myelin figures (Figure 3.5), whereas a broad polymorphism was found in the case of alkyl glycosides with a disaccharide headgroup. In this case lamellar and cubic phases were found in the dry state (Figure 3.12) and bicontinuous cubic phases of type 1 and 2, lamellar phases, columnar phases of type 1, micellar cubic phases of type 1 and lyotropic cholesteric phases in the contact preparation with water (Figure 3.15). The observed phase behaviour was correlated with the chemical structure. The hypothesis, that sterically problematic 1→6 linked sugar headgroups favour the occurrence of cubic phases could be proved.

While there are only a few examples of lyotropic cholesteric phases, this phase occurred in the case of long-chain alkyl glycosides with disaccharide headgroups frequently. Its existence was verified by small-angle neutron scattering, and it could be demonstrated that its occurrence requires a minimal chain length of the alkyl chain.

Glycosyl diacylglycerols were synthesised (Chapter 4) as model compounds which closely resemble nature. As these compounds were intended for use in binary mixtures in the final step, it was necessary to use glycosyl diacylglycerols bearing unsaturated fatty acid chains. Hence, the classical synthetic strategy according to Mannock (Figure 4.2) could not be used, since the final deprotecting step was known to interfere with unsaturated fatty acids. A new strategy was therefore developed, giving a quick and easy access within 6 steps to unsaturated glycosyl

diacylglycerols, starting with the peracetylated sugar and the suitably protected glycerol (Figures 4.6 and 4.7).

Glycosyl dioleoylglycerols with a monosaccharide headgroup displayed a columnar mesophase in the dry state and no further lyotropic phases, while with a disaccharide headgroup a broad lyotropic polymorphism was observed (Figures 4.10 and 4.12). These disaccharide derivatives displayed in the contact preparation with water besides a columnar phase a bicontinuous cubic phase, a lamellar phase and myelin figures. According to the general concept outlined in Chapter 2 (Figure 2.1), the disaccharide headgroup should already destabilise the columnar phase and exactly this was found for the lyotropic properties to occur. If the 1→4 linked disaccharide headgroup was replaced by a broad 1→6 linked headgroup, even in the anhydrous state a cubic and a lamellar phase were found in addition to a columnar phase, again proving the general hypothesis and the proposed effect of 1→6 linked headgroups. Again it was possible to link the observed mesogenic behaviour with the structure of the carbohydrate headgroup, which was changed systematically (Table 4.1).

The compounds synthesised were used in the final step (Chapter 5) to prepare binary mixtures, and it was possible to induce cubic phases in the mixture of a columnar and a lamellar component. The induced cubic phase was dependent on concentration as well as temperature, and proved to be a derivative of the lamellar phase. It was possible to deduce the influence of the carbohydrate structure on the stability of the induced cubic phase by comparison of the different phase diagrams, which have been obtained by changing the carbohydrate headgroup of the mixture components systematically (see page 85). For example, galactose caused the induced cubic phase to be less temperature dependent compared to glucose (Figure 5.13).

This last observation may be of great biological relevance, since galacto lipids are found in particular in plants which have to withstand a wide range of ambient temperatures during the different seasons while still maintaining their membrane properties.

But there is still an even more important general observation, which has been made whenever a cubic phase was found:

It took at elevated temperatures only a short time for the lamellar to cubic transition to occur throughout the whole sample, while at low temperatures this transition took several hours, if it happened at all. However, the formation of a seed of a cubic phase is expected to occur immediately. This seed of a cubic phase in a membrane is equivalent to a pore, which is necessary for a non-leaky fusion, whereas the transformation of the whole membrane into a cubic phase would destroy its barrier function. The quick formation of a seed of a cubic phase whilst the macroscopic phase transition is hindered for kinetical reasons – as found here – might be the crucial key-step in processes such as the cell fusion.

Zusammenfassung

Zahlreiche experimentelle Befunde deuten daraufhin, daß die von Lipiden gebildeten supramolekularen Strukturen und hier insbesondere die kubische Phasen von großer Bedeutung für Prozesse in Zellmembranen sind. Fundierten Erkenntnisse über die chemischen Strukturvoraussetzungen zur Erzeugung dieser bikontinuierlichen kubischen Phasen und Modellsysteme, die diese Phasen mit den gefundenen Effekten quantitativ korrelieren können, fehlten jedoch bisher.

Das Ziel dieser Arbeit war es daher, einfache Modellverbindungen zu synthetisieren und Struktur-Eigenschaftsbeziehungen im allgemeinen und für kubische Phasen im besonderen abzuleiten. Der Grundgedanke war dabei, daß die Stabilität kubischer Phasen auf einem neuen Strukturkonzept beruhen könnte, nämlich der Destabilisierung der gewöhnlichen lamellaren und kolumnaren Phasen durch sterisch problematische Kopfgruppen, so daß bikontinuierliche kubische Phasen relativ dazu stabilisiert werden (Abbildung 2.1).

Als einfachste Modellsysteme wurden zunächst Alkylglycoside dargestellt (Kapitel 3), deren Zuckerkopfgruppe systematisch modifiziert wurde. Die Synthese erfolgte ausgehend von den peracetylierten Zuckern als Glycosyldonor durch die Lewis-Säure katalysierte direkte Glycosylierung mit dem jeweiligen Alkohol. Diese Strategie vereinfacht die Synthese erheblich, da man auf diesem Weg aus ein und dem selben Glycosyldonor je nach den gewählten Reaktionsbedingungen das eine oder andere Anomer eines Glycosides erhält (Abbildung 3.3).

Alkylglycoside mit einer Monosaccharidekopfgruppe zeigten thermotrop eine S_A -Phase und im Kontakt mit Wasser Myelinfiguren (Abbildung 3.5), während im Falle einer Disaccharidkopfgruppe ein ausgeprägter Polymorphismus gefunden wurde. Hier traten im wasserfreien Zustand lamellare und kubische Phasen auf (Abbildung 3.12) und im Kontakt mit Wasser wurden bikontinuierliche kubische Phasen des Typs 1 und 2, lamellare Phasen, kolumnare Phasen des Typs 1, micellar kubische Phasen des Typs 1 sowie lyotrop cholesterische Phasen beobachtet (Abbildung 3.15). Das beobachtete Phasenverhalten konnte mit der chemischen Struktur korreliert werden, wobei der Grundgedanke, daß sterisch problematische 1→6 verknüpfte Zuckerkopfgruppen das Auftreten kubischer Phasen begünstigen, bestätigt wurde.

Während es nur wenige Beispiele für das Auftreten lyotrop cholesterischer Phasen gibt, trat diese Phase bei den langkettigen Alkylglycosiden mit einer Disaccharidkopfgruppe nahezu ubiquitär auf. Das Vorliegen einer lyotrop cholesterischen Phase wurde zusätzlich durch Kleinwinkel Neutronenstreuung bestätigt und es konnte nachgewiesen werden, daß für ihr auftreten eine minimale Kettenlänge nötig ist.

Im nächsten Schritt wurden Glycosyldiacylglycerole als naturähnlichere Modellverbindungen

synthetisiert (Kapitel 4). Da diese Verbindungen auch in binären Mischungen im letzten Schritt eingesetzt werden sollten, war es nötig, Glycosyldiacylglycerole darzustellen, die ungesättigte Fettsäureketten tragen. Aus diesem Grunde konnte die klassische von Mannoock entwickelte Synthesestrategie (Abbildung 4.2) nicht genutzt werden, da der Entschützungsprozess am Ende der Synthese bei ungesättigten Ketten bekanntermaßen zu Problemen führt. Es wurde daher eine neue Strategie entwickelt, die einen einfachen und schnellen Zugang in 6 Stufen zu ungesättigten Glycosyldiacylglycerolen gibt und vom peracetylierten Zucker und dem geeignet geschützten Glycerol ausgeht (Abbildungen 4.6 und 4.7).

Glycosyldiacylglycerole mit einer Monosaccharidkopfgruppe zeigten in wasserfreier Form eine kolumnare Phase und auch keine weiteren lyotropen Phasen, während im Falle einer Disaccharidkopfgruppe neben einer thermotropen kolumnaren Phase ein ausgeprägter lyotroper Polymorphismus gefunden wurde (Abbildungen 4.10 und 4.12). Diese Disaccharidderivate zeigten im Kontakt mit Wasser neben einer kolumnaren Phase eine bicontinuierliche kubische Phase, eine lamellare Phase und Myelinfiguren. Gemäß dem in Kapitel 2 vorgestelltem allgemeinen Konzept (Abbildung 2.1) sollte die Disaccharidkopfgruppe hier die kolumnare Phase destabilisieren und eine kubische Phase begünstigen und genau dies wurde hier beim lyotropen Verhalten auch gefunden.

Wurde die 1→4 verknüpfte Disaccharidkopfgruppe durch eine breite 1→6 verknüpfte Disaccharidkopfgruppe ersetzt, traten eine bicontinuierliche kubische Phase und eine lamellare Phase neben einer kolumnaren Phase sogar in wasserfreier Form auf. Dies bestätigte wiederum das allgemeine Konzept und den vermuteten Effekt von 1→6 verknüpften Kopfgruppen und es war wieder möglich, das mesogene Verhalten mit der Struktur der Kohlenhydratkopfgruppe zu korrelieren, die systematisch modifiziert wurde (Tabelle 4.1).

Die zuvor dargestellten Verbindungen wurden im letzten Schritt (Kapitel 5) in binären Mischungen eingesetzt und es gelang, eine kubische Phase in Mischungen einer kolumnaren und einer lamellaren Verbindung zu induzieren. Diese induzierte kubische Phase war sowohl konzentrations- als auch temperaturabhängig und wie sich zeigte ein Derivat der lamellaren Phase. Ferner war es möglich den Einfluß der Struktur der Kohlenhydratkopfgruppe auf die Stabilität der induzierten kubischen Phase abzuleiten durch Vergleich der unterschiedlichen Phasendiagramme, die durch einen systematischen Austausch der Kohlenhydratkopfgruppen der Mischungskomponenten erhalten wurden (siehe Seite 85). So nahm zum Beispiel die Temperaturabhängigkeit der induzierten kubischen Phase ab, wenn eine Glucosekopfgruppe gegen Galactose ausgetauscht wurde (Abbildung 5.13).

Diese Beobachtung könnte von großer biologischer Bedeutung sein, da Galactolipide vor allem in Pflanzen vorkommen, die natürlich innerhalb eines weiten Temperaturbereichs, den die Umgebungstemperatur innerhalb eines Jahres überstreicht, ihre Membraneigenschaften bewahren müssen.

Noch bedeutender könnte eine andere allgemeine Beobachtung sein, die immer gemacht wurde, wenn eine induzierte kubische Phase auftrat:

Die Umwandlung lamellar→kubisch vollzog sich bei erhöhten Temperaturen innerhalb kürzester Zeit und die gesamte Probe wandelte sich um. Bei Temperaturen im unteren Existenzbereich der kubischen Phase dauerte die Umwandlung jedoch oft Stunden, wenn sie überhaupt erfolgte und dies geschah dann oft nur in kleinen Bereichen. Nichts desto trotz sollte die Keimbildung einer kubischen Phase sofort erfolgen. Der Keim einer kubischen Phase in einer Membran entspricht einer Pore, wie sie für eine Fusion nötig ist, während eine vollständige Umwandlung der Membran in eine kubische Phase ihre Funktion als semipermeable Grenze zerstören würde. Die schnelle Bildung eines Keims einer kubischen Phase, wobei die makroskopische Phasenumwandlung kinetisch gehindert ist, –genau wie es hier beobachtet wurde – könnte genauer der entscheidende Schlüsselschritt in Prozessen wie der Zellfusion sein.

7. Experimental section

7.1 Materials and Methods

Thin-layer chromatography was performed on silica gel (Merck GF₂₅₄), and detection was effected by spraying with a solution of ethanol/sulphuric acid (9:1), followed by heating. Column chromatography was performed using silica gel 60 (230-240 mesh, Machery & Nagel). Optical rotations were recorded using a Perkin-Elmer 341 polarimeter. NMR spectra were recorded on a Bruker AMX-400 or a Bruker DRX 5001 spectrometer (m_c = centred multiplet, d = doublet, t = triplet, dd = double doublet, dt = double triplet). An Olympus BH optical polarising microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to identify thermal transitions and characterise anisotropic textures.

Sample preparation for lyotropic phase behaviour (X-ray diffraction)

The glycolipid samples were prepared as aqueous dispersions at high buffer content, i.e. above 80 wt% using 20 mM HEPES, in some cases also at lower water content (50 %). For this, the lipids were directly suspended in the buffer, and the suspensions were temperature-cycled several times between 5 and 70 °C and then stored at least 12 h at 4 °C before measurement.

FTIR spectroscopy

Infrared spectroscopic measurements were performed on FTIR spectrometers '5-DX' (Nicolet Instruments, Madison, WI) and IFS-55 (Bruker, Karlsruhe, Germany). The lipid samples were placed in a CaF₂ cuvette separated by a 12.5 μ m thick teflon spacer. Temperature scans were performed automatically between 10 and 70 °C with a heating rate of 3 °C/5 min. Every 3 °C, 50 interferograms were accumulated, apodised, Fourier-transformed, and converted to absorbance spectra. The gel to liquid crystalline phase transition $L_\beta \leftrightarrow L_\alpha$ (S_B to S_A in lamellar phases) was determined by evaluating the symmetric stretching vibration of the methylene groups $\nu_s(\text{CH}_2)$ with standard procedures. The location of $\nu_s(\text{CH}_2)$ - around 2850 cm^{-1} in the gel phase and 2853 cm^{-1} in the fluid phase - is a sensitive indicator of acyl chain order (Casal and Mantsch, 1984).

X-ray diffraction

X-ray diffraction measurements were performed at the European Molecular Biology

Laboratory (EMBL) outstation at the Hamburg Synchrotron Radiation Facility HASYLAB using the double-focussing monochromator-mirror camera X33. Diffraction patterns in the range of the scattering vector $0.07 < s < 1 \text{ nm}^{-1}$ ($s = 2 \sin \theta / \lambda$, 2θ the scattering angle and λ the wavelength = 0.15 nm) were recorded at 40 °C with exposure times of 2 or 3 min using a linear detector with delay line readout (Gabriel and Dauvergne, 1982). The s-axis calibration was done using tripalmitin as standard (periodicity 4.06 nm at room temperature). Further details of the data acquisition and evaluation system can be found elsewhere (Boulin and Kempf et al., 1986). In the diffraction patterns presented here, the logarithm of the diffraction intensities $\log I(s)$ is plotted against the scattering vectors. The evaluation of the X-ray spectra was made according to procedures described by Luzzati et al. (Luzzati et al., 1986) and in other papers (Brandenburg et al., 1990 and 1998) which allow the assignment of the spacing ratios of the main scattering maxima to defined three-dimensional structures. Here lamellar and cubic structures are of particular relevance, which can be characterised by the following features:

- (1) Lamellar (smectic phases): The reflections are grouped in equidistant ratios, i.e., at 1, 1/2, 1/3, 1/4 etc. of the lamellar repeat distance d_l .
- (2) Cubic: These are non-lamellar three-dimensional structures. Their various space groups differ in the ratio of their spacings. The relation between reciprocal spacing $s_{hkl} = 1/d_{hkl}$ and lattice constant a is $s_{hkl} = (h^2 + k^2 + l^2)^{1/2} / a$
(hkl=Miller indices of the respective set of plane).

In addition, X-ray wide-angle diffraction was performed in selected cases, in which the determination of the low-range order is possible. In the case of a hexagonal array of the lipid chains such as found for many phospholipids, the distance between neighbouring acyl chains, the lattice constant a , can be calculated from the main wide-angle reflection at a spacing ratio d by $a = 2/\sqrt{3} \times d$.

Small angle neutron scattering

A set of small-angle neutron scattering experiments was performed on the SANS1 instrument at the FRG1 research reactor of GKSS, Geesthacht, Germany (Stuhrmann et al., 1995). The range of scattering vectors q from 0.008 to 0.25 \AA^{-1} was covered by three combinations of

neutron wavelength (8.5 Å) and sample-to-detector distances (from 0.7 to 7 m). The wavelength resolution was 10% (full-width-at-half-maximum value).

The samples were kept in quartz cells with a path length of 1.5 mm at 23 °C. The raw spectra were corrected for backgrounds from the solvent, sample cell, and other sources by conventional procedures (Stuhrmann, 1989). The two-dimensional isotropic scattering spectra were azimuthally averaged, converted to an absolute scale, and corrected for detector efficiency by dividing by the incoherent scattering spectra of pure water (Wignall and Bates, 1986) which was measured with a 1-mm-path-length quartz cell.

The analysis of SANS data and the modelling were performed as described elsewhere (Minden et al., submitted).

7.2 Synthetic section

General synthetic procedures

Synthesis of peracetylated β -saccharides (*General procedure 1*)

The saccharide (10 mmol) was added in small portions to a stirred mixture of acetic acid anhydride (2 mmol of anhydride per hydroxyl group) and 1.64 g (20 mmol) sodium acetate, heated to 120 °C before addition of the sugar. After stirring for an additional 4 hours at 120 °C and the usual work up procedure, the β -anomer of the peracetylated saccharide was obtained as colourless crystals.

Synthesis of alkyl glycopyranosides (*General procedure 2*)

The peracetylated saccharide (10mmol) and the alcohol (15 mmol) were dissolved in 100 ml anhydrous dichloromethane under an atmosphere of dry nitrogen and afterwards the Lewis acid (10 mmol tin tetrachloride in the case of the synthesis of the α anomer and 14 mmol boron trifluoride etherate for the synthesis of the β anomer) was added. The mixture was stirred at ambient temperature until t.l.c. revealed the reaction to be complete. The preparation of the β anomer required a reaction time of 2-4 hours, that of the α anomer approximately 48 hours. After the reaction had been quenched with 100 ml of a saturated solution of sodium hydrogen carbonate, the organic layer was separated and the aqueous layer extracted twice with dichloromethane. The combined organic phases were washed twice with water (100 ml), dried over magnesium sulphate, filtrated and evaporated *in vacuo*. The resulting syrup was purified by column chromatography using as eluent:

- light petroleum (b.p. 50-70°C)-ethyl acetate 5:1 in the case of the monosaccharide derivatives and
- light petroleum (b.p. 50-70°C)-ethyl acetate 2:1 in the case of the disaccharide derivatives if nothing else is mentioned.

Deacetylation (*General procedure 3*)

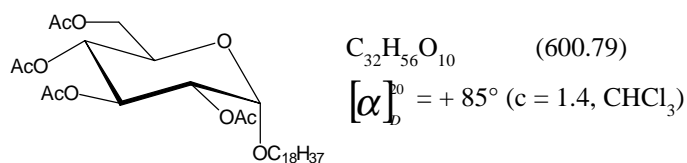
The compound was dissolved in dry methanol, and sodium methoxide was added (pH 8-9). The solution was stirred at ambient temperature until t.l.c. revealed the reaction to be complete, neutralised using Amberlyst IR 120 ion-exchange resin (protonated form), filtrated and evaporated *in vacuo*.

Glycosylation (*General procedure 4*)

To a solution of 1,2-di-*O*-benzyl-*sn*-glycerol (9.2 mmol), HgBr₂ (5 mmol) and Hg(CN)₂ (5 mmol) in 25 ml of dry acetonitrile, a solution of the acetobromo sugar (10 mmol) in 25 ml of dry acetonitrile was added under nitrogen over a period of 30 minutes at ambient temperature. When t.l.c. revealed the reaction to be complete, the reaction mixture was concentrated *in vacuo* to an oil, redissolved in 150 ml chloroform, filtered, washed three times with 100 ml of a 1M aqueous solution of KBr and subsequently once with 100 ml of water. The organic phase was dried with MgSO₄ and concentrated *in vacuo* to obtain a viscous residue which was purified by silica gel chromatography.

Esterification using DCC (*General procedure 5*)

A solution of the carbonic acid (1.1 equivalent), *N,N'*-dicyclohexylcarbodiimide (1.1 equivalent), the alcohol (1 equivalent) and a catalytic amount of 4-(1-pyrrolidiny)pyridine in dry dichloromethane was stirred at room temperature until t.l.c. revealed the reaction to be complete. *N,N'*-dicyclohexylurea formed during the course of the reaction was filtered off, the solution concentrated *in vacuo* and the resulting residue purified by silica gel chromatography.

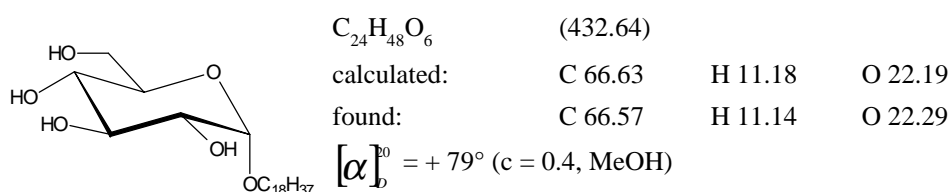
Stearyl-2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranoside 1

Penta-*O*-acetyl- β -D-glucopyranose and stearyl alcohol were reacted using *General procedure 2*. Yield: 1.67 g (28 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): δ = 5.48 (dd, 1H, H-3), 5.05 (dd, 1H, H-4), 5.06 (d, 1H, H-1), 4.85 (dd, 1H, H-2), 4.26 (dd, 1H, H-6a), 4.09 (dd, 1H, H-6b), 4.02 (ddd, 1H, H-5), 3.68 (dt, 1H, H- α a), 3.42 (dt, 1H, H- α b), 2.12, 2.06, 2.03, 2.01 (each s, 3H, OAc), 1.54-1.64 (m, 2H, β - CH_2), 1.20-1.38 (m, 30H, - CH_2 -), 0.88 (t, 3H, - CH_3);

$^3J_{1,2} = 3.6$, $^3J_{2,3} = 10.2$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 10.2$, $^3J_{5,6a} = 4.6$, $^3J_{5,6b} = 2.0$, $^2J_{6a,6b} = 12.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta-CH_2} = 6.6$, $^3J_{\alpha b, \beta-CH_2} = 6.6$ Hz.

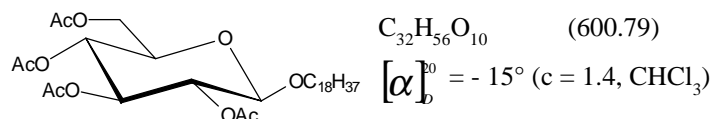
^{13}C -NMR (100 MHz, $CDCl_3$ + TMS): δ = 170.67, 170.20, 170.15, 169.64 (C=O, OAc), 95.65 (C-1), 70.99 (C-2), 70.31 (C-3), 68.78 (C- α), 68.68 (C-4), 67.15 (C-5), 61.98 (C-6), 31.94, 29.72, 29.67, 29.37, 29.28, 26.05, 22.71 (- CH_2 -), 20.73, 20.69, 20.65 (- CH_3 , OAc), 14.13 (- CH_3).

Stearyl- α -D-glucopyranoside 2

1.5 g (2.50 mmol) stearyl-2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranoside **1** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 1.00 g (92 %).

1H -NMR (400 MHz, d_4 -MeOH): δ = 4.81 (d, 1H, H-1), 3.84 (dd, 1H, H-6a), 3.78 (dt, 1H, H- α a), 3.71 (dd, 1H, H-6b), 3.68 (dd, 1H, H-3), 3.61 (ddd, 1H, H-5), 3.48 (dt, 1H, H- α b), 3.42 (dd, 1H, H-2), 3.33 (dd, 1H, H-4), 1.68 (m_C , 2H, β - CH_2), 1.24 -1.50 (m, 30H, - CH_2 -), 0.95 (t, 3H, - CH_3);

$^3J_{1,2} = 3.6$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 10.2$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 2.5$, $^3J_{5,6b} = 5.6$, $^2J_{6a,6b} = 11.7$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta-CH_2} = 6.6$, $^3J_{\alpha b, \beta-CH_2} = 6.6$ Hz.

Stearyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside 3

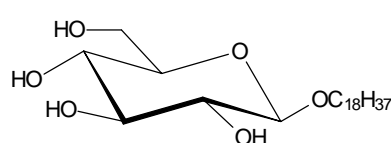
Penta-*O*-acetyl- β -D-glucopyranose and stearyl alcohol were reacted using *General procedure 2*. Yield: 1.67 g (28 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.21 (dd, 1H, H-3), 5.09 (dd, 1H, H-4), 4.99 (dd, 1H, H-2), 4.49 (d, 1H, H-1), 4.27 (dd, 1H, H-6a), 4.14 (dd, 1H, H-6b), 3.87 (dt, 1H, H- α), 3.69 (ddd, 1H, H-5), 3.47 (dt, 1H, H- α b), 2.09, 2.04, 2.03, 2.01 (je s, 3H, OAc), 1.48-1.63 (m, 2H, β - CH_2), 1.17-1.34 (m, 30H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

$^3\text{J}_{1,2} = 8.1$, $^3\text{J}_{2,3} = 9.7$, $^3\text{J}_{3,4} = 9.7$, $^3\text{J}_{4,5} = 9.7$, $^3\text{J}_{5,6a} = 4.6$, $^3\text{J}_{5,6b} = 2.6$, $^2\text{J}_{6a,6b} = 12.2$, $^2\text{J}_{\alpha a,\alpha b} = 9.7$, $^3\text{J}_{\alpha a,\beta\text{-CH}_2} = 6.7$, $^3\text{J}_{\alpha b,\beta\text{-CH}_2} = 6.9$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 + TMS): δ = 170.71, 170.34, 169.41, 169.28 (C=O, OAc), 100.86 (C-1), 72.91 (C-3), 71.77 (C-5), 71.39 (C-2), 70.28 (C- α), 68.53 (C-4), 62.04 (C-6), 31.94, 29.71, 29.63, 29.41, 29.37, 29.35, 25.83, 22.70 ($-\text{CH}_2-$), 20.75, 20.64, 20.61 ($-\text{CH}_3$, OAc), 14.12 ($-\text{CH}_3$).

Stearyl- β -D-glucopyranoside 4



$\text{C}_{24}\text{H}_{48}\text{O}_6$ (432.64)

calculated: C 66.63 H 11.18 O 22.19

found: C 66.44 H 11.09 O 22.47

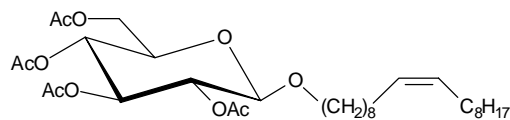
$[\alpha]_D^{20} = -23^\circ$ (c = 0.5, MeOH)

1.73 g (2.88 mmol) stearyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside **3** were deprotected using the *General procedure 3*. Yield: 1.15 g (93 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.28 (d, 1H, H-1), 3.94 (dt, 1H, H- α), 3.90 (dd, 1H, H-6a), 3.70 (dd, 1H, H-6b), 3.57 (dt, 1H, H- α b), 3.26-3.42 (m, 3H, H-3, H-4, H-5), 3.2 (dd, 1H, H-2), 1.66 (m_c, 2H, β - CH_2), 1.26-1.46 (m, 30H, $-\text{CH}_2-$), 0.94 (t, 3H, $-\text{CH}_3$);

$^3\text{J}_{1,2} = 7.6$, $^3\text{J}_{2,3} = 9.2$, $^3\text{J}_{5,6a} = 2.0$, $^3\text{J}_{5,6b} = 5.1$, $^2\text{J}_{6a,6b} = 11.7$, $^2\text{J}_{\alpha a,\alpha b} = 9.7$, $^3\text{J}_{\alpha a,\beta\text{-CH}_2} = 7.1$, $^3\text{J}_{\alpha b,\beta\text{-CH}_2} = 6.6$ Hz.

cis-9'-octadecenyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside 5



$\text{C}_{32}\text{H}_{54}\text{O}_{10}$ (598.77)

$[\alpha]_D^{20} = -14^\circ$ (c = 1.8, CHCl_3)

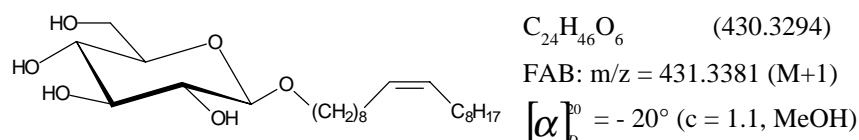
Penta-*O*-acetyl- β -D-glucopyranose and oleyl alcohol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70°C)-ethyl acetate 4:1. Yield: 2.18 g (36 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.28-5.41 (m, 2H, H-olefinic), 5.21 (dd, 1H, H-3), 5.09 (dd, 1H, H-4), 4.99 (dd, 1H, H-2), 4.49 (d, 1H, H-1), 4.27 (dd, 1H, H-6a), 4.14 (dd, 1H, H-6b), 3.87 (dt, 1H, H- α), 3.69 (ddd, 1H, H-5), 3.47 (dt, 1H, H- α b), 2.09, 2.04, 2.03, 2.01 (je s, 3H, OAc), 1.96-2.05 (m, 4H, $-\text{CH}_2-$ allylic), 1.48-1.64 (m, 2H, β - CH_2), 1.20-1.37 (m, 22H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 4.6$, $^3J_{5,6b} = 2.6$, $^2J_{6a,6b} = 12.2$, $^2J_{\alpha,\alpha\beta} = 9.7$, $^3J_{\alpha,\beta\text{-CH}_2} = 6.6$, $^3J_{\alpha\beta,\beta\text{-CH}_2} = 6.9$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): $\delta = 170.70$, 170.34, 169.42, 169.27 (C=O, OAc), 129.99, 129.80 (C-olefinic), 100.86 (C-1), 72.92 (C-3), 71.78 (C-5), 71.39 (C-2), 70.26 (C- α), 68.54 (C-4), 62.04 (C-6), 31.91, 29.78, 29.52, 29.41, 29.32, 29.27, 27.23, 27.21, 25.83, 22.69 (-CH₂-), 20.74, 20.64, 20.61 (-CH₃, OAc), 14.12 (-CH₃).

cis-9'-octadecenyl- β -D-glucopyranoside **6**

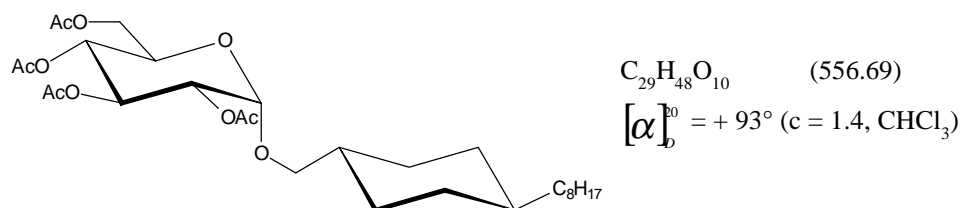


1.47 g (2.46 mmol) oleyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside **5** were deprotected using the *General procedure 3*. The product was purified via gel filtration (Serva LH-20 in methanol). Yield: 1.02 g (96 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): $\delta = 5.34$ -5.45 (m, 2H, H-olefinic), 4.28 (d, 1H, H-1), 3.94 (dt, 1H, H- α), 3.90 (dd, 1H, H-6a), 3.70 (dd, 1H, H-6b), 3.57 (dt, 1H, H- $\alpha\beta$), 3.25-3.41 (m, 3H, H-3, H-4, H-5), 3.21 (dd, 1H, H-2), 1.97-2.13 (m, 4H, H-allylic), 1.66 (m_c, 2H, β -CH₂), 1.28-1.47 (m, 30H, -CH₂-), 0.94 (t, 3H, -CH₃);

$^3J_{1,2} = 7.6$, $^3J_{2,3} = 9.2$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 5.6$, $^2J_{6a,6b} = 12.2$, $^2J_{\alpha,\alpha\beta} = 9.7$, $^3J_{\alpha,\beta\text{-CH}_2} = 6.6$, $^3J_{\alpha\beta,\beta\text{-CH}_2} = 6.6$ Hz.

4'-octylcyclohexylmethyl-2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranoside **7**

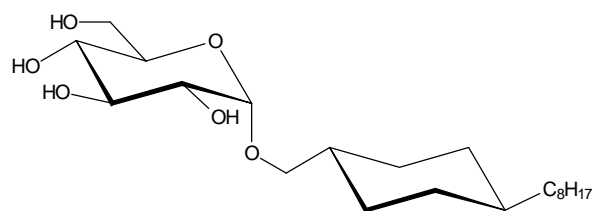


Penta-*O*-acetyl- β -D-glucopyranose and 4'-octylcyclohexylmethylalcohol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70°C)-acetone 8:1. Yield: 1.56 g (28 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): $\delta = 5.48$ (dd, 1H, H-3), 5.05 (dd, 1H, H-4), 5.06 (d, 1H, H-1), 4.85 (dd, 1H, H-2), 4.26 (dd, 1H, H-6a), 4.09 (dd, 1H, H-6b), 4.02 (ddd, 1H, H-5), 3.48 (dd, 1H, H- α), 3.21 (dd, 1H, H- $\alpha\beta$), 2.12, 2.06, 2.03, 2.01 (je s, 3H, OAc), 1.66-1.80 (m, 4H, cyclohexyl), 1.44-1.59 (m, 2H, cyclohexyl), 1.08-1.34 (m, 14H, -CH₂-), 0.80-0.97 (m, 7H, -CH₃, cyclohexyl);

$^3J_{1,2} = 3.6$, $^3J_{2,3} = 10.2$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 10.2$, $^3J_{5,6a} = 4.6$, $^3J_{5,6b} = 2.0$, $^2J_{6a,6b} = 12.2$, $^2J_{\alpha,\alpha\beta} = 9.7$, $^3J_{\alpha,\beta\text{-CH}_2} = 6.6$, $^3J_{\alpha\beta,\beta\text{-CH}_2} = 6.1$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): $\delta = 170.68$, 170.22, 170.18, 169.67 (C=O, OAc), 95.81 (C-1), 74.39 (C- α), 71.08 (C-2), 70.36 (C-3), 68.70 (C-4), 67.12 (C-5), 61.99 (C-6), 37.89, 37.73 (CH-cyclohexyl), 37.39, 32.60, 31.93, 29.99, 29.88, 29.75, 29.67, 29.35, 26.97, 22.70 (-CH₂-), 20.74, 20.66 (-CH₃, OAc), 14.12 (-CH₃).

4'-octylcyclohexylmethyl- α -D-glucofuranoside 8
 $C_{21}H_{40}O_6$ (388.54)

calculated: C 64.92 H 10.38 O 24.70

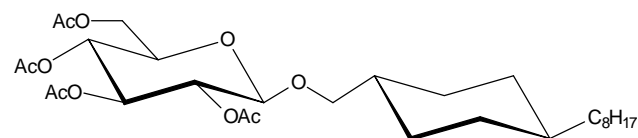
found: C 64.75 H 10.75 O 24.50

 $[\alpha]_D^{20} = +77^\circ$ (c = 0.8, MeOH)

0.94 g (1.69 mmol) 4'-octylcyclohexylmethyl-2,3,4,6-tetra-*O*-acetyl- α -D-glucofuranoside **7** were deprotected using the *General procedure 3*. Yield: 0.62 g (95 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.78 (d, 1H, H-1), 3.83 (dd, 1H, H-6a), 3.70 (dd, 1H, H-6b), 3.68 (dd, 1H, H-3), 3.60 (ddd, 1H, H-5), 3.56 (dd, 1H, H- α), 3.42 (dd, 1H, H-2), 3.25-3.43 (m, 2H, H-4, H- α b), 1.77-1.98 (m, 4H, cyclohexyl), 1.65 (m_c , 1H, cyclohexyl), 1.25-1.41 (m, 14H, $-\text{CH}_2-$), 1.17-1.25 (m, 1H, cyclohexyl), 0.88-1.10 (m, 7H, $-\text{CH}_3$, cyclohexyl);

$^3J_{1,2} = 4.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 2.5$, $^3J_{5,6b} = 5.6$, $^2J_{6a,6b} = 11.7$, $^2J_{\alpha a, \alpha b} = 9.1$, $^3J_{\alpha a, \text{cyclohexyl}} = 7.1$ Hz.

4'-octylcyclohexylmethyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucofuranoside 9
 $C_{29}H_{48}O_{10}$ (556.69)

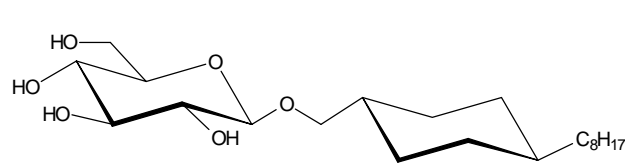
 $[\alpha]_D^{20} = -20^\circ$ (c = 0.7, CHCl_3)

Penta-*O*-acetyl- β -D-glucofuranose and 4'-octylcyclohexylmethylalcohol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70°C)-acetone 6:1. Yield: 2.16 g (39 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.20 (dd, 1H, H-3), 5.08 (dd, 1H, H-4), 4.99 (dd, 1H, H-2), 4.46 (d, 1H, H-1), 4.26 (dd, 1H, H-6a), 4.13 (dd, 1H, H-6b), 3.24 (dd, 1H, H- α a), 3.70 (dd, 1H, H- α b), 3.67 (ddd, 1H, H-5), 2.08, 2.03, 2.02, 2.01 (je s, 3H, OAc), 1.66-1.80 (m, 4H, cyclohexyl), 1.44-1.59 (m, 2H, cyclohexyl), 1.08-1.34 (m, 14H, $-\text{CH}_2-$), 0.80-0.97 (m, 7H, $-\text{CH}_3$, cyclohexyl);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 4.6$, $^3J_{5,6b} = 2.6$, $^2J_{6a,6b} = 12.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \text{cyclohexyl}} = 7.1$, $^3J_{\alpha b, \text{cyclohexyl}} = 6.1$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 170.72, 170.35, 169.42, 168.28 (C=O, OAc), 101.17 (C-1), 75.97 (C- α), 72.88 (C-3), 71.76 (C-5), 71.40 (C-2), 68.56 (C-4), 62.04 (C-6), 38.04, 37.76 (CH-cyclohexyl), 37.39, 32.64, 32.60, 31.93, 29.99, 29.69, 29.67, 29.50, 29.35, 26.96, 22.70 ($-\text{CH}_2-$), 20.76, 20.65, 20.61 ($-\text{CH}_3$, OAc), 14.12 ($-\text{CH}_3$).

4'-octylcyclohexylmethyl- β -D-glucopyranoside 10
 $C_{21}H_{40}O_6$ (388.54)

calculated: C 64.92 H 10.38 O 24.70

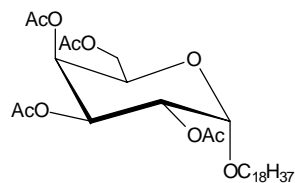
found: C 64.87 H 10.48 O 24.65

 $[\alpha]_D^{20} = -24^\circ$ (c = 0.8, MeOH)

1.70 g (3.05 mmol) 4'-octylcyclohexylmethyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside **9** were deprotected using the *General procedure 3*. Yield: 1.15 g (97 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.26 (d, 1H, H-1), 3.90 (dd, 1H, H-6a), 3.75 (dd, 1H, H- α a), 3.70 (dd, 1H, H-6b), 3.25-3.41 (m, 4H, H-3, H-4, H-5, H- α b), 3.21 (dd, 1H, H-2), 1.77-1.95 (m, 4H, cyclohexyl), 1.61 (m_C, 1H, cyclohexyl), 1.25-1.41 (m, 14H, -CH₂-), 1.17-1.25 (m, 1H, cyclohexyl), 0.87-1.08 (m, 7H, -CH₃, cyclohexyl);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.2$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 5.1$, $^2J_{6a,6b} = 11.7$, $^2J_{\alpha a, \alpha b} = 9.2$, $^3J_{\alpha a, \text{cyclohexyl}} = 6.6$ Hz.

Stearyl-2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranoside 11
 $C_{32}H_{56}O_{10}$ (600.79)

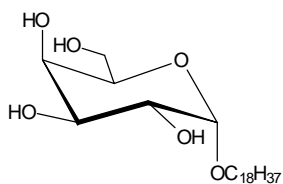
 $[\alpha]_D^{20} = +84^\circ$ (c = 1.0, CHCl₃)

Penta-*O*-acetyl- β -D-galactopyranose and stearyl alcohol were reacted using *General procedure 2*. Yield: 1.69 g (28 %).

$^1\text{H-NMR}$ (400 MHz, CDCl₃ + TMS): δ = 5.46 (dd, 1H, H-4), 5.35 (dd, 1H, H-3), 5.08-5.14 (m, 2H, H-1, H-2), 4.22 (ddd, 1H, H-5), 4.11 (dd, 1H, H-6a), 4.08 (dd, 1H, H-6b), 3.68 (dt, 1H, H- α a), 3.42 (dt, 1H, H- α b), 2.14, 2.07, 2.04, 1.99 (je s, 3H, OAc), 1.54-1.64 (m, 2H, β -CH₂), 1.20-1.38 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{3,4} = 3.6$, $^3J_{4,5} = 1.0$, $^3J_{5,6a} = 6.1$, $^3J_{5,6b} = 7.1$, $^2J_{6a,6b} = 11.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.7$, $^3J_{\alpha b, \beta\text{-CH}_2} = 6.7$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl₃ + TMS): δ = 170.44, 170.28, 170.05 (C=O, OAc), 96.10 (C-1), 68.72 (C- α), 68.31 (C-2), 68.18 (C-4), 67.72 (C-3), 66.17 (C-5), 61.85 (C-6), 31.94, 29.71, 29.67, 29.38, 29.33, 26.10, 22.71, (-CH₂-), 20.79, 20.70, 20.67 (-CH₃, OAc), 14.13 (-CH₃).

Stearyl- α -D-galactopyranoside 12
 $C_{24}H_{48}O_6$ (432.64)

calculated: C 66.63 H 11.18 O 22.19

found: C 66.56 H 11.11 O 22.33

 $[\alpha]_D^{20} = +83^\circ$ (c = 0.5, MeOH)

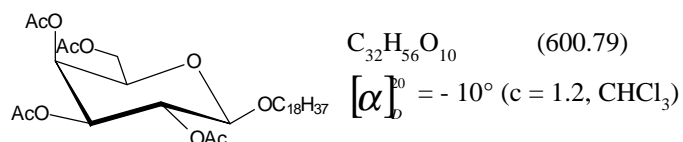
1.1 g (1.83 mmol) stearyl-2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranoside **11** were deprotected using the *General*

procedure 3. The product was recrystallised from methanol. Yield: 0.72 g (91 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.84 (d, 1H, H-1), 3.93 (dd, 1H, H-4), 3.85 (ddd, 1H, H-5), 3.71-3.83 (m, 5H, H-2, H-3, H-6a, H-6b, H- α), 3.48 (dt, 1H, H- α b), 1.62- 1.75 (m, 2H, β -CH $_2$), 1.29 -1.46 (m, 30H, -CH $_2$ -), 0.95 (t, 3H, -CH $_3$);

$^3J_{1,2}$ = 3.6, $^3J_{3,4}$ = 3.1, $^3J_{4,5}$ = 1.5, $^3J_{5,6a}$ = 6.1, $^3J_{5,6b}$ = 6.1, $^2J_{\alpha a, \alpha b}$ = 9.7, $^3J_{\alpha b, \beta\text{-CH}_2}$ = 6.6 Hz.

Stearyl-2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranoside **13**



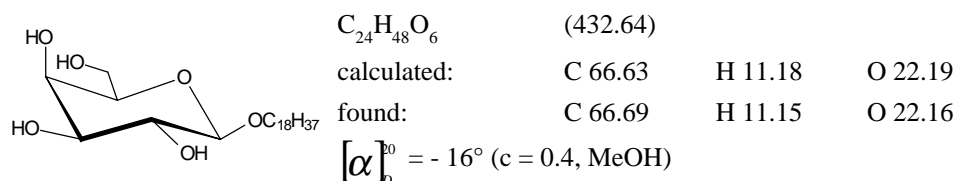
Penta-*O*-acetyl- β -D-galactopyranose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.0 g (50 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.41 (dd, 1H, H-4), 5.23 (dd, 1H, H-2), 5.04 (dd, 1H, H-3), 4.47 (d, 1H, H-1), 4.21 (dd, 1H, H-6a), 4.15 (dd, 1H, H-6b), 3.88-3.95 (m, 2H, H- α a, H-5), 3.49 (dt, 1H, H- α b), 2.17, 2.01. (je s, 3H, OAc), 2.07 (s, 6H, OAc), 1.51-1.67 (m, 2H, β -CH $_2$), 1.20-1.44 (m, 30H, -CH $_2$ -), 0.90 (t, 3H, -CH $_3$);

$^3J_{1,2}$ = 8.2, $^3J_{2,3}$ = 10.2, $^3J_{3,4}$ = 3.6, $^3J_{4,5}$ = 1.4, $^3J_{5,6a}$ = 6.3, $^3J_{5,6b}$ = 6.9, $^2J_{6a,6b}$ = 11.4, $^2J_{\alpha a, \alpha b}$ = 9.6, $^3J_{\alpha b, \beta\text{-CH}_2}$ = 6.9 Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 + TMS): δ = 170.41, 170.31, 170.22, 169.37 (C=O, OAc), 101.39 (C-1), 71.01 (C-3), 70.59 (C-5), 70.33 (C- α), 68.98 (C-2), 67.11 (C-4), 61.30 (C-6), 31.94, 29.71, 29.63, 29.44, 29.37, 25.84, 22.70 (-CH $_2$ -), 20.75, 20.69, 20.61 (-CH $_3$, OAc), 14.12 (-CH $_3$).

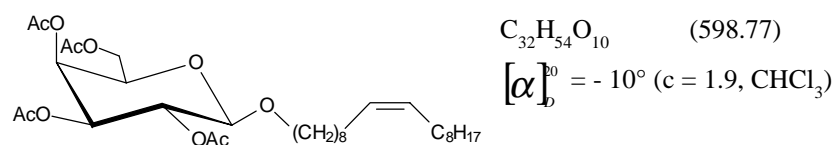
Stearyl- β -D-galactopyranoside **14**



2.87 g (4.77 mmol) stearyl-2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranoside **13** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 1.84 g (89 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.25 (d, 1H, H-1), 3.94 (dt, 1H, H- α a), 3.87 (dd, 1H, H-4), 3.80 (dd, 1H, H-6a), 3.76 (dd, 1H, H-6b), 3.58 (dt, 1H, H- α b), 3.51-3.57 (m, 2H, H-2, H-5), 3.49 (dd, 1H, H-3), 1.67 (m, 2H, β -CH $_2$), 1.28 -1.46 (m, 30H, -CH $_2$ -), 0.95 (t, 3H, -CH $_3$);

$^3J_{1,2}$ = 7.1, $^3J_{2,3}$ = 9.7, $^3J_{3,4}$ = 3.1, $^3J_{4,5}$ = 1.0, $^3J_{5,6a}$ = 6.6, $^3J_{5,6b}$ = 5.6, $^2J_{6a,6b}$ = 11.2, $^2J_{\alpha a, \alpha b}$ = 9.2, $^3J_{\alpha a, \beta\text{-CH}_2}$ = 6.6, $^3J_{\alpha b, \beta\text{-CH}_2}$ = 6.6 Hz.

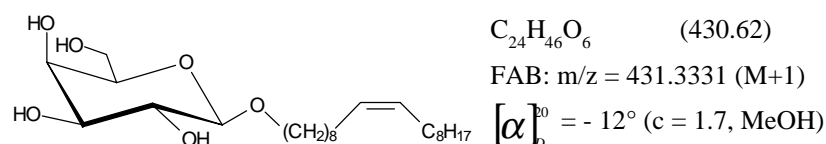
cis-9'-octadecenyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside 15

Penta-O-acetyl-β-D-galactopyranose and oleyl alcohol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70°C)-ethyl acetate 4:1. Yield: 3.17 g (53 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): δ = 5.39 (dd, 1H, H-4), 5.28-5.38 (m, 2H, H-olefinic), 5.21 (dd, 1H, H-2), 5.02 (dd, 1H, H-3), 4.45 (d, 1H, H-1), 4.19 (dd, 1H, H-6a), 4.13 (dd, 1H, H-6b), 3.85-3.93 (m, 2H, H-5, H- α), 3.47 (dt, 1H, H- α b), 2.15 (s, 3H, OAc), 2.05 (s, 6H, OAc), 1.98 (s, 3H, OAc), 1.93-2.07 (m, 4H, $-CH_2-$ allylic), 1.48-1.64 (m, 2H, β - CH_2), 1.20-1.37 (m, 22H, $-CH_2-$), 0.88 (t, 3H, $-CH_3$);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 10.2$, $^3J_{3,4} = 3.1$, $^3J_{4,5} = 1.0$, $^3J_{5,6a} = 6.6$, $^3J_{5,6b} = 7.1$, $^2J_{6a,6b} = 11.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha b, \beta-CH_2} = 6.6$ Hz.

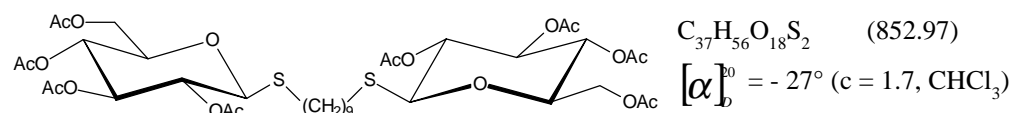
^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): δ = 170.41, 170.31, 170.22, 169.36 (C=O, OAc), 129.99, 129.80 (C-olefinic), 101.39 (C-1), 71.01 (C-3), 70.60 (C-5), 70.31 (C- α), 68.99 (C-2), 67.11 (C-4), 61.30 (C-6), 31.91, 29.78, 29.53, 29.43, 29.33, 29.28, 27.22, 25.83, 22.69 ($-CH_2-$), 20.74, 20.68, 20.61 ($-CH_3$, OAc), 14.12 ($-CH_3$).

cis-9'-octadecenyl-β-D-galactopyranoside 16

2.78 g (4.64 mmol) oleyl-2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside **15** were deprotected using the *General procedure 3*. The product was purified via column chromatography using chloroform-methanol 94:6 as eluent and a further gel filtration (Serva LH-20 in methanol). Yield: 1.71 g (86%).

1H -NMR (400 MHz, d_4 -MeOH): δ = 5.28-5.46 (m, 2H, H-olefinic), 4.24 (d, 1H, H-1), 3.93 (dt, 1H, H- α a), 3.87 (dd, 1H, H-4), 3.79 (dd, 1H, H-6a), 3.76 (dd, 1H, H-6b), 3.5-61 (m, 3H, H-2, H-5, H- α b), 3.49 (dd, 1H, H-3), 1.96-2.14 (m, 4H, H-allylic), 1.66 (m_c, 2H, β - CH_2), 1.27-1.46 (m, 30H, $-CH_2-$), 0.94 (t, 3H, $-CH_3$);

$^3J_{1,2} = 7.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 3.1$, $^3J_{4,5} = 1.0$, $^3J_{5,6a} = 6.6$, $^3J_{5,6b} = 5.6$, $^2J_{6a,6b} = 11.5$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta-CH_2} = 6.6$ Hz.

Nonan-1,9-diyl-bis(2',3',4',6'-tetra-O-acetyl-β-D-thioglucopyranoside) 17

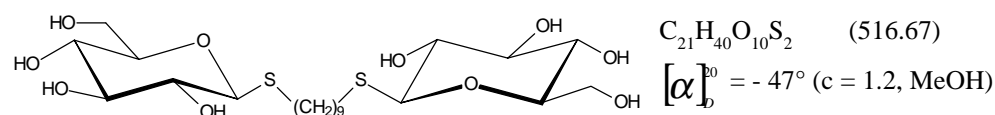
10 mmol penta-*O*-acetyl- β -D-glucopyranose and 5 mmol 1,9-nonanedithiol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70°C)-diethyl ether 1:3. Yield: 2.50 g (59 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.22 (dd, 2H, H-3, H-3'), 5.09 (dd, 2H, H-4, H-4'), 5.03 (dd, 2H, H-2, H-2'), 4.48 (d, 2H, H-1, H-1'), 4.25 (dd, 2H, H-6a, H-6a'), 4.14 (dd, 2H, H-6b, H-6b'), 3.91 (dd, 2H, H-5, H-5'), 2.60-2.74 (m, 4H, α - CH_2 , α' - CH_2), 2.08, 2.06, 2.03, 2.01 (je s, 6H, OAc), 1.54-1.64 (m, 4H, β - CH_2 , β' - CH_2), 1.32-1.42 (m, 4H, γ - CH_2 , γ' - CH_2), 1.24-1.32 (m, 6H, $-\text{CH}_2-$);

$^3\text{J}_{1,2/1',2'} = 10.2$, $^3\text{J}_{2,3/2',3'} = 9.7$, $^3\text{J}_{3,4/3',4'} = 9.7$, $^3\text{J}_{4,5/4',5'} = 9.7$, $^3\text{J}_{5,6a/5',6a'} = 4.6$, $^3\text{J}_{5,6b/5',6b'} = 2.5$, $^2\text{J}_{6a,6b/6a',6b'} = 12.2$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 + TMS): δ = 170.63, 170.20, 169.42, 169.39 (C=O, OAc), 83.63 (C-1), 75.88 (C-5), 73.93 (C-3), 69.91 (C-2), 68.37 (C-4), 62.21 (C-6), 29.96, 29.60, 29.39, 29.11, 28.79 ($-\text{CH}_2-$), 20.75, 20.63, 20.60 ($-\text{CH}_3$, OAc).

Nonan-1,9-diyl-bis(β -D-thioglucopyranoside) 18

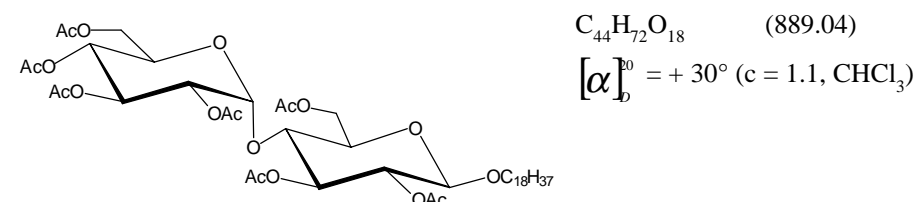


1.8 g (2.1 mmol) nonan-1,9-diyl-bis(2',3',4',6'-tetra-*O*-acetyl- β -D-thioglucopyranoside) **17** were deprotected using the *General procedure 3*. Yield: 1.03 g (95 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.27 (d, 2H, H-1, H-1'), 3.78 (dd, 2H, H-6a, H-6a'), 3.58 (dd, 2H, H-6b, H-6b'), 3.15-3.30 (m, 6H, H-3, H-3', H-4, H-4', H-5, H-5'), 3.11 (dd, 2H, H-2, H-2'), 2.56-2.72 (m, 4H, α - CH_2 , α' - CH_2), 1.56 (m_c, 4H, β - CH_2 , β' - CH_2), 1.34 (m_c, 4H, γ - CH_2 , γ' - CH_2), 1.22 -1.29 (m, 6H, $-\text{CH}_2-$);

$^3\text{J}_{1,2/1',2'} = 9.7$, $^3\text{J}_{5,6b/5',6b'} = 5.1$, $^2\text{J}_{6a,6b/6a',6b'} = 12.2$ Hz.

Stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-glucopyranoside 19



Octa-*O*-acetyl- β -D-maltobiose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.55 g (40 %).

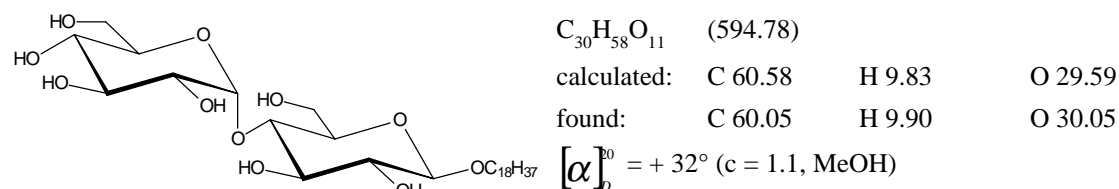
$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.42 (d, 1H, H-1'), 5.36 (dd, 1H, H-3'), 5.25 (dd, 1H, H-3), 5.05 (dd, 1H, H-4'), 4.86 (dd, 1H, H-2'), 4.81 (dd, 1H, H-2), 4.51 (d, 1H, H-1), 4.47 (dd, 1H, H-6a), 4.26 (dd, 1H, H-

6a'), 4.23 (dd, 1H, H-6b), 4.04 (dd, 1H, H-6b'), 4.00 (dd, 1H, H-4), 3.96 (ddd, 1H, H-5'), 3.84 (dt, 1H, H- α), 3.67 (ddd, 1H, H-5), 3.46 (dt, 1H, H- α b), 2.14, 2.10, 2.05, 2.03, 2.01 (each s, 3H, OAc), 2.00 (s, 6H, OAc), 1.50-1.60 (m, 2H, β -CH₂), 1.20-1.34 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 7.6$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 2.5$, $^3J_{5,6b} = 4.6$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 4.1$, $^3J_{2,3'} = 10.2$, $^3J_{3,4'} = 10.2$, $^3J_{4,5'} = 10.2$, $^3J_{5',6a'} = 4.1$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.6$, $^3J_{\alpha b, \beta\text{-CH}_2} = 7.1$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl₃ + TMS): $\delta = 170.54, 170.50, 170.28, 169.97, 169.61, 169.44$ (C=O, OAc), 100.32 (C-1), 95.54 (C-1'), 75.51 (C-3), 72.84 (C-4), 72.27, 72.09 (C-2, C-5), 70.25 (C- α), 70.03 (C-2'), 69.40 (C-3'), 68.51 (C-5'), 68.08 (C-4'), 62.95 (C-6), 61.55 (C-6'), 31.94, 29.71, 29.67, 29.63, 29.41, 29.37, 29.34, 25.84, 22.70 (-CH₂-), 20.94, 20.85, 20.69, 20.64, 20.62, 20.59 (-CH₃, OAc), 14.13 (-CH₃).

Stearyl-4-*O*-(α -D-glucopyranosyl)- β -D-glucopyranoside **20**

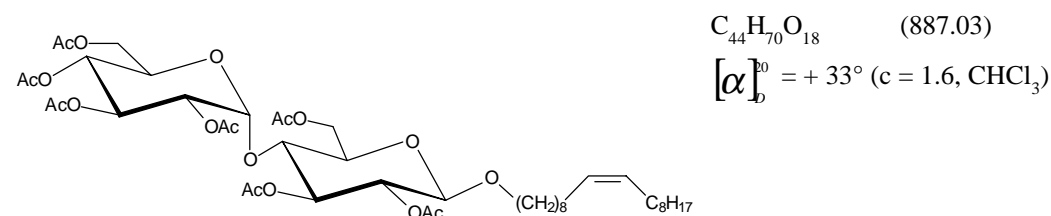


3.0 g (3.37 mmol) stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-glucopyranoside **19** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 1.78 g (89 %).

$^1\text{H-NMR}$ (400 MHz, d₄-MeOH): $\delta = 5.20$ (d, 1H, H-1'), 4.31 (d, 1H, H-1), 3.28-3.99 (m, 12H, H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α , H- α b), 3.48 (dd, 1H, H-2'), 3.26 (dd, 1H, H-2), 1.61-1.71 (m, 2H, β -CH₂), 1.27-1.48 (m, 30H, -CH₂-), 0.95 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{1,2'} = 3.6$, $^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.3$, $^3J_{2,3'} = 9.7$ Hz.

Cis-9-octadecenyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-glucopyranoside **21**



Octa-*O*-acetyl- β -D-maltoside and oleyl alcohol were reacted using *General procedure 2*. Yield: 3.08 g (35 %).

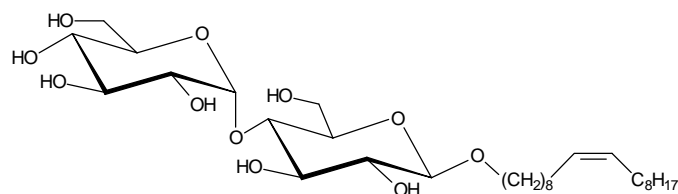
$^1\text{H-NMR}$ (400 MHz, CDCl₃ + TMS): $\delta = 5.42$ (d, 1H, H-1'), 5.36 (dd, 1H, H-3'), 5.29-5.40 (m, 2H, H-olefinic), 5.25 (dd, 1H, H-3), 5.05 (dd, 1H, H-4'), 4.86 (dd, 1H, H-2'), 4.81 (dd, 1H, H-2), 4.51 (d, 1H, H-1), 4.47 (dd, 1H, H-6a), 4.26 (dd, 1H, H-6a'), 4.23 (dd, 1H, H-6b), 4.04 (dd, 1H, H-6b'), 4.00 (dd, 1H, H-4), 3.96 (ddd, 1H,

H-5'), 3.84 (dt, 1H, H- α a), 3.67 (ddd, 1H, H-5), 3.46 (dt, 1H, H- α b), 2.14, 2.10, 2.05, 2.03, 2.01 (each s, 3H, OAc), 2.00 (s, 6H, OAc), 1.93-2.06 (m, 4H, H-allylic), 1.50-1.60 (m, 2H, β -CH₂), 1.20-1.34 (m, 22H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 2.6$, $^3J_{5,6b} = 4.1$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 4.1$, $^3J_{2',3'} = 10.2$, $^3J_{3',4'} = 10.2$, $^3J_{4',5'} = 10.2$, $^3J_{5',6a'} = 4.1$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.6$, $^3J_{\alpha b, \beta\text{-CH}_2} = 7.1$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl₃ + TMS): $\delta = 170.54$, 170.49, 170.27, 169.97, 169.59, 169.43 (C=O, OAc), 129.99, 129.79 (C-olefinic), 100.32 (C-1), 95.54 (C-1'), 75.51 (C-3), 72.84 (C-4), 72.27 (C-2), 72.09 (C-5), 70.23 (C- α), 70.03 (C-2'), 69.39 (C-3'), 68.51 (C-5'), 68.08 (C-4'), 62.95 (C-6), 61.55 (C-6'), 31.91, 29.78, 29.52, 29.40, 29.32, 29.27, 27.22, 25.84, 22.69 (-CH₂-), 20.94, 20.85, 20.68, 20.63, 20.61, 20.58 (-CH₃, OAc), 14.12 (-CH₃).

Cis-9-octadecenyl-4-*O*-(α -D-glucopyranosyl)- β -D-glucopyranoside **22**



C₃₀H₅₆O₁₁ (592.3823)

FAB: m/z = 615.35 (M+Na)

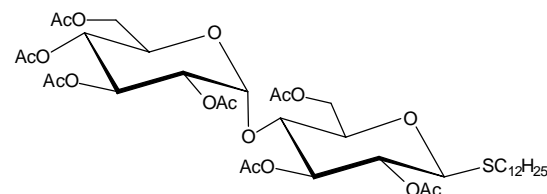
$[\alpha]_D^{20} = +32^\circ$ (c = 0.7, MeOH)

2.30 g (2.59 mmol) *cis*-9-octadecenyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-glucopyranoside **21** were deprotected using the *General procedure 3*. The product was purified via column chromatography using chloroform-methanol 87:13 as eluent and a subsequent gel filtration (Serva LH-20 in methanol). Yield: 1.10 g (72 %).

$^1\text{H-NMR}$ (400 MHz, d₄-MeOH): d = 5.34-5.47 (m, 2H, H-olefinic), 5.20 (d, 1H, H-1'), 4.31 (d, 1H, H-1), 3.28-3.99 (m, 12H, H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α a, H- α b), 3.48 (dd, 1H, H-2'), 3.26 (dd, 1H, H-2), 1.98-2.15 (m, 4H, H-allylic), 1.61-1.71 (m, 2H, β -CH₂), 1.27-1.48 (m, 22H, -CH₂-), 0.95 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{1,2'} = 3.6$, $^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.3$, $^3J_{2',3'} = 9.7$ Hz.

Dodecyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-thioglucopyranoside **23**



C₃₈H₆₀O₁₇S (820.94)

$[\alpha]_D^{20} = +30^\circ$ (c = 1.4, CHCl₃)

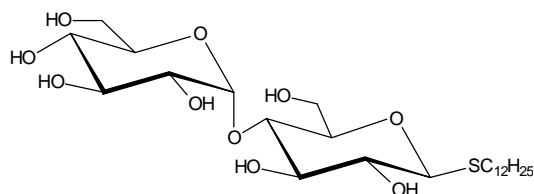
Octa-*O*-acetyl- β -D-maltobiose and dodecane thiol were reacted using *General procedure 2*. Eluent for column chromatography: light petroleum (b.p. 50-70 °C)-ethyl acetate 5:1+ 5 % methanol. The product was recrystallised twice from butanol. Yield: 6.00 g (73 %).

$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 5.41$ (d, 1H, H-1'), 5.36 (dd, 1H, H-3'), 5.28 (dd, 1H, H-3), 5.05 (dd, 1H, H-4'), 4.86 (dd, 1H, H-2), 4.86 (dd, 1H, H-2'), 4.52 (d, 1H, H-1), 4.46 (dd, 1H, H-6a), 4.25 (dd, 1H, H-6a'), 4.22 (dd, 1H, H-6b), 4.05 (dd, 1H, H-6b'), 3.99 (dd, 1H, H-4), 3.95 (ddd, 1H, H-5'), 3.69 (ddd, 1H, H-5), 2.56-2.72 (m, 2H, $\alpha\text{-CH}_2$), 2.14, 2.10, 2.05, 2.04, 2.03, 2.01, 2.00 (each s, 3H, OAc), 1.50-1.62 (m, 2H, $\beta\text{-CH}_2$), 1.18-1.42 (m, 18H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

$^3J_{1,2} = 10.2$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 2.5$, $^3J_{5,6b} = 4.6$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 4.1$, $^3J_{2',3'} = 9.9$, $^3J_{3',4'} = 9.9$, $^3J_{4',5'} = 9.9$, $^3J_{5',6a'} = 4.0$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.53$, 170.42, 170.15, 169.93, 169.65, 169.43 (C=O, OAc), 95.60 (C-1'), 83.27 (C-1), 76.46 (C-3), 76.09 (C-5), 72.74 (C-4), 70.89 (C-2), 69.99 (C-2'), 69.34 (C-3'), 68.55 (C-5'), 68.02 (C-4'), 63.12 (C-6), 61.52 (C-6'), 30.18 (C- α), 31.92, 29.69, 29.66, 29.64, 29.60, 29.54, 29.35, 29.18, 28.80, 22.69 ($-\text{CH}_2-$), 20.94, 20.83, 20.70, 20.60 ($-\text{CH}_3$, OAc), 14.13 ($-\text{CH}_3$).

Dodecyl-4-*O*-(α -D-glucopyranosyl)- β -D-thioglucopyranoside **24**



$\text{C}_{24}\text{H}_{46}\text{O}_{10}\text{S}$ (526.68)

$[\alpha]_D^{20} = +28^\circ$ (c = 1.5, MeOH)

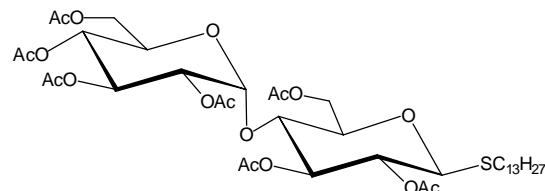
5.56 g (6.77 mmol) dodecyl-2,3,6-tri-*O*-acetyl-4-*O*-

(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-thioglucopyranoside **23** were deprotected using the *General procedure 3*. Yield: 3.56 g (100 %).

$^1\text{H-NMR}$ (400 MHz, $d_4\text{-MeOH}$): $\delta = 5.21$ (d, 1H, H-1'), 4.40 (d, 1H, H-1), 3.24-3.95 (m, 10H, H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b'), 3.48 (dd, 1H, H-2'), 3.40 (dd, 1H, H-2), 2.79 (dt, 1H, H- α a), 2.72 (dt, 1H, H- α b), 1.61-1.73 (m, 2H, $\beta\text{-CH}_2$), 1.24-1.50 (m, 18H, $-\text{CH}_2-$), 0.94 (t, 3H, $-\text{CH}_3$);

$^3J_{1,2} = 9.7$, $^3J_{2,3} = 9.2$, $^3J_{1,2'} = 4.1$, $^3J_{2',3'} = 9.7$, $^2J_{\alpha a, \alpha b} = 12.2$, $^3J_{\alpha a, \beta\text{-CH}_2} = 7.1$, $^3J_{\alpha b, \beta\text{-CH}_2} = 7.6$ Hz.

Tridecyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-thioglucopyranoside **25**



$\text{C}_{39}\text{H}_{62}\text{O}_{17}\text{S}$ (834.97)

$[\alpha]_D^{20} = +30^\circ$ (c = 1.3, CHCl_3)

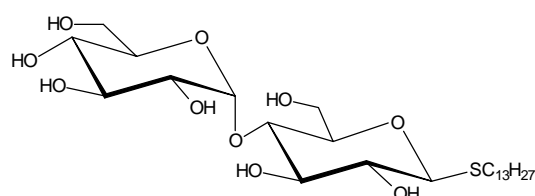
Octa-*O*-acetyl- β -D-maltobiose and tridecane thiol were reacted using *General procedure 2*. Additionally to the usual chromatographic purification according to *General procedure 2*, the product was recrystallised twice from butanol. Yield: 5.16 g (62 %).

$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 5.41$ (d, 1H, H-1'), 5.36 (dd, 1H, H-3'), 5.28 (dd, 1H, H-3), 5.05 (dd, 1H, H-4'), 4.86 (dd, 1H, H-2), 4.86 (dd, 1H, H-2'), 4.52 (d, 1H, H-1), 4.46 (dd, 1H, H-6a), 4.25 (dd, 1H, H-6a'), 4.22 (dd, 1H, H-6b), 4.05 (dd, 1H, H-6b'), 3.99 (dd, 1H, H-4), 3.95 (ddd, 1H, H-5'), 3.69 (ddd, 1H, H-5), 2.56-2.72 (m, 2H, $\alpha\text{-CH}_2$), 2.14, 2.10, 2.05, 2.04, 2.03, 2.01, 2.00 (each s, 3H, OAc), 1.50-1.62 (m, 2H, $\beta\text{-CH}_2$), 1.18-1.42 (m, 20H, $\text{-CH}_2\text{-}$), 0.88 (t, 3H, -CH_3);

$^3J_{1,2} = 10.2$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 2.5$, $^3J_{5,6b} = 4.6$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 4.1$, $^3J_{2,3'} = 9.9$, $^3J_{3,4'} = 9.9$, $^3J_{4,5'} = 9.9$, $^3J_{5',6a'} = 4.0$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.58$, 170.53, 170.43, 170.16, 169.94, 169.66, 169.43 (C=O, OAc), 95.62 (C-1'), 83.29 (C-1), 76.48 (C-3), 76.12 (C-5), 72.80 (C-4), 70.92 (C-2), 70.02 (C-2'), 69.37 (C-3'), 68.57 (C-5'), 68.06 (C-4'), 63.14 (C-6), 61.55 (C-6'), 30.18 (C- α), 31.93, 29.69, 29.66, 29.61, 29.54, 29.36, 29.19, 28.81, 22.70 ($\text{-CH}_2\text{-}$), 20.93, 20.82, 20.69, 20.60 (-CH_3 , OAc), 14.12 (-CH_3).

Tridecyl-4-*O*-(α -D-glucopyranosyl)- β -D-thioglucopyranoside **26**



$\text{C}_{25}\text{H}_{48}\text{O}_{10}\text{S}$ (540.71)

$[\alpha]_D^{20} = +28^\circ$ ($c = 1.7$, MeOH)

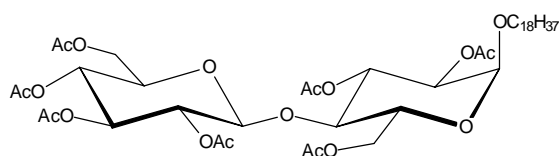
4.77 g (5.71 mmol) tridecyl-2,3,6-tri-*O*-acetyl-4-*O*-

(2',3',4',6'-tetra-*O*-acetyl- α -D-glucopyranosyl)- β -D-thioglucopyranoside **25** were deprotected using the *General procedure 3*. Yield: 2.98 g (97 %).

$^1\text{H-NMR}$ (400 MHz, $d_4\text{-MeOH}$): $\delta = 5.21$ (d, 1H, H-1'), 4.40 (d, 1H, H-1), 3.24-3.95 (m, 10H, H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b'), 3.48 (dd, 1H, H-2'), 3.40 (dd, 1H, H-2), 2.79 (dt, 1H, H- α a), 2.72 (dt, 1H, H- α b), 1.61-1.73 (m, 2H, $\beta\text{-CH}_2$), 1.24-1.50 (m, 20H, $\text{-CH}_2\text{-}$), 0.94 (t, 3H, -CH_3);

$^3J_{1,2} = 9.7$, $^3J_{2,3} = 9.2$, $^3J_{1,2'} = 4.1$, $^3J_{2',3'} = 9.7$, $^2J_{\alpha a, \alpha b} = 12.2$, $^3J_{\alpha a, \beta\text{-CH}_2} = 7.1$, $^3J_{\alpha b, \beta\text{-CH}_2} = 7.6$ Hz.

Stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- α -D-glucopyranoside **27**



$\text{C}_{44}\text{H}_{72}\text{O}_{18}$ (889.04)

$[\alpha]_D^{20} = +39^\circ$ ($c = 1.1$, CHCl_3)

Octa-*O*-acetyl- β -D-cellobiose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.46 g (39 %).

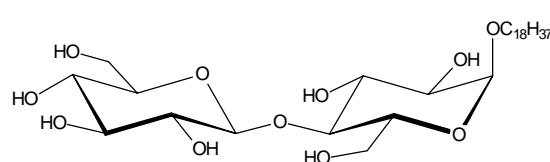
$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 5.45$ (d, 1H, H-3), 5.15 (dd, 1H, H-3'), 5.08 (dd, 1H, H-4'), 4.97 (d,

1H, H-1), 4.93 (dd, 1H, H-2'), 4.77 (dd, 1H, H-2), 4.51 (d, 1H, H-1'), 4.47 (dd, 1H, H-6a), 4.37 (dd, 1H, H-6a'), 4.13 (dd, 1H, H-6b), 4.04 (dd, 1H, H-6b'), 3.92 (dd, 1H, H-5), 3.70 (ddd, 1H, H-4), 3.61-3.69 (m, 2H, H-5', H- α), 3.38 (dt, 1H, H- α b), 2.13, 2.09, 2.04, 2.03, 2.02, 2.01, 1.98 (each s, 3H, OAc), 1.52-1.62 (m, 2H, β -CH₂), 1.18-1.36 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 3.6$, $^3J_{2,3} = 10.2$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 4.9$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 7.6$, $^3J_{2',3'} = 9.6$, $^3J_{3',4'} = 9.6$, $^3J_{4',5'} = 9.6$, $^3J_{5',6a'} = 4.4$, $^3J_{5',6b'} = 2.3$, $^2J_{6a',6b'} = 12.5$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha b, \beta-CH_2} = 7.1$ Hz.

¹³C-NMR (100 MHz, CDCl₃ + TMS): $\delta = 170.52$, 170.42, 170.33, 170.27, 169.58, 169.30, 169.05 (C=O, OAc), 100.88 (C-1'), 95.57 (C-1), 76.89 (C-4), 73.10 (C-3'), 71.96 (C-5'), 71.75 (C-2'), 71.19 (C-2), 69.81 (C-3), 68.74 (C- α), 68.10 (C-5), 67.86 (C-4'), 61.91 (C-6), 61.62 (C-6'), 31.94, 29.72, 29.67, 29.37, 29.26, 26.03, 22.70 (-CH₂-), 20.86, 20.71, 20.67, 20.58, 20.56 (-CH₃, OAc), 14.12 (-CH₃).

Stearyl-4-O-(β -D-glucopyranosyl)- α -D-glucopyranoside **28**



$C_{30}H_{58}O_{11}$ (594.78)

calculated: C 60.58 H 9.83 O 29.59

found: C 60.55 H 9.91 O 29.54

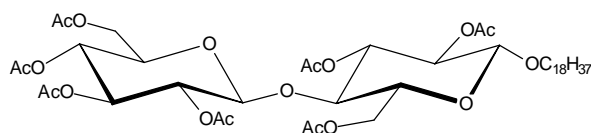
$[\alpha]_D^{20} = +68^\circ$ (c = 0.6, DMSO)

1.60 g (1.79 mmol) stearyl-2,3,6-tri-O-acetyl-4-O-(2',3',4',6'-tetra-O-acetyl- β -D-glucopyranosyl)- α -D-glucopyranoside **27** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 0.90 g (96 %).

¹H-NMR (400 MHz, d₄-MeOH): $\delta = 4.80$ (d, 1H, H-1), 4.43 (d, 1H, H-1'), 3.23-3.96 (m, 14H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α a, H- α b), 1.62-1.73 (m, 2H, β -CH₂), 1.29-1.39 (m, 30H, -CH₂-), 0.94 (t, 3H, -CH₃);

$^3J_{1,2} = 3.6$, $^3J_{1,2'} = 7.6$ Hz.

Stearyl-2,3,6-tri-O-acetyl-4-O-(2',3',4',6'-tetra-O-acetyl- β -D-glucopyranosyl)- β -D-glucopyranoside **29**



$C_{44}H_{72}O_{18}$ (889.04)

$[\alpha]_D^{20} = -19^\circ$ (c = 1.6, CHCl₃)

Octa-O-acetyl- β -D-cellobiose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.55 g (40 %).

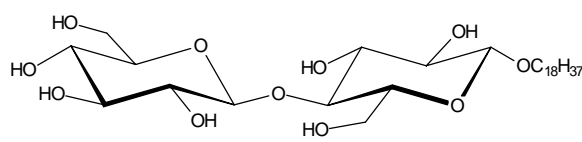
¹H-NMR (400 MHz, CDCl₃ + TMS): $\delta = 5.18$ (d, 1H, H-3), 5.14 (dd, 1H, H-3'), 5.07 (dd, 1H, H-4'), 4.92 (dd, 1H, H-2'), 4.89 (dd, 1H, H-2), 4.50 (d, 1H, H-1'), 4.47-4.54 (dd, 1H, H-6a), 4.44 (d, 1H, H-1), 4.37 (dd, 1H,

H-6a \prime), 4.09 (dd, 1H, H-6b), 4.04 (dd, 1H, H-6b \prime), 3.82 (dt, 1H, H- α), 3.77 (dd, 1H, H-4), 3.65 (ddd, 1H, H-5 \prime), 3.58 (ddd, 1H, H-5), 3.44 (dt, 1H, H- α b), 2.12, 2.09, 2.03, 2.02, 2.01, 2.01, 1.98 (each s, 3H, OAc), 1.47-1.59 (m, 2H, β -CH₂), 1.21-1.32 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 7.6$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 5.1$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 8.1$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 4.6$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha a,\beta\text{-CH}_2} = 6.6$, $^3J_{\alpha b,\beta\text{-CH}_2} = 7.1$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl₃ + TMS): $\delta = 170.50, 170.33, 170.22, 169.85, 169.55, 169.31, 169.05$ (C=O, OAc), 100.80, 100.70 (C-1', C-1), 76.58 (C-4), 72.98 (C-3'), 72.66, 72.58 (C-5, C-3), 71.98 (C-5'), 71.66 (C-2', C-2), 70.26 (C- α), 67.86 (C-4'), 61.97 (C-6), 61.60 (C-6'), 31.93, 29.71, 29.63, 29.41, 29.37, 25.83, 22.70 (-CH₂-), 20.87, 20.67, 20.58, 20.55 (-CH₃, OAc), 14.13 (-CH₃).

Stearyl-4-*O*-(β -D-glucopyranosyl)- β -D-glucopyranoside **30**



C₃₀H₅₈O₁₁ (594.78)

calculated: C 60.58 H 9.83 O 29.59

found: C 60.55 H 9.96 O 29.49

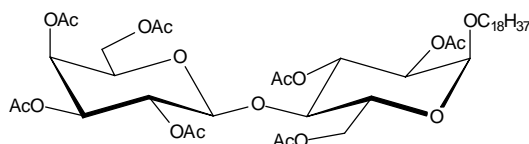
$[\alpha]_D^{20} = -7^\circ$ (c = 0.7, DMSO)

3.28 g (3.69 mmol) stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- β -D-glucopyranoside **29** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 2.09 g (95 %).

$^1\text{H-NMR}$ (400 MHz, d₄-MeOH): d = 4.45 (d, 1H, H-1'), 4.32 (d, 1H, H-1), 3.22-3.97 (m, 14H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α , H- α b), 1.61-1.71 (m, 2H, β -CH₂), 1.25-1.45 (m, 30H, -CH₂-), 0.94 (t, 3H, -CH₃);

$^3J_{1,2} = 7.6$, $^3J_{1,2'} = 7.6$ Hz.

Stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-galactopyranosyl)- α -D-glucopyranoside **31**



C₄₄H₇₂O₁₈ (889.04)

$[\alpha]_D^{20} = +45^\circ$ (c = 1.0, CHCl₃)

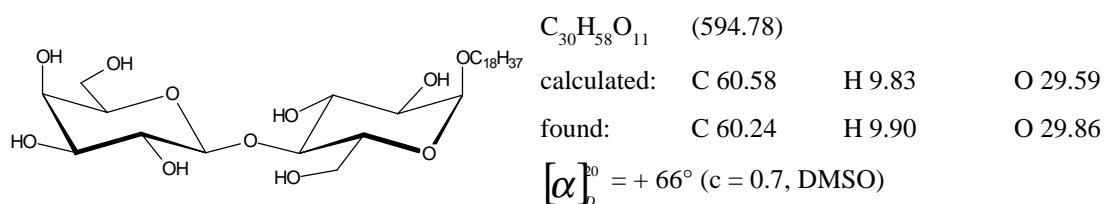
Octa-*O*-acetyl- β -D-lactose and stearyl alcohol were reacted using *General procedure 2*. Yield: 2.43 g (27%).

$^1\text{H-NMR}$ (400 MHz, CDCl₃ + TMS): $\delta = 5.48$ (dd, 1H, H-3), 5.35 (dd, 1H, H-4'), 5.12 (dd, 1H, H-2'), 4.97 (d, 1H, H-1), 4.96 (dd, 1H, H-3'), 4.77 (dd, 1H, H-2), 4.48 (d, 1H, H-1'), 4.44 (dd, 1H, H-6a), 4.04-4.18 (m, 3H, H-6b, H-6a', H-6b'), 3.93 (ddd, 1H, H-5), 3.87 (ddd, 1H, H-5'), 3.73 (dd, 1H, H-4), 3.65 (dt, 1H, H- α a), 3.39 (dt, 1H, H- α b), 2.16, 2.13, 2.06, 2.04, 1.97 (each s, 3H, OAc), 2.05 (s, 3H, OAc), 1.52-1.64 (m, 2H, β -CH₂), 1.18-1.36 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 4.1$, $^3J_{2,3} = 10.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 4.6$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 8.1$, $^3J_{2',3'} = 10.5$,
 $^3J_{3',4'} = 3.6$, $^3J_{4',5'} = 1.5$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.6$, $^3J_{\alpha b, \beta\text{-CH}_2} = 6.6$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.45$, 170.40, 170.35, 170.19, 170.11, 169.51, 169.06 (C=O, OAc), 101.19 (C-1'), 95.57 (C-1), 76.67 (C-4), 71.26 (C-2), 71.13 (C-3'), 70.66 (C-5'), 70.09 (C-3), 69.21 (C-2'), 68.74 (C- α), 68.06 (C-5), 66.65 (C-4'), 62.03 (C-6), 60.83 (C-6'), 31.94, 29.71, 29.67, 29.37, 29.24, 26.02, 22.70 (-CH₂-), 20.94, 20.87, 20.72, 20.66, 20.52 (-CH₃, OAc), 14.13 (-CH₃).

Stearyl-4-*O*-(β -D-galactopyranosyl)- α -D-glucopyranoside **32**

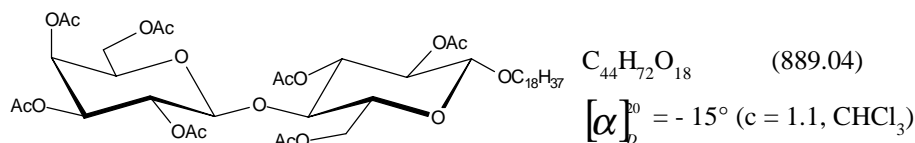


1.49 g (1.67 mmol) stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-galactopyranosyl)- α -D-glucopyranoside **31** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 0.96 g (96 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): $\delta = 4.80$ (d, 1H, H-1), 4.39 (d, 1H, H-1'), 3.45-3.94 (m, 14H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α , H- α b), 1.61-1.74 (m, 2H, β -CH₂), 1.27-1.47 (m, 30 H, -CH₂-), 0.93 (t, 3H, -CH₃);

$^3J_{1,2} = 3.6$, $^3J_{1,2'} = 7.6$ Hz.

Stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-galactopyranosyl)- β -D-glucopyranoside **33**



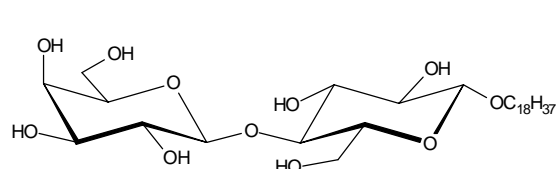
Octa-*O*-acetyl- β -D-lactose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.11 g (35%).

$^1\text{H-NMR}$ (400 MHz, C_6D_6): $\delta = 5.54$ (dd, 1H, H-2'), 5.47 (dd, 1H, H-4'), 5.41 (dd, 1H, H-3), 5.26 (dd, 1H, H-2), 5.10 (dd, 1H, H-3'), 4.52 (dd, 1H, H-6a), 4.31 (d, 1H, H-1'), 4.22 (d, 1H, H-1), 4.14 (dd, 1H, H-6b), 4.05-4.12 (m, 2H, H-6a', H-6b'), 3.81 (dt, 1H, H- α a), 3.63 (dd, 1H, H-4), 3.43 (ddd, 1H, H-5'), 3.34 (dt, 1H, H- α b), 3.20 (ddd, 1H, H-5), 1.97, 1.93, 1.84, 1.73, 1.70, 1.64, 1.54 (each s, 3H, OAc), 1.46-1.54 (m, 2H, β -CH₂), 1.20-1.37 (m, 30H, -CH₂-), 0.91 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 6.1$, $^2J_{6a,6b} = 12.2$, $^3J_{1,2'} = 8.1$, $^3J_{2',3'} = 10.4$,
 $^3J_{3',4'} = 3.6$, $^3J_{4',5'} = 1.0$, $^3J_{5',6a'} = 6.9$, $^3J_{5',6b'} = 6.6$, $^2J_{\alpha a, \alpha b} = 9.6$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.1$, $^3J_{\alpha b, \beta\text{-CH}_2} = 6.6$ Hz.

^{13}C -NMR (125 MHz, C_6D_6): δ = 170.24, 170.14, 169.97, 169.90, 169.58, 169.41, 169.15 (C=O, OAc), 101.85 (C-1'), 100.96 (C-1), 77.44 (C-4), 73.99 (C-3), 72.99 (C-5), 72.62 (C-2), 71.73 (C-3'), 71.01 (C-5'), 70.05 (C- α), 69.91 (C-2'), 67.10 (C-4'), 62.91 (C-6), 61.08 (C-6'), 32.48, 30.35, 30.27, 30.25, 30.08, 29.97, 29.91, 26.46, 23.26 ($-\text{CH}_2-$), 20.99, 20.65, 20.63, 20.50, 20.36, 20.27, 19.96 ($-\text{CH}_3$, OAc), 14.51 ($-\text{CH}_3$).

Stearyl-4-*O*-(β -D-galactopyranosyl)- β -D-glucopyranoside **34**



$\text{C}_{30}\text{H}_{58}\text{O}_{11}$ (594.78)

calculated: C 60.58 H 9.83 O 29.59

found: C 60.34 H 9.87 O 29.79

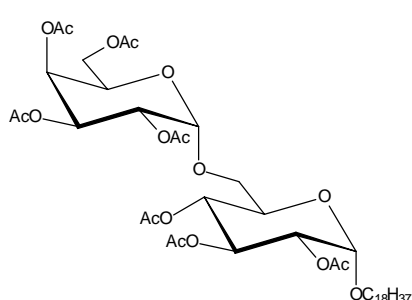
$[\alpha]_D^{20} = -6$ ($c = 0.3$, DMSO)

2.5 g (2.81 mmol) stearyl-2,3,6-tri-*O*-acetyl-4-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-galactopyranosyl)- β -D-glucopyranoside **33** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 1.57 g (94 %).

^1H -NMR (400 MHz, d_4 -MeOH): δ = 4.40 (d, 1H, H-1'), 4.32 (d, 1H, H-1), 3.25-3.97 (m, 14H, H-2, H-2', H-3, H-3', H-4, H-4', H-5, H-5', H-6a, H-6a', H-6b, H-6b', H- α , H- α b), 1.61-1.71 (m, 2H, β - CH_2), 1.27-1.46 (m, 30 H, $-\text{CH}_2-$), 0.94 (t, 3H, $-\text{CH}_3$);

$^3J_{1,2} = 7.6$, $^3J_{1,2'} = 8.1$ Hz.

Stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- α -D-glucopyranoside **35**



$\text{C}_{44}\text{H}_{72}\text{O}_{18}$ (889.04)

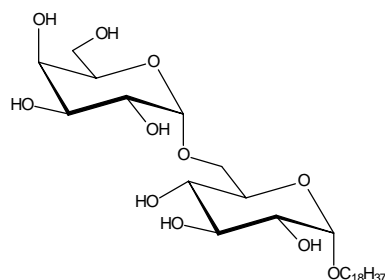
$[\alpha]_D^{20} = +115^\circ$ ($c = 1.2$, CHCl_3)

3.39 g (5 mmol) octa-*O*-acetyl- β -D-melibiose and 2.03 g (7.5 mmol) stearyl alcohol were reacted using *General procedure 2*. Yield: 1.86 g (42%).

^1H -NMR (500 MHz, CDCl_3 + TMS): δ = 5.48 (dd, 1H, H-3), 5.46 (dd, 1H, H-4'), 5.33 (dd, 1H, H-3'), 5.18 (d, 1H, H-1'), 5.11 (dd, 1H, H-2'), 5.03 (dd, 1H, H-4), 5.01 (d, 1H, H-1), 4.79 (dd, 1H, H-2), 4.25 (ddd, 1H, H-5'), 4.11 (dd, 1H, H-6a'), 4.05 (dd, 1H, H-6b'), 3.98 (ddd, 1H, H-5), 3.72 (dd, 1H, H-6a), 3.69 (dt, 1H, H- α a), 3.53 (dd, 1H, H-6b), 3.41 (dt, 1H, H- α b), 2.14, 2.12, 2.06, 2.05, 2.04, 2.01, 1.98 each (s, 3H, OAc), 1.54-1.64 (m, 2H, β - CH_2), 1.22-1.38 (m, 30H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

$^3J_{1,2} = 3.5$, $^3J_{2,3} = 10.1$, $^3J_{3,4} = 9.8$, $^3J_{4,5} = 10.1$, $^3J_{5,6a} = 5.4$, $^3J_{5,6b} = 2.2$, $^2J_{6a,6b} = 11.3$, $^3J_{1',2'} = 3.5$, $^3J_{2',3'} = 10.7$, $^3J_{3',4'} = 3.5$, $^3J_{4',5'} = 1.0$, $^3J_{5',6a'} = 6.0$, $^3J_{5',6b'} = 6.9$, $^2J_{6a',6b'} = 11.4$, $^2J_{\alpha a,\alpha b} = 9.8$, $^3J_{\alpha a,\beta-CH_2} = 6.5$, $^3J_{\alpha b,\beta-CH_2} = 6.6$ Hz.
 ^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): $\delta = 170.55$, 170.42 , 170.23 , 170.19 , 169.82 , 169.58 (C=O, OAc), 96.18 (C-1'), 95.34 (C-1), 71.05 (C-2), 70.39 (C-3), 69.21 (C-4), 68.61 (C- α), 68.16 , 68.11 , 68.09 (C-5,C-4', C-2'), 67.52 (C-3'), 66.41 (C-5'), 66.03 (C-6), 61.81 (C-6'), 31.93 , 29.72 , 29.68 , 29.43 , 29.37 , 29.28 , 26.08 , 22.70 ($-CH_2-$), 20.79 , 20.72 , 20.70 , 20.68 , 20.64 ($-CH_3$, OAc), 14.12 ($-CH_3$).

Stearyl-6-*O*-(α -D-galactopyranosyl)- α -D-glucopyranoside **36**



$C_{30}H_{58}O_{11}$ (594.78)

calculated: C 60.58 H 9.83 O 29.59

found: C 60.56 H 9.95 O 29.49

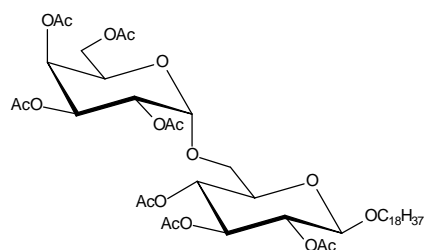
$[\alpha]_D^{20} = +128^\circ$ (c = 0.8, DMSO)

1.22 g (1.37 mmol) stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- α -D-glucopyranoside **35** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 0.77 g (94 %).

1H -NMR (400 MHz, d_4 -MeOH): $\delta = 4.91$ (d, 1H, H-1'), 4.82 (d, 1H, H-1), 3.99 (dd, 1H, H-6a), 3.91 - 3.98 (m, 2H, H-4', H-5'), 3.71 - 3.83 (m, 7H, H-2', H-3', H-6a', H-6b', H-5, H-6b, H- α a), 3.68 (dd, 1H, H-3), 3.49 (dt, 1H, H- α b), 3.45 (dd, 1H, H-2), 3.43 (dd, 1H, H-4), 1.61 - 1.75 (m, 2H, β - CH_2), 1.26 - 1.51 (m, 30H, $-CH_2-$), 0.94 (t, 3H, $-CH_3$);

$^3J_{1,2} = 4.1$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 4.1$, $^2J_{6a,6b} = 10.2$, $^3J_{1',2'} = 3.1$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha b,\beta-CH_2} = 6.6$ Hz.

Stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- β -D-glucopyranoside **37**



$C_{44}H_{72}O_{18}$ (889.04)

$[\alpha]_D^{20} = +52^\circ$ (c = 1.1, $CHCl_3$)

3.39 g (5 mmol) octa-*O*-acetyl- β -D-melibiose and 2.03 g (7.5 mmol) stearyl alcohol were reacted using *General procedure 2*. Yield: 1.77 g (40 %).

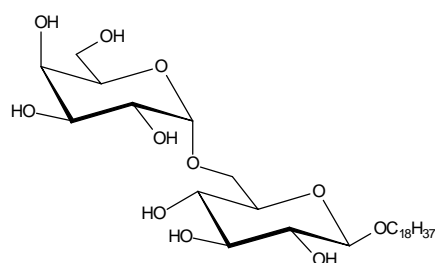
1H -NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 5.45$ (dd, 1H, H-4'), 5.35 (dd, 1H, H-3'), 5.21 (dd, 1H, H-3), 5.16 (d, 1H, H-1'), 5.11 (dd, 1H, H-2'), 5.07 (dd, 1H, H-4), 4.93 (d, 1H, H-2), 4.48 (d, 1H, H-1), 4.25 (ddd, 1H, H-5'),

4.11 (dd, 1H, H-6a'), 4.06 (dd, 1H, H-6b'), 3.83 (dt, 1H, H- α a), 3.76 (dd, 1H, H-6a), 3.65 (ddd, 1H, H-5), 3.58 (dd, 1H, H-6b), 3.45 (dt, 1H, H- α b), 2.13, 2.12, 2.05, 2.04, 2.03, 2.00, 1.98 (each s, 3H, OAc), 1.48-1.60 (m, 2H, β -CH₂), 1.19-1.34 (m, 30H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{5,6a} = 5.1$, $^3J_{5,6b} = 2.5$, $^2J_{6a,6b} = 11.2$, $^3J_{1,2'} = 3.6$, $^3J_{2',3'} = 10.7$, $^3J_{3',4'} = 3.1$, $^3J_{4',5'} = 1.0$, $^3J_{5',6a'} = 5.6$, $^3J_{5',6b'} = 6.6$, $^2J_{6a',6b'} = 11.2$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha a,\beta\text{-CH}_2} = 6.1$, $^3J_{\alpha b,\beta\text{-CH}_2} = 6.6$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl₃ + TMS): $\delta = 170.56, 170.35, 170.21, 169.87, 169.36, 169.31$ (C=O, OAc), 100.56 (C-1), 96.47 (C-1'), 72.93 (C-3), 72.66 (C-5), 71.38 (C-2), 70.02 (C- α), 69.08 (C-4), 68.09, 68.02 (C-4', C-2'), 67.47 (C-3'), 66.48 (C-5'), 66.45 (C-6), 61.67 (C-6'), 31.94, 29.72, 29.66, 29.44, 29.40, 29.37, 25.90, 22.70 (-CH₂-), 20.80, 20.71, 20.67, 20.65 (-CH₃, OAc), 14.13 (-CH₃).

Stearyl-6-*O*-(α -D-galactopyranosyl)- β -D-glucopyranoside **38**



$\text{C}_{30}\text{H}_{58}\text{O}_{11}$ (594.78)

calculated: C 60.58 H 9.83 O 29.59

found: C 60.47 H 9.94 O 29.59

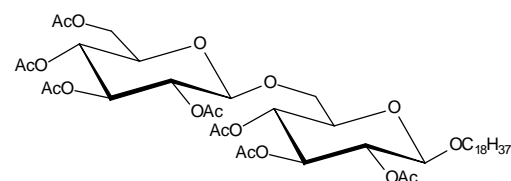
$[\alpha]_D^{20} = +57^\circ$ (c = 0.8, DMSO)

1.40 g (1.57 mmol) stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- β -D-glucopyranoside **37** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 0.87 g (93 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): d = 4.90 (d, 1H, H-1'), 4.32 (d, 1H, H-1), 4.03 (dd, 1H, H-6a), 3.91-3.96 (m, 2H, H-4', H-5'), 3.90 (dt, 1H, H- α a), 3.70-3.81 (m, 5H, H-2', H-3', H-6a', H-6b', H-6b), 3.60 (dt, 1H, H- α b), 3.51 (ddd, 1H, H-5), 3.44 (dd, 1H, H-4), 3.39 (dd, 1H, H-3), 3.23 (dd, 1H, H-2), 1.63-1.72 (m, 2H, β -CH₂), 1.28-1.46 (m, 30H, -CH₂-), 0.95 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 4.1$, $^3J_{5,6b} = 2.0$, $^2J_{6a,6b} = 11.2$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha a,\beta\text{-CH}_2} = 7.1$, $^3J_{\alpha b,\beta\text{-CH}_2} = 6.6$ Hz.

Stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- β -D-glucopyranoside **39**



$\text{C}_{44}\text{H}_{72}\text{O}_{18}$ (889.04)

$[\alpha]_D^{20} = -18^\circ$ (c = 1.7, CHCl₃)

Octa-*O*-acetyl- β -D-gentiobiose and stearyl alcohol were reacted using *General procedure 2*. Yield: 3.74 g

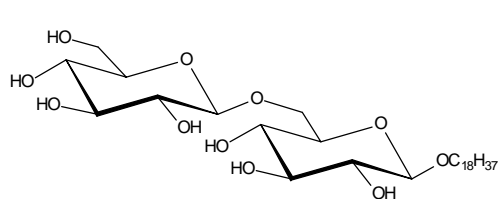
(42%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.19 (dd, 1H, H-3), 5.18 (dd, 1H, H-3'), 5.07 (dd, 1H, H-4'), 4.99 (dd, 1H, H-2'), 4.94 (dd, 1H, H-2), 4.88 (dd, 1H, H-4), 4.60 (d, 1H, H-1'), 4.45 (d, 1H, H-1), 4.28 (dd, 1H, H-6a'), 4.12 (dd, 1H, H-6b'), 3.82-3.91 (m, 2H, H-6a, H- α a), 3.58-3.71 (m, 3H, H-5, H-5', H-6b), 3.46 (dt, 1H, H- α b), 2.09, 2.04, 2.03, 2.03, 2.02, 2.00, 1.99 (each s, 3H, OAc), 1.49-1.62 (m, 2H, β - CH_2), 1.22-1.32 (m, 30H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

$^3\text{J}_{1,2} = 8.1$, $^3\text{J}_{2,3} = 9.7$, $^3\text{J}_{3,4} = 9.7$, $^3\text{J}_{4,5} = 9.7$, $^3\text{J}_{1,2'} = 8.1$, $^3\text{J}_{2',3'} = 9.7$, $^3\text{J}_{3',4'} = 9.7$, $^3\text{J}_{4',5'} = 9.7$, $^3\text{J}_{5',6a'} = 4.6$, $^3\text{J}_{5',6b'} = 2.0$, $^2\text{J}_{6a',6b'} = 12.2$, $^2\text{J}_{\alpha a,\alpha b} = 9.7$, $^3\text{J}_{\alpha b,\beta-\text{CH}_2} = 6.7$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 170.61, 170.25, 170.19, 169.65, 169.41, 169.29, 169.22 (C=O, OAc), 100.81 (C-1'), 100.60 (C-1), 73.37 (C-5), 72.84, 72.81 (C-3', C-3), 71.99 (C-5'), 71.42 (C-2), 71.15 (C-2'), 70.11 (C- α), 69.25 (C-4), 68.38 (C-6), 68.31 (C-4'), 61.84 (C-6'), 31.93, 29.72, 29.67, 29.65, 29.40, 29.37, 25.89, 22.70 ($-\text{CH}_2-$), 20.73, 20.64, 20.59 ($-\text{CH}_3$, OAc), 14.13 ($-\text{CH}_3$).

Stearyl-6-*O*-(β -D-glucopyranosyl)- β -D-glucopyranoside **40**



$\text{C}_{30}\text{H}_{58}\text{O}_{11}$ (594.78)

calculated: C 60.58 H 9.83 O 29.59

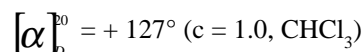
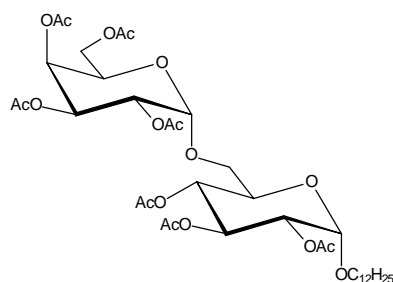
found: C 60.55 H 9.93 O 29.52

$[\alpha]_b^{20} = -32^\circ$ (c = 0.7, DMSO)

3.24 g (3.64 mmol) stearyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- β -D-glucopyranoside **39** were deprotected using the *General procedure 3*. The product was recrystallised from methanol. Yield: 1.91 g (88 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.42 (d, 1H, H-1), 4.30 (d, 1H, H-1'), 4.19 (dd, 1H, H-6a), 3.92 (dt, 1H, H- α a), 3.91 (dd, 1H, H-6a'), 3.83 (dd, 1H, H-6b), 3.71 (dd, 1H, H-6b'), 3.58 (dt, 1H, H- α b), 3.44-3.51 (m, 1H, H-5), 3.16-3.43 (m, 7H, H-2, H-2', H-3, H-3', H-4, H-4', H-5'), 1.61-1.71 (m, 2H, β - CH_2), 1.27-1.47 (m, 30H, $-\text{CH}_2-$), 0.95 (t, 3H, $-\text{CH}_3$);

$^3\text{J}_{1,2} = 7.6$, $^3\text{J}_{5,6a} = 2.0$, $^3\text{J}_{5,6b} = 5.6$, $^2\text{J}_{6a,6b} = 11.2$, $^3\text{J}_{1',2'} = 7.6$, $^3\text{J}_{5',6a'} = 2.0$, $^3\text{J}_{5',6b'} = 5.6$, $^2\text{J}_{6a',6b'} = 12.2$, $^2\text{J}_{\alpha a,\alpha b} = 9.7$, $^3\text{J}_{\alpha a,\beta-\text{CH}_2} = 6.7$, $^3\text{J}_{\alpha b,\beta-\text{CH}_2} = 6.7$ Hz.

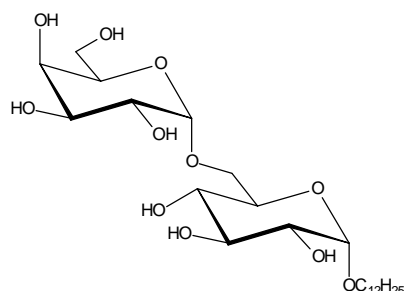
Dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- α -D-glucopyranoside **41**

3.39 g (5 mmol) octa-*O*-acetyl- β -D-melibiose and 2.03 g (7.5 mmol) dodecyl alcohol were reacted using *General procedure 2*. Yield: 1.60 g (40 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 5.48 (dd, 1H, H-3), 5.46 (dd, 1H, H-4'), 5.33 (dd, 1H, H-3'), 5.18 (d, 1H, H-1'), 5.11 (dd, 1H, H-2'), 5.03 (dd, 1H, H-4), 5.01 (d, 1H, H-1), 4.79 (dd, 1H, H-2), 4.25 (ddd, 1H, H-5'), 4.11 (dd, 1H, H-6a'), 4.05 (dd, 1H, H-6b'), 3.98 (ddd, 1H, H-5), 3.72 (dd, 1H, H-6a), 3.69 (dt, 1H, H- α), 3.53 (dd, 1H, H-6b), 3.41 (dt, 1H, H- α b), 2.14, 2.12, 2.06, 2.05, 2.04, 2.01, 1.98 each (s, 3H, OAc), 1.54-1.64 (m, 2H, β - CH_2), 1.22-1.38 (m, 18H, $-\text{CH}_2-$), 0.88 (t, 3H, $-\text{CH}_3$);

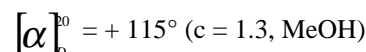
$^3\text{J}_{1,2} = 3.5$, $^3\text{J}_{2,3} = 10.1$, $^3\text{J}_{3,4} = 9.8$, $^3\text{J}_{4,5} = 10.1$, $^3\text{J}_{5,6a} = 5.4$, $^3\text{J}_{5,6b} = 2.2$, $^2\text{J}_{6a,6b} = 11.3$, $^3\text{J}_{1',2'} = 3.5$, $^3\text{J}_{2',3'} = 11.0$, $^3\text{J}_{3',4'} = 3.5$, $^3\text{J}_{4',5'} = 1.0$, $^3\text{J}_{5',6a'} = 6.0$, $^3\text{J}_{5',6b'} = 6.9$, $^2\text{J}_{6a',6b'} = 11.2$, $^2\text{J}_{\alpha,\alpha b} = 9.8$, $^3\text{J}_{\alpha,\beta-\text{CH}_2} = 6.5$, $^3\text{J}_{\alpha b,\beta-\text{CH}_2} = 6.6$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 170.54, 170.42, 170.23, 170.19, 169.82, 169.58 (C=O, OAc), 96.17 (C-1'), 95.34 (C-1), 71.05 (C-2), 70.39 (C-3), 69.21 (C-4), 68.61 (C- α), 68.16, 68.09 (C-5, C-4', C-2'), 67.52 (C-3'), 66.41 (C-5'), 66.03 (C-6), 61.81 (C-6'), 31.92, 29.71, 29.66, 29.41, 29.36, 29.28, 26.07, 22.69 ($-\text{CH}_2-$), 20.79, 20.72, 20.70, 20.68, 20.64 ($-\text{CH}_3$, OAc), 14.12 ($-\text{CH}_3$).

Dodecyl-6-*O*-(α -D-galactopyranosyl)- α -D-glucopyranoside **42**

calculated: C 56.45 H 9.08 O 34.47

found: C 56.63 H 9.23 O 34.14



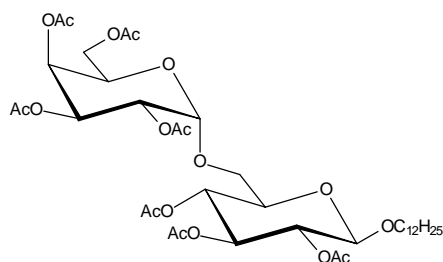
1.23 g (1.53 mmol) dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- α -D-galactopyranosyl)- α -D-glucopyranoside **41** were deprotected using the *General procedure 3*. Yield: 0.75 g (96 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.91 (d, 1H, H-1'), 4.82 (d, 1H, H-1), 3.99 (dd, 1H, H-6a), 3.91-3.98 (m, 2H, H-4', H-5'), 3.71-3.83 (m, 7H, H-2', H-3', H-6a', H-6b', H-5, H-6b, H- α a), 3.68 (dd, 1H, H-3), 3.49 (dt, 1H, H- α b), 3.45 (dd, 1H, H-2), 3.43 (dd, 1H, H-4), 1.61-1.75 (m, 2H, β - CH_2), 1.28-1.48 (m, 18H, $-\text{CH}_2-$), 0.94

(t, 3H, -CH₃);

³J_{1,2} = 4.1, ³J_{2,3} = 9.2, ³J_{3,4} = 9.2, ³J_{4,5} = 9.2, ³J_{5,6a} = 4.1, ²J_{6a,6b} = 10.7, ³J_{1',2'} = 3.1, ²J_{αa,αb} = 9.7, ³J_{αb,β-CH₂} = 6.6 Hz.

Dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-glucopyranoside 43



C₃₈H₆₀O₁₈ (804.88)

[α]_D²⁰ = +47° (c = 1.1, CHCl₃)

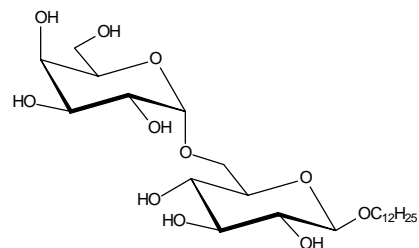
3.39 g (5 mmol) octa-*O*-acetyl-β-D-melibiose and 2.03 g (7.5 mmol) dodecyl alcohol were reacted using *General procedure 2*. Yield: 1.52 g (38 %).

¹H-NMR (400 MHz, CDCl₃ + TMS): δ = 5.45 (dd, 1H, H-4'), 5.35 (dd, 1H, H-3'), 5.21 (dd, 1H, H-3), 5.16 (d, 1H, H-1'), 5.11 (dd, 1H, H-2'), 5.07 (dd, 1H, H-4), 4.93 (d, 1H, H-2), 4.48 (d, 1H, H-1), 4.25 (ddd, 1H, H-5'), 4.11 (dd, 1H, H-6a'), 4.06 (dd, 1H, H-6b'), 3.83 (dt, 1H, H-αa), 3.76 (dd, 1H, H-6a), 3.65 (ddd, 1H, H-5), 3.58 (dd, 1H, H-6b), 3.45 (dt, 1H, H-αb), 2.13, 2.12, 2.05, 2.04, 2.03, 2.00, 1.98 (each s, 3H, OAc), 1.48-1.60 (m, 2H, β-CH₂), 1.19-1.34 (m, 18H, -CH₂-), 0.88 (t, 3H, -CH₃);

³J_{1,2} = 8.1, ³J_{2,3} = 9.7, ³J_{3,4} = 9.7, ³J_{4,5} = 9.7, ³J_{5,6a} = 5.1, ³J_{5,6b} = 2.5, ²J_{6a,6b} = 11.2, ³J_{1',2'} = 3.6, ³J_{2',3'} = 10.7, ³J_{3',4'} = 3.1, ³J_{4',5'} = 1.0, ³J_{5',6a'} = 5.6, ³J_{5',6b'} = 6.6, ²J_{6a',6b'} = 11.2, ²J_{αa,αb} = 9.7, ³J_{αa,β-CH₂} = 6.1, ³J_{αb,β-CH₂} = 6.6 Hz.

¹³C-NMR (125 MHz, CDCl₃ + TMS): δ = 170.56, 170.35, 170.21, 169.87, 169.36, 169.31 (C=O, OAc), 100.56 (C-1), 96.47 (C-1'), 72.93 (C-3), 72.66 (C-5), 71.38 (C-2), 70.02 (C-α), 69.08 (C-4), 68.09, 68.02 (C-4', C-2'), 67.47 (C-3'), 66.48 (C-5'), 66.45 (C-6), 61.67 (C-6'), 31.94, 29.72, 29.66, 29.44, 29.40, 29.37, 25.90, 22.70 (-CH₂-), 20.80, 20.71, 20.67, 20.65 (-CH₃, OAc), 14.13 (-CH₃).

Dodecyl-6-*O*-(α-D-galactopyranosyl)-β-D-glucopyranoside 44



C₂₄H₄₆O₁₁ (510.62)

calculated: C 56.45 H 9.08 O 34.47

found: C 56.09 H 9.21 O 34.70

[α]_D²⁰ = +40° (c = 1.2, MeOH)

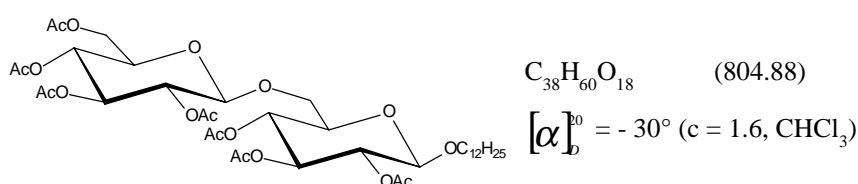
0.77 g (0.96 mmol) dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-

glucopyranoside **43** were deprotected using the *General procedure 3*. Yield: 0.44 g (90 %).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.90 (d, 1H, H-1'), 4.32 (d, 1H, H-1), 4.02 (dd, 1H, H-6a), 3.91-3.96 (m, 2H, H-4', H-5'), 3.89 (dt, 1H, H- α a), 3.70-3.81 (m, 5H, H-2', H-3', H-6a', H-6b', H-6b), 3.59 (dt, 1H, H- α b), 3.51 (ddd, 1H, H-5), 3.44 (dd, 1H, H-4), 3.39 (dd, 1H, H-3), 3.22 (dd, 1H, H-2), 1.61-1.71 (m, 2H, β -CH₂), 1.28-1.46 (m, 30H, -CH₂-), 0.94 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.2$, $^3J_{3,4} = 9.2$, $^3J_{4,5} = 9.2$, $^3J_{5,6a} = 4.1$, $^3J_{5,6b} = 2.0$, $^2J_{6a,6b} = 11.2$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha a,\beta\text{-CH}_2} = 7.1$, $^3J_{\alpha b,\beta\text{-CH}_2} = 6.6$ Hz.

Dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- β -D-glucopyranoside **45**



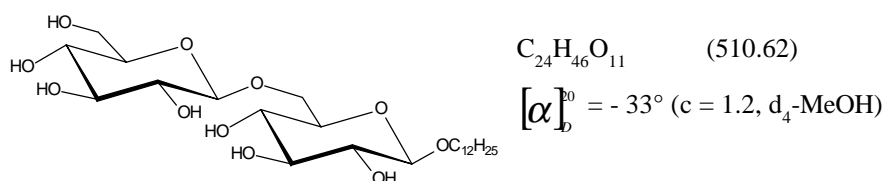
3.39 g (5.0 mmol) octa-*O*-acetyl- β -D-gentiobiose and 2.03 g (7.5 mmol) dodecyl alcohol were reacted using *General procedure 2*. Yield: 1.6 g (40 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.19 (dd, 1H, H-3), 5.18 (dd, 1H, H-3'), 5.07 (dd, 1H, H-4'), 4.99 (dd, 1H, H-2'), 4.94 (dd, 1H, H-2), 4.88 (dd, 1H, H-4), 4.60 (d, 1H, H-1'), 4.45 (d, 1H, H-1), 4.28 (dd, 1H, H-6a'), 4.12 (dd, 1H, H-6b'), 3.82-3.91 (m, 2H, H-6a, H- α a), 3.58-3.71 (m, 3H, H-5, H-5', H-6b), 3.46 (dt, 1H, H- α b), 2.09, 2.04, 2.03, 2.03, 2.02, 2.00, 1.99 (each s, 3H, OAc), 1.49-1.62 (m, 2H, β -CH₂), 1.22-1.32 (m, 18H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3J_{1,2} = 8.1$, $^3J_{2,3} = 9.7$, $^3J_{3,4} = 9.7$, $^3J_{4,5} = 9.7$, $^3J_{1,2'} = 8.1$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4,5'} = 9.7$, $^3J_{5',6a'} = 4.6$, $^3J_{5',6b'} = 2.0$, $^2J_{6a',6b'} = 12.2$, $^2J_{\alpha a,\alpha b} = 9.7$, $^3J_{\alpha b,\beta\text{-CH}_2} = 6.7$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 170.61, 170.25, 170.19, 169.65, 169.41, 169.29, 169.22 (C=O, OAc), 100.81 (C-1'), 100.60 (C-1), 73.37 (C-5), 72.84, 72.81 (C-3', C-3), 71.99 (C-5'), 71.42 (C-2), 71.15 (C-2'), 70.11 (C- α), 69.25 (C-4), 68.38 (C-6), 68.31 (C-4'), 61.84 (C-6'), 31.93, 29.72, 29.67, 29.65, 29.40, 29.37, 25.89, 22.70 (-CH₂-), 20.73, 20.64, 20.59 (-CH₃, OAc), 14.13 (-CH₃).

Dodecyl-6-*O*-(β -D-glucopyranosyl)- β -D-glucopyranoside **46**



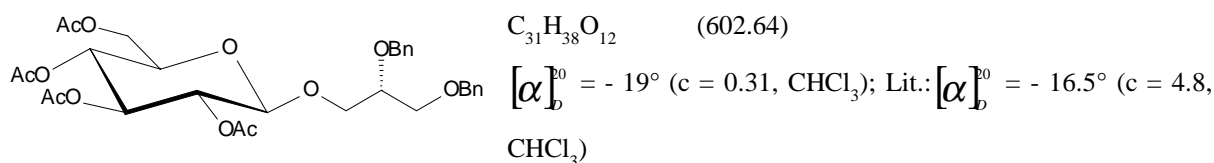
1.1 g (1.37 mmol) dodecyl-2,3,4-tri-*O*-acetyl-6-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)- β -D-

glucopyranoside **45** were deprotected using the *General procedure 3*. Yield: 0.65 g (93%).

$^1\text{H-NMR}$ (400 MHz, d_4 -MeOH): δ = 4.42 (d, 1H, H-1), 4.30 (d, 1H, H-1'), 4.19 (dd, 1H, H-6a), 3.92 (dt, 1H, H- α a), 3.91 (dd, 1H, H-6a'), 3.83 (dd, 1H, H-6b), 3.71 (dd, 1H, H-6b'), 3.58 (dt, 1H, H- α b), 3.44-3.51 (m, 1H, H-5), 3.16-3.43 (m, 7H, H-2, H-2', H-3, H-3', H-4, H-4', H-5'), 1.61-1.71 (m, 2H, β -CH₂), 1.27-1.47 (m, 18H, -CH₂-), 0.95 (t, 3H, -CH₃);

$^3J_{1,2} = 7.6$, $^3J_{5,6a} = 2.0$, $^3J_{5,6b} = 5.6$, $^2J_{6a,6b} = 11.2$, $^3J_{1',2'} = 7.6$, $^3J_{5',6a'} = 2.0$, $^3J_{5',6b'} = 5.6$, $^2J_{6a',6b'} = 12.2$, $^2J_{\alpha a, \alpha b} = 9.7$, $^3J_{\alpha a, \beta\text{-CH}_2} = 6.7$, $^3J_{\alpha b, \beta\text{-CH}_2} = 6.7$ Hz.

1,2-di-*O*-benzyl-3-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)-*sn*-glycerol **61**

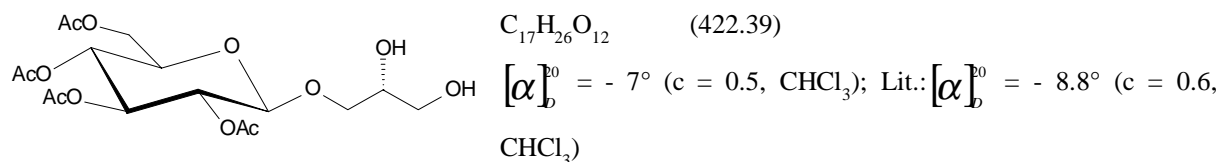


4.11 g (10 mmol) of acetobromo glucose and 2.5 g (9.17 mmol) 1,2-di-*O*-benzyl-*sn*-glycerol were reacted using *General procedure 4*. Yield: 4.40 g (80 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 +TMS): δ = 7.26-7.37 (m, 10H, H-aromatic), 5.18 (dd, 1H, H-3'), 5.08 (dd, 1H, H-4'), 4.99 (dd, 1H, H-2'), 4.65 (m_c, 2H, CH₂-benzylic), 4.56 (d, 1H, CH₂-benzylic), 4.52 (d, 1H, H-1'), 4.51 (d, 1H, CH₂-benzylic), 4.25 (dd, 1H, H-6_a'), 4.11 (dd, 1H, H-6_b'), 3.96 (m, 1H, H-3a), 3.69-3.77 (m, 2H, H-2, H-3b), 3.64 (ddd, 1H, H-5'), 3.59 (dd, 1H, H-1a), 3.56 (dd, 1H, H-1b), 2.06, 2.02, 1.99, 1.94 (each s, 3H, OAc); $^3J_{1',2'} = 7.6$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 4.6$, $^3J_{5',6b'} = 2.5$, $^2J_{6a',6b'} = 12.2$, $^3J_{1a,2} = 4.2$, $^3J_{1b,2} = 5.2$, $^2J_{1a,1b} = 10.6$, $^3J_{3a,2} = 4.3$, $^2J_{3a,3b} = 9.9$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 +TMS): δ = 170.66, 170.26, 169.40, 169.27 (C=O, OAc), 138.49, 138.21, 128.42, 128.36, 127.68, 127.63 (C-aromatic), 101.08 (C-1'), 76.87 (C-2), 73.49 (C-benzylic), 72.83 (C-3), 72.16 (C-benzylic), 71.82 (C-5), 71.34 (C-2), 69.76 (C-1), 69.29 (C-3), 68.45 (C-4), 61.95 (C-6), 20.72, 20.59 (-CH₃, OAc).

3-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)-*sn*-glycerol **62**



A mixture of 4.21 g (6.98 mmol) **61** and 0.4 g Pd/C (10%) in 100 ml ethanol containing 2 ml glacial acetic acid was stirred under one atmosphere of hydrogen until t.l.c. showed the reaction to be complete. The catalyst was removed by filtration, and the mother liquor evaporated *in vacuo*. The resulting residue was purified by

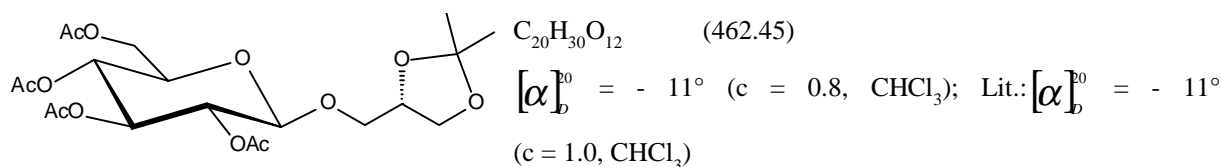
silica gel chromatography (chloroform-methanol 9:1). Yield: 2.92 g (99 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3+TMS): δ = 5.22 (dd, 1H, H-3'), 5.07 (dd, 1H, H-4'), 5.00 (dd, 1H, H-2'), 4.55 (d, 1H, H-1'), 4.22 (dd, 1H, H-6a'), 4.20 (dd, 1H, H-6b'), 3.78-3.88 (m, 3H, H-3a, H-3b, H-2), 3.74 (ddd, 1H, H-5'), 3.69 (dd, 1H, H-1a), 3.60 (dd, 1H, H-1b), 2.00-2.30 (bs, 2H, -OH), 2.10, 2.06, 2.03, 2.01 (each s, 3H, OAc);

$^3J_{1',2'} = 7.9$, $^3J_{2',3'} = 9.8$, $^3J_{3',4'} = 9.8$, $^3J_{4',5'} = 9.8$, $^3J_{5',6a'} = 4.4$, $^3J_{5',6b'} = 3.5$, $^2J_{6a',6b'} = 12.6$, $^3J_{1a,2} = 3.8$, $^3J_{1b,2} = 4.7$, $^2J_{1a,b} = 11.4$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3+TMS): δ = 170.65, 170.19, 169.55, 169.41 (C=O, OAc), 101.46 (C-1'), 72.95 (C-3), 72.54 (C-3'), 72.01 (C-5'), 71.25 (C-2'), 70.43 (C-2), 68.38 (C-4'), 63.38 (C-1), 61.88 (C-6'), 20.71, 20.68, 20.59 (-CH₃, OAc).

1,2-di-*O*-isopropylidene-3-*O*-(2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl)-*sn*-glycerol **72**

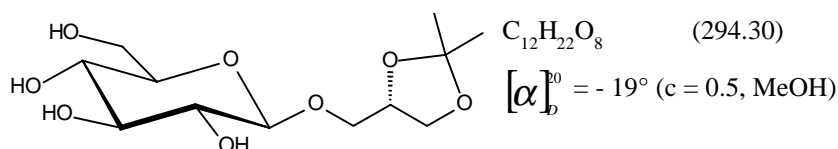


2.85 g (6.75 mmol) **62** were dissolved in 90 ml acetone and 11.3 ml (92.16 mmol) 2,2-dimethoxypropane and 225 mg (1.31 mmol) *p*-toluenesulfonic acid were added. After stirring for 1 hour at room temperature the solution was neutralised with triethylamine and evaporated to dryness. The crude material was redissolved in 170 ml chloroform and washed twice with 100 ml of a saturated solution of NaHCO_3 and once with 100 ml water. The organic phase was dried (MgSO_4), the solvent removed *in vacuo* and the residue recrystallised from diisopropyl ether. Yield: 3.03 g (97 %).

$^1\text{H-NMR}$ (400 MHz, C_6D_6): δ = 5.46 (dd, 1H, H-3'), 5.36 (dd, 1H, H-2'), 5.32 (dd, 1H, H-4'), 4.37 (d, 1H, H-1'), 4.30 (dd, 1H, H-6a'), 4.09 (dd, 1H, H-6b'), 4.04-4.11 (m, 1H, H-2), 3.85 (dd, 1H, H-3a), 3.80 (dd, 1H, H-3b), 3.77 (dd, 1H, H-1a), 3.54 (dd, 1H, H-1b), 3.25 (ddd, 1H, H-5'), 1.85 (s, 3H, OAc), 1.77 (s, 6H, OAc), 1.75 (s, 3H, OAc), 1.49 (s, 3H, -CH₃ ketal), 1.33 (s, 3H, -CH₃ ketal);

$^3J_{1',2'} = 7.6$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 4.5$, $^3J_{5',6b'} = 2.5$, $^2J_{6a',6b'} = 12.2$, $^3J_{1a,2} = 4.1$, $^3J_{1b,2} = 6.1$, $^2J_{1a,1b} = 10.7$, $^3J_{3a,2} = 6.1$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 8.7$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, C_6D_6): δ = 169.05 (C=O, OAc), 109.55 (C-ketal), 101.54 (C-1'), 74.86 (C-2), 73.62 (C-3'), 72.47 (C-5'), 72.02 (C-2'), 69.58 (C-1), 69.01 (C-4'), 66.73 (C-3), 62.00 (C-6'), 27.14, 25.63 (-CH₃, ketal), 20.56, 20.46, 20.38 (-CH₃, OAc).

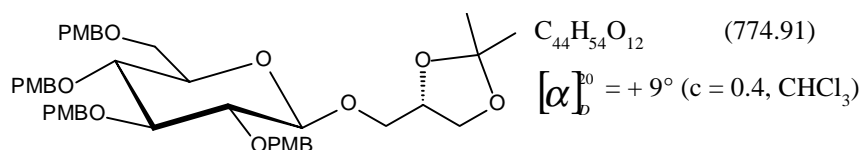
1,2-di-*O*-isopropylidene-3-*O*-(β-D-glucopyranosyl)-*sn*-glycerol 73

2.93 g (6.33 mmol) **72** were deprotected using *General procedure 3*. Yield 1.71 g (92 %).

$^1\text{H-NMR}$ (400 MHz, MeOH): $\delta = 4.37$ (m, 1H, H-2), 4.33 (d, 1H, H-1'), 4.11 (dd, 1H, H-3a), 3.96 (dd, 1H, H-1a), 3.90 (dd, 1H, H-6a'), 3.85 (dd, 1H, H-3b), 3.70 (dd, 1H, H-6b'), 3.64 (dd, 1H, H-1b), 3.36-3.42 (m, 1H, H-3'), 3.29-3.33 (m, 2H, H-5', H-4'), 3.23 (dd, 1H, H-2'), 1.43 (s, 3H, CH₃ ketal), 1.36 (s, 3H, CH₃ ketal);

$^3J_{1',2'} = 7.6$, $^3J_{2',3'} = 9.2$, $^3J_{5',6a'} = 1.5$, $^3J_{5',6b'} = 5.6$, $^2J_{6a',b'} = 11.7$, $^3J_{1a,2} = 5.6$, $^3J_{1b,2} = 6.1$, $^2J_{1a,1b} = 10.7$, $^3J_{3a,2} = 6.1$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 8.7$ Hz.

$^{13}\text{C-NMR}$ (400 MHz, MeOH): $\delta = 110.94$ (C-ketal), 105.10 (C-1'), 78.39, 71.99 (C-3', C-4', C-5'), 76.37 (C-2), 75.43 (C-2'), 71.82 (C-6'), 68.12 (C-3), 63.13 (C-1), 27.45 (CH₃ ketal), 25.99 (CH₃ ketal).

1,2-di-*O*-isopropylidene-3-*O*-[2',3',4',6'-tetra-*O*-(4''-methoxybenzyl)-β-D-glucopyranosyl]-*sn*-glycerol 74

1.61 g (5.47 mmol) **73** were dissolved under nitrogen in 50 ml dry N,N-dimethylformamide. The solution was cooled in an ice-water bath and 1.05 g (43.8 mmol) NaH were added portionwise at 0 °C. The mixture was subsequently brought to ambient temperature, 5.9 ml (43.8 mmol) *p*-methoxybenzylchloride were added dropwise and the resulting mixture was stirred at ambient temperature overnight. Methanol was added carefully to destroy excess NaH and the solvent was evaporated *in vacuo*. The residue was dissolved in 150 ml ethyl acetate, washed twice with 50 ml of a saturated solution of NaHCO₃ and once with 50 ml water. The organic layer was dried (MgSO₄) and evaporated to dryness. The residue was purified by column chromatography (petroleum ether [50/70]-ethyl acetate 2:1). Yield 2.15 g (51 %).

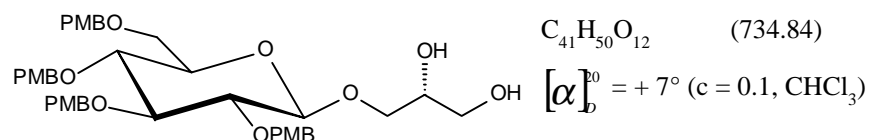
$^1\text{H-NMR}$ (500 MHz, C₆D₆): $\delta = 7.43$, 7.37, 7.28, 7.23 (each d, 2H, H aromatic), 6.80-6.88 (m, 8H, H aromatic), 5.10, 5.08, 4.94, 4.93, 4.80, 4.63, 4.51, 4.44 (each d, 1H, CH₂-benzylic), 4.42 (d, 1H, H-1'), 4.28 (m, 1H, H-2), 4.04 (dd, 1H, H-3a), 3.93 (m, 2H, H-1a, H-1b), 3.72-3.81 (m, 4H, H-3', H-4', H-6a', H-6b'), 3.66 (m, 1H, H-2'), 3.61 (dd, 1H, H-3b), 3.42-3.48 (m, 1H, H-5'), 3.32-3.37 (m, 12H, OCH₃), 1.48 (s, 3H, CH₃ ketal), 1.34 (s, 3H, CH₃ ketal);

$^3J_{1',2'} = 7.9$, $^3J_{3a,2} = 4.4$, $^3J_{3b,2} = 6.3$, $^2J_{3a,3b} = 10.4$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, C₆D₆): $\delta = 160.04$, 159.99, 132.05, 131.81, 131.68, 131.21 (C_{quaternary} aromatic), 130.29, 129.98, 129.90, 129.86, 114.39, 114.32, 114.29 (C-aromatic), 109.64 (C-ketal), 104.72 (C-1'), 85.12, 78.27 (C-3', C-4'), 82.61 (C-2'), 75.82 (C-5'), 75.57 (C-benzylic), 75.14 (C-2), 74.99, 74.78, 73.54 (C-benzylic),

70.50 (C-3), 69.37 (C-6'), 67.37 (C-1), 55.02 (C methoxy), 27.43, 25.85 (CH₃ ketal).

3-O-[2',3',4',6'-tetra-O-(4''-methoxybenzyl)-β-D-glucopyranosyl]-sn-glycerol **75**



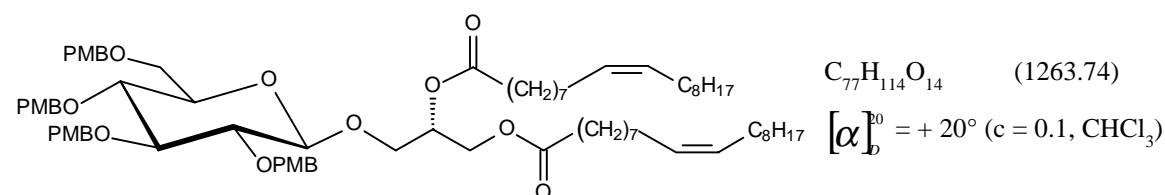
1.64 g (2.12 mmol) **74** were dissolved in 20 ml 70 % acetic acid and stirred for 3 hours at 50 °C. The solvent was evaporated under reduced pressure and the resulting oil was co-evaporated twice with toluene and purified by chromatography on silica gel (chloroform-methanol 98:2). Yield: 967 mg (62 %).

¹H-NMR (400 MHz, C₆D₆): δ = 7.40, 7.38, 7.31, 7.20 (each d, 2H, H aromatic), 6.81-6.89 (m, 8H, H aromatic), 5.07, 4.99, 4.91, 4.89, 4.81, 4.56, 4.46, 4.40 (each d, 1H, CH₂ benzylic), 4.36 (d, 1H, H-1'), 3.88 (m, 1H, H-2), 3.81 (dd, 1H, H-3a), 3.67-3.75 (m, 3H, H-4', H-6a', H-3b), 3.55-3.65 (m, 4H, H-1a, H-2', H-3', H-6b'), 3.45-3.54 (m, 2H, H-1b, H-5'), 3.34-3.36 (m, 12H, OCH₃);

³J_{1,2'} = 7.9, ³J_{3a,2} = 2.8, ²J_{3a,3b} = 11.7 Hz.

¹³C-NMR (125 MHz, C₆D₆): δ = 160.08, 160.02, 159.99, 159.91, 131.81, 131.52, 131.31, 130.70 (C_{quaternary} aromatic), 130.13, 130.06, 129.97, 129.79, 114.32, 114.29, 114.24, 114.22 (C-aromatic), 105.00 (C-1'), 85.00 (C-4'), 82.40, 78.14 (C-2', C-3'), 75.51 (C-benzylic), 75.25 (C-5'), 74.83, 74.73 (C-benzylic), 74.13 (C-3), 73.52 (C-benzylic) 71.72 (C-2), 69.32 (C-6'), 63.86 (C-1), 54.94 (C methoxy).

1,2-di-O-oleoyl-3-O-[2',3',4',6'-tetra-O-(4''-methoxybenzyl)-β-D-glucopyranosyl]-sn-glycerol **76**



930 mg (1.27 mmol) **75** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 3:1). Yield: 1.04g (65 %).

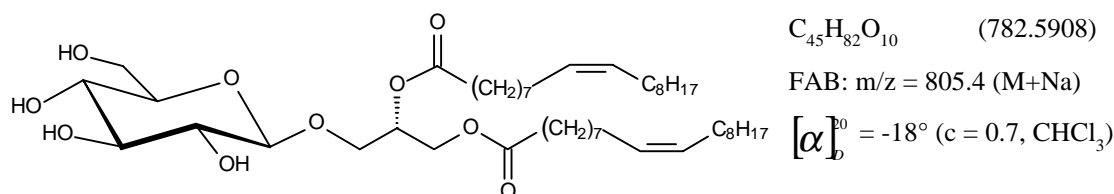
¹H-NMR (400 MHz, C₆D₆): δ = 7.50, 7.38, 7.33, 7.24, 6.91, 6.89, 6.87, 6.83 (each d, 2H, aromatic), 5.51-5.63 (m, 5H, H-olefinic, H-2), 5.14, 5.11, 4.95, 4.94, 4.85, 4.64, 4.55, 4.49 (each d, 1H, CH₂ benzylic), 4.56-4.63 (dd, 1H, H-1a), 4.41 (d, 1H, H-1'), 4.42 (dd, 1H, H-1b), 4.12 (dd, 1H, H-3a), 3.74-3.81 (m, 4H, H-3', H-4', H-6a', H-6b'), 3.64-3.74 (m, 2H, H-2', H-3b), 3.45-3.51 (m, 1H, H-5'), 3.39 (s, 3H, OCH₃), 3.36 (s, 3H, -OCH₃), 3.35 (s, 6H, -OCH₃), 2.19-2.31 (m, 4H, α-CH₂), 2.07-2.19 (m, 8H, H-allylic), 1.59-1.70 (m, 4H, β-CH₂), 1.21-

1.49 (m, 40H, -CH₂-), 0.96 (t, 6H, -CH₃);

³J_{1,2'} = 7.6, ³J_{1a,2} = 5.3, ²J_{1a,1b} = 10.9 Hz.

¹³C-NMR (100 MHz, C₆D₆): δ = 173.33, 172.93 (C=O, oleoyl), 130.50, 130.45, 130.22, 130.10, 130.04, 129.87, 114.43, 114.39, 114.32, 114.30 (C-aromatic, C-olefinic), 105.15 (C-1'), 85.13, 82.50, 78.19 (C-2', C-3', C-4'), 75.61 (C benzylic), 75.55 (C-5'), 74.96, 74.92 (C -benzylic), 73.60 (C-benzylic), 70.23 (C-2), 69.28 (C-6'), 68.30 (C-3), 62.67 (C-1), 55.03 (C methoxy), 34.49, 34.4 (C-α, C-α'), 31.92, 29.78, 29.73, 29.54, 29.35, 29.33, 29.22, 29.15, 29.12, 29.09 (C-alkyl), 27.24, 27.19 (C-allylic), 25.25 (C-β, C-β'), 22.69 (C-alkyl), 14.12 (C-methyl).

1,2-di-O-oleoyl-3-O-(β-D-glucopyranosyl)-sn-glycerol 77



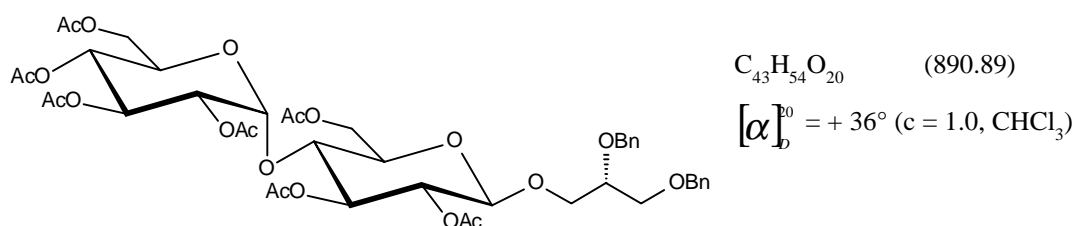
504 mg (0.39 mmol) **76** and 1.93 g (3.51 mmol) ceric ammonium nitrate were dissolved in 20 ml acetonitrile/water 18:1 and stirred for 1 hour at ambient temperature. After completion, the reaction mixture was diluted with 100 ml dichloromethane, washed with 50 ml water, 50 ml sodium hydrogen sulfite, 50 ml sodium hydrogen carbonate and again with water. The organic layer was dried (MgSO₄) and evaporated to dryness. The crude material was purified by silica gel chromatography (chloroform-methanol 98:2) and subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 180 mg (58 %).

¹H-NMR (400 MHz, CDCl₃+TMS+MeOD): δ = 5.31-5.39 (m, 4H, H olefinic), 5.24-5.30 (m, 1H, H-2), 4.37 (dd, 1H, H-1a), 4.30 (d, 1H, H-1'), 4.20 (dd, 1H, H-1b), 3.91 (dd, 1H, H-3a), 3.86 (dd, 1H, H-6a'), 3.77 (dd, 1H, H-6b'), 3.71 (dd, 1H, H-3b), 3.43-3.51 (m, 2H, H-3', H-4'), 3.25-3.36 (m, 2H, H-2', H-5'), 2.29-2.36 (m, 4H, α-CH₂), 1.92-2.08 (m, 8H, H-allylic), 1.56-1.66 (m, 4H, β-CH₂), 1.20-1.38 (m, 40H, -CH₂-), 0.88 (t, 6H, -CH₃);

³J_{1,2'} = 7.6, ³J_{5',6a'} = 3.1, ³J_{5',6b'} = 5.1, ²J_{6a',6b'} = 12.2, ³J_{1a,2} = 3.6, ³J_{1b,2} = 6.6, ²J_{1a,1b} = 11.7, ³J_{3a,2} = 5.1, ³J_{3b,2} = 6.1, ²J_{3a,b} = 10.7 Hz.

¹³C-NMR (100 MHz, CDCl₃+TMS+MeOD): δ = 173.84, 173.61 (C=O, oleoyl), 130.07, 129.72 (C-olefinic), 103.56 (C-1'), 76.17, 70.04 (C-3', C-4'), 75.83, 73.57 (C-2', C-5'), 70.23 (C-2), 68.30 (C-3), 62.67 (C-1), 62.10 (C-6'), 34.31, 34.13 (C αCH₂), 31.93, 29.79, 29.75, 29.55, 29.35, 29.21, 29.16, 29.12, 29.08, 27.25, 27.20, 22.70 (C-alkyl), 24.90, 24.87 (C βCH₂), 14.13 (C methyl).

1,2-di-*O*-benzyl-3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- α -D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl- β -D-glucopyranosyl]-*sn*-glycerol **81**



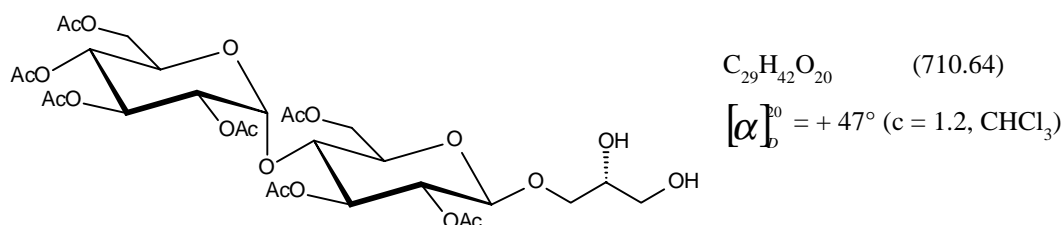
8.40 g (12.02 mmol) of acetobromo maltose and 3.0 g (11.02) mmol 1,2-di-*O*-benzyl-*sn*-glycerol were reacted using *General procedure 4*. Yield: 6.37 g (65 %).

1H -NMR (500 MHz, $CDCl_3$ + TMS): δ = 7.28-7.38 (m, 10H, H-aromatic), 5.40 (d, 1H, H-1'), 5.36 (dd, 1H, H-3'), 5.23 (dd, 1H, H-3'), 5.05 (dd, 1H, H-4'), 4.86 (dd, 1H, H-2'), 4.83 (dd, 1H, H-2'), 4.64 (s, 2H, CH_2 -benzylic), 4.56 (d, 1H, H-1'), 4.55 (d, 1H, CH_2 -benzylic), 4.51 (d, 1H, CH_2 -benzylic), 4.45 (dd, 1H, H-6a), 4.25 (dd, 1H, H-6a'), 4.21 (dd, 1H, H-6b), 4.04 (dd, 1H, H-6b'), 3.99 (dd, 1H, H-4'), 3.94-3.98 (m, 1H, H-5'), 3.93 (dd, 1H, H-3a), 3.73 (m, 1H, H-2), 3.70 (dd, 1H, H-3b), 3.63 (ddd, 1H, H-5'), 3.58 (dd, 1H, H.1a), 3.55 (dd, 1H, H-1b), 2.11, 2.10, 2.05, 2.03, 2.00, 1.99, 1.93 (each s, 3H, OAc);

$^3J_{1',2'} = 7.8$, $^3J_{2',3'} = 9.5$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.5$, $^3J_{5',6a'} = 2.5$, $^3J_{5',6b'} = 4.4$, $^2J_{6a',6b'} = 12.0$, $^3J_{1'',2''} = 4.1$, $^3J_{2'',3''} = 10.6$, $^3J_{3'',4''} = 9.5$, $^3J_{4'',5''} = 10.4$, $^3J_{5'',6a''} = 3.8$, $^3J_{5'',6b''} = 1.9$, $^2J_{6a'',6b''} = 12.6$, $^3J_{1a,2} = 4.4$, $^3J_{1b,2} = 5.7$, $^2J_{1a,1b} = 10.4$, $^3J_{3a,2} = 5.0$, $^3J_{3b,2} = 5.1$, $^2J_{3a,3b} = 10.1$ Hz.

^{13}C -NMR (100 MHz, $CDCl_3$ + TMS): δ = 170.54, 170.46, 170.20, 169.95, 169.60, 169.43 (C=O, OAc), 138.47, 138.18 ($C_{\text{quaternary}}$ aromatic), 128.42, 128.36, 127.69, 127.63 (C-aromatic), 100.52 (C-1'), 95.56 (C-1'), 76.79 (C-2), 75.39 (C-3'), 73.48 (C-benzylic), 72.77 (C-4'), 72.17 (C-2'), 72.12 (C-benzylic), 72.11 (C-5'), 70.02 (C-2'), 69.74 (C-1), 69.36 (C-3'), 69.29 (C-3), 68.50 (C-5'), 68.03 (C-4'), 62.84 (C-6'), 61.51 (C-6'), 20.91, 20.83, 20.69, 20.62, 20.59 ($-CH_3$, OAc).

3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- α -D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl- β -D-glucopyranosyl]-*sn*-glycerol **82**



A mixture of 5.90 g (6.62 mmol) **81** and 0.4 g Pd/C (10%) in 130 ml ethanol containing 20 ml ethyl acetate and 3.5 ml glacial acetic acid was stirred under one atmosphere of hydrogen until t.l.c. showed the reaction to be complete. The catalyst was filtered off, the mother liquor evaporated *in vacuo*, and the resulting residue

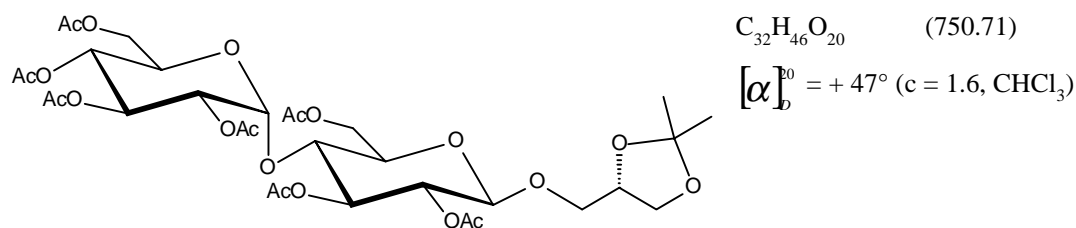
purified by silica gel chromatography (chloroform-methanol 95:5). Yield: 4.35 g (92 %).

$^1\text{H-NMR}$ (500 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 5.41$ (d, 1H, H-1''), 5.36 (dd, 1H, H-3''), 5.27 (dd, 1H, H-3'), 5.05 (dd, 1H, H-4''), 4.86 (dd, 1H, H-2''), 4.84 (dd, 1H, H-2'), 4.57 (d, 1H, H-1'), 4.55-4.61 (m, 1H, H-6a'), 4.26 (dd, 1H, H-6a''), 4.19 (dd, 1H, H-6b'), 4.07 (dd, 1H, H-6b''), 3.98 (dd, 1H, H-4'), 3.94-4.00 (m, 1H, H-5'), 3.76-3.89 (m, 3H, H-2, H-3a, H-3b), 3.72 (ddd, 1H, H-5'), 3.69 (m, 1H, H-1a), 3.58 (dd, 1H, H-1b), 2.15, 2.11, 2.05, 2.04, 2.03, 2.01, 2.00 (each s, 3H, OAc);

$^3J_{1',2'} = 7.6$, $^3J_{2',3'} = 9.4$, $^3J_{3',4'} = 9.4$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 2.7$, $^3J_{5',6b'} = 4.9$, $^2J_{6a',6b'} = 12.2$, $^3J_{1'',2''} = 4.1$, $^3J_{2'',3''} = 10.7$, $^3J_{3'',4''} = 9.7$, $^3J_{4'',5''} = 10.3$, $^3J_{5'',6a''} = 4.1$, $^3J_{5'',6b''} = 2.6$, $^2J_{6a'',6b''} = 12.2$, $^3J_{1b,2} = 4.6$, $^2J_{1a,1b} = 11.2$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.54$, 170.15, 169.96, 169.78, 169.43 (C=O, OAc), 101.02 (C-1'), 95.61 (C-1''), 75.07 (C-3'), 73.02 (C-3), 72.59 (C-4'), 72.40 (C-5'), 72.07 (C-2'), 70.52 (C-2), 70.00 (C-2''), 69.32 (C-3''), 68.60 (C-5''), 68.01 (C-4''), 63.38 (C-1), 62.52 (C-6''), 61.51 (C-6'), 20.89, 20.81, 20.70, 20.66, 20.60, 20.57 (-CH₃, OAc).

1,2-di-*O*-isopropylidene-3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- α -D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl- β -D-glucopyranosyl]-*sn*-glycerol 83



4.25 g (5.98 mmol) **82** were dissolved in 60 ml acetone. 10.0 ml (81.56 mmol) 2,2-dimethoxypropane and 200 mg (1.16 mmol) *p*-toluenesulfonic acid were added and the mixture stirred at ambient temperature. After completion the solution was neutralised with triethylamine and evaporated to dryness. The crude material was redissolved in 150 ml chloroform and washed twice with 100 ml of a saturated solution of NaHCO_3 and once with 100 ml water. The organic layer was dried (MgSO_4) and the solvent evaporated under reduced pressure. Yield: 4.18 g (93 %).

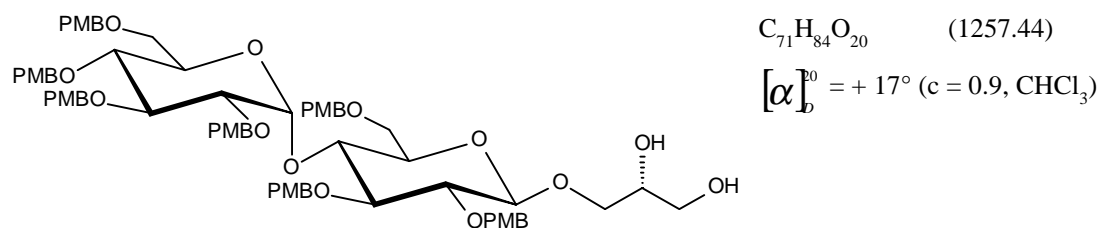
$^1\text{H-NMR}$ (500 MHz, C_6D_6): $\delta = 5.86$ (dd, 1H, H-3''), 5.54 (d, 1H, H-1''), 5.40 (dd, 1H, H-4''), 5.37 (dd, 1H, H-3'), 5.06 (dd, 1H, H-2''), 5.05 (dd, 1H, H-2'), 4.45 (dd, 1H, H-6a''), 4.33 (d, 1H, H-1'), 4.34 (dd, 1H, H-6a'), 4.33 (dd, 1H, H-6b''), 4.18 (ddd, 1H, H-5'), 4.08 (dd, 1H, H-6b'), 3.98 (m, 1H, H-2), 3.88 (dd, 1H, H-4'), 3.75 (dd, 1H, H-1a), 3.70 (dd, 1H, H-1b), 3.65 (dd, 1H, H-3a), 3.46 (dd, 1H, H-3b), 2.80 (ddd, 1H, H-5'), 1.95, 1.80, 1.75, 1.69, 1.67 (each s, 3H, OAc), 1.81 (s, 6H, OAc);

$^3J_{1',2'} = 8.1$, $^3J_{2',3'} = 9.5$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.2$, $^3J_{5',6a'} = 3.0$, $^3J_{5',6b'} = 4.1$, $^2J_{6a',6b'} = 12.2$, $^3J_{1'',2''} = 4.1$, $^3J_{2'',3''} = 10.7$, $^3J_{3'',4''} = 9.7$, $^3J_{4'',5''} = 9.7$, $^3J_{5'',6a''} = 3.6$, $^3J_{5'',6b''} = 3.0$, $^2J_{6a'',6b''} = 12.2$, $^3J_{1a,2} = 6.1$, $^3J_{1b,2} = 6.6$, $^2J_{1a,1b} = 8.1$, $^3J_{3a,2} = 4.1$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 10.6$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.64$, 170.49, 170.34, 170.22, 170.00, 169.48 (C=O, OAc), 109.57 (C-ketal), 101.08 (C-1'), 96.11 (C-1''), 76.15 (C-3'), 74.91 (C-2), 72.81, 72.77 (C-4', C-2'), 72.42 (C-5'),

71.04 (C-2'), 70.07 (C-3''), 69.54 (C-3), 69.45 (C-5''), 69.11 (C-4''), 66.57 (C-1), 62.95 (C-6'), 62.10 (C-6''), 27.09, 25.62 (-CH₃, ketal), 20.99, 20.71, 20.64, 20.60, 20.55, 20.47, 20.38 (-CH₃, OAc).

3-O-[4'-O-(2'',3'',4'',6''-tetra-O-{4'''-methoxybenzyl}- α -D-glucopyranosyl)-2',3',6'-tri-O-{4'''-methoxybenzyl}- β -D-glucopyranosyl]-sn-glycerol **86**



4.08 g (5.43 mmol) **83** were deprotected using *General procedure 3*. The thus obtained compound **84** was dissolved under nitrogen in 40 ml dry N,N-dimethylformamide. The solution was cooled to 0°C and 1.71 g (71.46 mmol) NaH were added portionwise. After the addition of NaH was complete the mixture was brought to ambient temperature, 9.72 ml (71.46 mmol) *p*-methoxybenzyl chloride were added dropwise and the resulting mixture was stirred at ambient temperature overnight. Methanol was added carefully to destroy excess NaH and the solvent was evaporated *in vacuo*. The residue was dissolved in 150 ml ethyl acetate, washed twice with 50 ml of a saturated solution of NaHCO₃ and once with 50 ml water. The organic layer was dried (MgSO₄) and evaporated to dryness. The residue was purified by column chromatography (petroleum ether [50/70]-ethyl acetate 7:5) to obtain compound **85**. This was added to 40 ml 70 % acetic acid and stirred for 4 hours at 50 °C. The solvent was evaporated under reduced pressure and the resulting oil was co-evaporated twice with toluene and purified by chromatography on silica gel (petroleum ether [50/70]-ethyl acetate 1:2). Yield: 1.92 g (28 %).

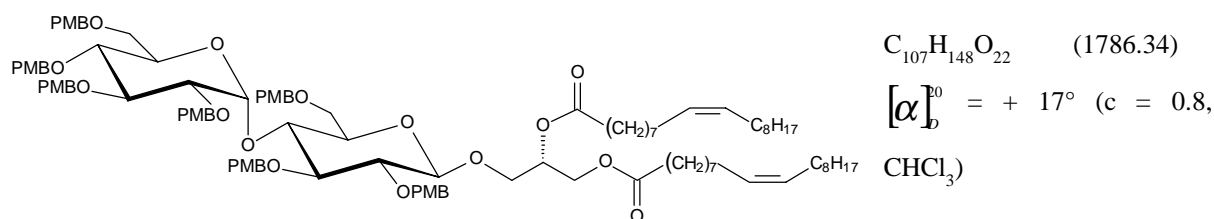
¹H-NMR (500 MHz, C₆D₆): δ = 7.40 (d, 2H, H-aromatic), 7.37 (d, 4H, H-aromatic), 7.32, 7.30, 7.29, 7.27 (each d, 2H, H-aromatic), 6.80-6.88 (m, 12H, H-aromatic), 6.78 (d, 2H, H-aromatic), 5.93 (d, 1H, H-1'), 5.12, 5.10, 5.04, 5.01, 5.00, 4.93, 4.72, 4.68, 4.65, 4.60, 4.55, 4.54, 4.51, 4.44 (d, 1H, CH₂-benzylic), 4.37 (d, 1H, H-1'), 4.31 (dd, 1H, H-4'), 4.30 (dd, 1H, H-3''), 4.20 (ddd, 1H, H-5''), 3.99 (dd, 1H, H-6a'), 3.86-3.96 (m, 4H, H-2, H-3', H-6b', H-4''), 3.84 (dd, 1H, H-6a''), 3.75-3.79 (m, 2H, H-3a, H-6b''), 3.71 (dd, 1H, H-3b), 3.60-3.67 (m, 3H, H-1a, H-2', H-2''), 3.47-3.55 (m, 2H, H-1b, H-5'), 3.32, 3.35, 3.36, 3.365, 3.37 (each s, 3H, -OCH₃), 3.34 (s, 6H, -OCH₃);

³J_{1',2'} = 7.6, ³J_{3',4'} = 9.2, ³J_{4',5'} = 9.2, ³J_{5',6a'} = 5.2, ²J_{6a',6b'} = 10.7, ³J_{1'',2''} = 3.5, ³J_{2'',3''} = 9.5, ³J_{3'',4''} = 9.5, ³J_{4'',5''} = 10.1, ³J_{5'',6a''} = 4.1, ³J_{5'',6b''} = 1.6, ²J_{6a'',6b''} = 10.7, ³J_{3b,2} = 6.6, ²J_{3a,3b} = 11.4 Hz.

¹³C-NMR (125 MHz, C₆D₆): δ = 160.22, 160.16, 160.10, 160.02, 159.83, 132.28, 132.10, 131.88, 131.61, 131.36, 130.99 (C_{quaternary} aromatic), 130.35, 130.32, 130.25, 130.13, 130.01, 129.93, 129.07, (C-aromatic, C-olefinic), 114.54, 114.47, 114.43 (C-aromatic), 104.93 (C-1'), 97.50 (C-1''), 85.29 (C-3'), 82.57 (C-3''), 82.30 (C-2'), 80.54 (C-2''), 78.79 (C-4'), 75.68, 75.40 (C-benzylic), 75.16 (C-5'), 74.78, 74.13 (C-benzylic),

74.10 (C-4'), 73.93, 73.79, 73.77, 73.42 (C-benzylic, C-3), 72.55 (C-5'), 71.89 (C-2), 69.97 (C-6'), 69.69 (C-6''), 64.08 (C-1), 55.18, 55.15, 55.12, 55.09 (C-methoxy).

1,2-di-O-oleoyl-3-O-[4'-O-(2'',3'',4'',6''-tetra-O-{4''''-methoxybenzyl}- α -D-glucopyranosyl)-2',3',6'-tri-O-{4''''-methoxybenzyl}- β -D-glucopyranosyl]-sn-glycerol **87**

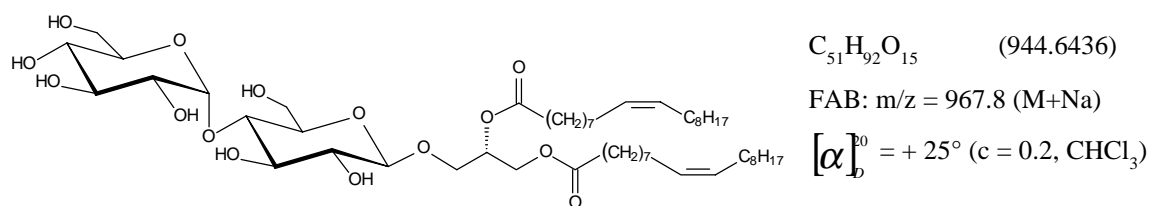


1.54 g (1.22 mmol) **86** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 4:1). Yield: 1.48 g (68 %).

1H -NMR (500 MHz, C_6D_6): δ = 7.41, 7.39, 7.38, 7.36, 7.29, 7.28, 7.26 (each d, 2H, H-aromatic), 6.88 (d, 2H, H-aromatic), 6.80-6.87 (m, 10H, H-aromatic), 6.77 (d, 2H, H-aromatic), 5.99 (d, 1H, H-1'), 5.46-5.61 (m, 5H, H-2, H-olefinic), 5.13 (d, 2H, CH_2 -benzylic), 5.06, 5.05 (each d, 1H, CH_2 -benzylic), 5.01 (d, 2H, CH_2 -benzylic), 4.73, 4.72 (each d, 1H, CH_2 -benzylic), 4.53-4.66 (m, 6H, CH_2 -benzylic, H-1a), 4.40-4.48 (m, 3H, CH_2 -benzylic, H-1b, H-4'), 4.39 (d, 1H, H-1'), 4.34 (dd, 1H, H-3'), 4.27 (ddd, 1H, H-5'), 4.11 (dd, 1H, H-6a'), 4.05 (dd, 1H, H-3a), 3.95 (dd, 1H, H-3'), 3.93 (dd, 1H, H-4'), 3.91 (dd, 1H, H-6b'), 3.86 (dd, 1H, H-6a''), 3.78 (dd, 1H, H-6b''), 3.62-3.72 (m, 3H, H-3b, H-2', H-2''), 3.49 (m, 1H, H-5'), 3.41, 3.36, 3.353, 3.351, 3.34, 3.33, 3.31 (each s, 3H, OCH_3), 2.24-2.30 (m, 2H, α - CH_2), 2.19-2.24 (m, 2H, α' - CH_2), 2.05-2.19 (m, 8H, CH_2 -allylic), 1.58-1.70 (m, 4H, β - CH_2 , β' - CH_2), 1.20-1.45 (m, 40H, $-CH_2-$), 0.96 (t, 3H, $-CH_3$);

$^3J_{1,2'} = 7.6$, $^3J_{2,3'} = 9.0$, $^3J_{3,4'} = 9.2$, $^3J_{5',6a'} = 4.4$, $^3J_{5',6b'} = 2.3$, $^2J_{6a',6b'} = 10.7$, $^3J_{1'',2''} = 3.2$, $^3J_{2'',3''} = 9.5$, $^3J_{3'',4''} = 9.4$, $^3J_{4'',5''} = 9.5$, $^3J_{5'',6a''} = 4.2$, $^3J_{5'',6b''} = 2.0$, $^2J_{6a'',6b''} = 10.6$, $^3J_{3a,2} = 4.4$, $^2J_{3a,3b} = 10.8$ Hz.

^{13}C -NMR (100 MHz, C_6D_6): δ = 173.12, 172.92 (C=O, oleoyl), 160.02, 159.95, 159.89, 159.67, 132.25, 132.06, 131.89, 131.62, 131.35, 131.33, 131.31 ($C_{\text{quaternary}}$ aromatic), 130.51, 130.44, 130.28, 130.12, 130.03, 129.90, 129.88, 129.81, 128.94 (C-aromatic, C-olefinic), 114.39, 114.34, 114.32, 114.29 (C-aromatic), 104.55 (C-1'), 97.37 (C-1''), 85.24 (C-3'), 82.56 (C-3''), 81.99 (C-2'), 80.51 (C-2''), 78.70 (C-4'), 75.66 (C-5'), 75.57, 75.28, 74.60, 73.93, 73.68 (C-benzylic), 73.64 (C-4'), 73.60, 73.24 (C-benzylic), 72.34 (C-5'), 70.86 (C-2), 69.72, 69.61 (C-6', C-6''), 68.26 (C-3), 63.47 (C-1), 55.09, 55.02, 55.00, 54.97 (C-methoxy), 34.76, 34.48 (C- α , C- α'), 32.56, 30.51, 30.45, 30.25, 30.01, 29.89, 29.84, 29.81, 29.72 (C-alkyl), 27.97, 27.95 (C-allyl), 25.57, 25.51 (C- β , C- β'), 23.36 (C-alkyl), 14.63 (C-methyl).

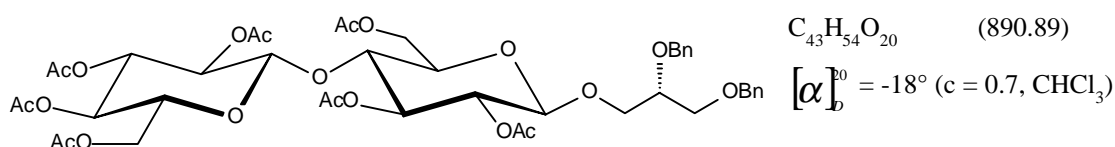
1,2-di-*O*-oleoyl-3-*O*-[4'-*O*-(α -D-glucopyranosyl)- β -D-glucopyranosyl]-*sn*-glycerol 88

1.33 g (0.74 mmol) **87** and 6.25 g (11.40 mmol) ceric ammonium nitrate were dissolved in a mixture of 22 ml acetonitrile and 1.2 ml water and stirred at ambient temperature. After completion, the precipitate was filtered off and dissolved in chloroform, washed with 50 ml water, 50 ml sodium hydrogen sulfite, 50 ml sodium hydrogen carbonate and again with water. The organic layer was dried ($MgSO_4$) and evaporated to dryness. The crude material was purified by silica gel chromatography (chloroform-methanol 95:5) and a subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 265 mg (38 %).

1H -NMR (500 MHz, d_4 -MeOH + TMS): $\delta = 5.23$ -5.42 (m, 5H, H-2, H-olefinic), 5.15 (d, 1H, H-1'), 4.45 (dd, 1H, H-1a), 4.30 (d, 1H, H-1'), 4.21 (dd, 1H, H-1b), 3.98 (dd, 1H, H-3a), 3.89 (dd, 1H, H-6a'), 3.79-3.86 (m, 2H, H-6b', H-6a''), 3.74 (dd, 1H, H-3b), 3.64-3.72 (m, 2H, H-5'', H-6b''), 3.62 (t, 2H, H-3', H-3''), 3.55 (dd, 1H, H-4'), 3.45 (dd, 1H, H-2'), 3.37 (ddd, 1H, H-5'), 3.27 (dd, 1H, H-4'), 3.25 (dd, 1H, H-2'), 2.32 (t, 2H, α - CH_2), 2.33 (t, 2H, α' - CH_2), 1.90-2.12 (m, 8H, $-CH_2$ -allylic), 1.56-1.66 (m, 4H, β - CH_2 , β' - CH_2), 1.22-1.40 (m, 40H, $-CH_2$ -), 0.90 (t, 6H, $-CH_3$);

$^3J_{1',2'} = 7.9$, $^3J_{2',3'} = 9.1$, $^3J_{3',4'} = 9.1$, $^3J_{4',5'} = 9.3$, $^3J_{5',6a'} = 1.9$, $^3J_{5',6b'} = 4.4$, $^2J_{6a',6b'} = 12.3$, $^3J_{1'',2''} = 3.8$, $^3J_{2'',3''} = 9.8$, $^3J_{3'',4''} = 9.2$, $^3J_{1a,2} = 2.8$, $^3J_{1b,2} = 6.6$, $^3J_{1a,1b} = 12.0$, $^3J_{3a,2} = 5.4$, $^3J_{3b,2} = 6.0$, $^2J_{3a,3b} = 11.0$ Hz.

^{13}C -NMR (100 MHz, d_4 -MeOH + TMS): $\delta = 174.91$, 174.58 (C=O, OAc), 130.78, 130.60 (C-olefinic), 104.53 (C-1'), 102.83 (C-1''), 81.10 (C-4'), 77.44, 74.88 (C-3', C-3''), 76.52 (C-5'), 74.57 (C-5''), 74.30 (C-2'), 73.95 (C-2''), 71.49 (C-2), 71.31 (C-4''), 68.71 (C-3), 63.85 (C-1), 62.64 (C-6''), 61.94 (C-6'), 35.04, 34.88 (C- α , C- α'), 32.91, 30.70, 30.62, 30.48, 30.30, 30.22, 30.18, 30.08, 30.05, 30.02, 28.04, 25.86, 23.60 (C-alkyl), 14.44 (C-methyl).

1,2-di-*O*-benzyl-3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- β -D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl- β -D-glucopyranosyl]-*sn*-glycerol 92

6.52 g (9.32 mmol) of acetobromo cellobiose and 2.54 g (9.32 mmol) 1,2-di-*O*-benzyl-*sn*-glycerol were reacted using *General procedure 4*. Yield: 5.45 g (66 %).

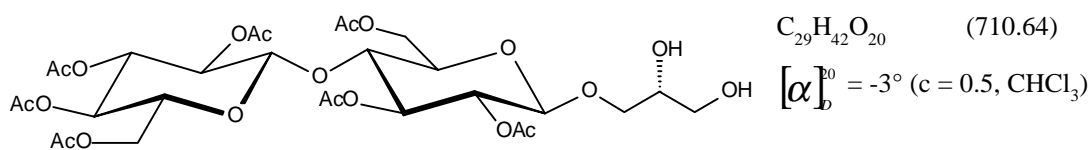
1H -NMR (400 MHz, $CDCl_3$ +TMS): $\delta = 7.24$ -7.37 (m, 10H, H-aromatic), 5.15, 5.14 (each dd, 1H; H-3', H-3''),

5.06 (dd, 1H, H-4''), 4.92, 4.90 (each dd, 1H; H-2', H-2''), 4.66 (d, 1H, CH₂-benzylic), 4.62 (d, 1H, CH₂-benzylic), 4.54 (d, 1H, CH₂-benzylic), 4.50 (d, 1H, CH₂-benzylic), 4.49 (d, 2H, H-1', H-1''), 4.48 (dd, 1H, H-6a'), 4.36 (dd, 1H, H-6a''), 4.07 (dd, 1H, H-6b'), 4.04 (dd, 1H, H-6b''), 3.92 (dd, 1H, H-3a), 3.76 (dd, 1H, H-4'), 3.71-3.76 (m, 1H, H-2), 3.68 (dd, 1H, H-3b), 3.64 (ddd, 1H, H-5''), 3.53-3.60 (m, 2H, H-1a, H-1b), 3.53 (ddd, 1H, H-5'), 2.09, 2.08, 2.03, 2.01, 2.00, 1.98, 1.93 (each s, 3H, OAc);

³J_{1',2'} = 7.6, ³J_{2',3'} = 9.3, ³J_{3',4'} = 9.7, ³J_{4',5'} = 9.7, ³J_{5',6a'} = 2.0, ²J_{5',6b'} = 5.2, ²J_{6a',6b'} = 12.6, ³J_{1'',2''} = 7.6, ³J_{2'',3''} = 9.3, ³J_{3'',4''} = 9.7, ³J_{4'',5''} = 9.7, ³J_{5'',6a''} = 4.6, ³J_{5'',6b''} = 2.5, ²J_{6a'',6b''} = 12.6, ³J_{3a,2} = 4.6, ³J_{3b,2} = 5.1, ²J_{3a,3b} = 10.2 Hz.

¹³C-NMR (100 MHz, CDCl₃+TMS): δ = 170.49, 170.30, 170.22, 169.78, 169.55, 169.30, 169.03 (C=O, OAc), 138.49, 138.18 (C_{quaternary} aromatic), 128.43, 128.36, 127.61, 127.59 (C-aromatic), 100.87, 100.82 (C-1', C-1''), 76.84, 76.48 (C-4', C-2), 73.49 (C-benzylic), 72.97, 72.50 (C-3', C-3''), 72.66 (C-5'), 72.12 (C-benzylic), 71.98 (C-5''), 71.63, 71.60 (C-2', C-2''), 69.74 (C-1), 69.29 (C-3), 67.82 (C-4''), 61.86, 61.57 (C-6', C-6''), 20.86, 20.66, 20.62, 20.55 (-CH₃, OAc).

3-O-[4'-O-(2'',3'',4'',6''-tetra-O-acetyl-β-D-glucopyranosyl)-2',3',6'-tri-O-acetyl-β-D-glucopyranosyl]-sn-glycerol **93**



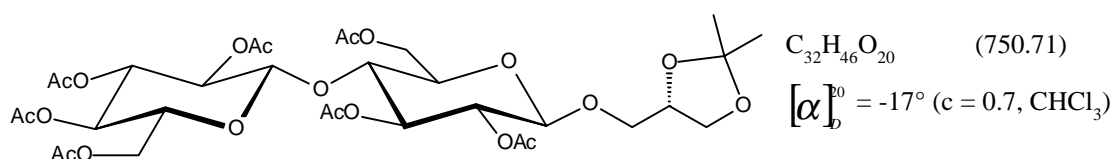
A mixture of 5.26 g (5.90 mmol) **92** and 0.4 g Pd/C (10%) in 100 ml ethanol containing 9 ml ethyl acetate and 2.5 ml glacial acetic acid was stirred under one atmosphere of hydrogen until t.l.c. showed the reaction to be complete. Chloroform was added until the white precipitate was completely dissolved. The catalyst was filtered off, the mother liquor evaporated *in vacuo*, and the resulting residue recrystallised from ethanol. Yield: 3.80 g (91 %).

¹H-NMR (400 MHz, CDCl₃+TMS): δ = 5.19 (dd, 1H, H-3'), 5.15 (dd, 1H, H-3''), 5.06 (dd, 1H, H-4'), 4.93 (dd, 1H, H-2'), 4.91 (dd, 1H, H-2''), 4.59 (dd, 1H, H-6a'), 4.52 (d, 1H, H-1'), 4.50 (d, 1H, H-1''), 4.36 (dd, 1H, H-6a''), 4.07 (dd, 1H, H-6b'), 4.05 (dd, 1H, H-6b''), 3.72-3.87 (m, 3H, H-2, H-3a, H-3b), 3.75 (dd, 1H, H-4'), 3.60-3.70 (m, 3H, H-1a, H-5', H-5''), 3.56 (dd, 1H, H-1b), 2.14, 2.09, 2.05, 2.03, 2.02, 2.01, 1.98 (each s, 3H, OAc);

³J_{1',2'} = 8.1, ³J_{2',3'} = 9.7, ³J_{3',4'} = 9.6, ³J_{4',5'} = 9.6, ³J_{5',6a'} = 2.0, ³J_{5',6b'} = 5.6, ²J_{6a',6b'} = 12.2, ³J_{1'',2''} = 8.1, ³J_{2'',3''} = 9.6, ³J_{3'',4''} = 9.6, ³J_{4'',5''} = 9.6, ³J_{5'',6a''} = 4.5, ³J_{5'',6b''} = 2.5, ²J_{6a'',6b''} = 12.2, ³J_{1b,2} = 5.1, ²J_{1a,1b} = 11.2 Hz.

¹³C-NMR (100 MHz, CDCl₃+TMS): δ = 170.48, 170.37, 170.23, 169.76, 169.70, 169.31, 169.04 (C=O, OAc), 101.40, 100.79 (C-1', C-1''), 76.44 (C-4'), 73.20 (C-3), 72.94, 72.05 (C-5', C-5''), 72.90 (C-3'), 72.22 (C-3''), 71.62 (C-2'), 71.47 (C-2''), 70.52 (C-2), 67.79 (C-4''), 63.37 (C-1), 61.65 (C-6'), 61.57 (C-6''), 20.80, 20.70, 20.67, 20.54 (-CH₃, OAc).

1,2-di-*O*-isopropylidene-3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- β -D-glucopyranosyl)-2',3',6'-tri-*O*-acetyl- β -D-glucopyranosyl]-*sn*-glycerol **94**



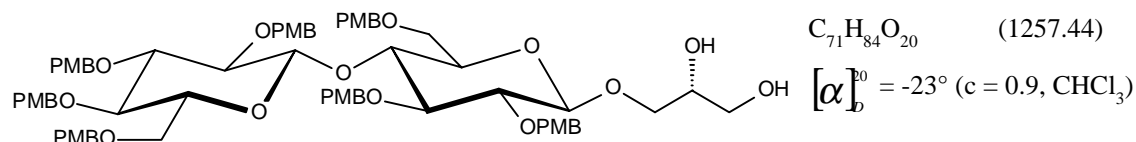
3.70 g (5.21 mmol) **93** were dissolved in 60 ml acetone, 8.7 ml (71.40 mmol) 2,2-dimethoxypropane and 174 mg (1.01 mmol) *p*-toluenesulfonic acid were added and the mixture stirred at ambient temperature. After completion, the solution was neutralised with triethylamine and evaporated to dryness. The crude material was redissolved in 150 ml chloroform and washed twice with 100 ml of a saturated solution of $NaHCO_3$ and once with 100 ml water. The organic layer was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Yield: 3.85 g (99 %).

1H -NMR (400 MHz, C_6D_6): δ = 5.36 (dd, 1H, H-3'), 5.33 (dd, 1H, H-3''), 5.22 (dd, 1H, H-2'), 5.19 (dd, 1H, H-4'), 5.14 (dd, 1H, H-2''), 4.47 (dd, H-6a'), 4.36 (dd, H-6a''), 4.31 (d, 1H, H-1'), 4.27 (d, 1H, H-1''), 4.07 (dd, 1H, H-6b'), 4.00-4.06 (m, 1H, H-2), 3.90 (dd, 1H, H-6b''), 3.75-3.82 (m, 2H, H-3a, H-3b), 3.73 (dd, 1H, H-1a), 3.57 (dd, 1H, H-4'), 3.50 (dd, 1H, H-1b), 3.27 (ddd, 1H, H-5'), 3.07 (ddd, 1H, H-5''), 1.91 (s, 6H, OAc), 1.84 (s, 3H, OAc), 1.71 (s, 3H, OAc), 1.70 (s, 3H, OAc), 1.69 (s, 6H, OAc), 1.42 (s, 3H, $-CH_3$ ketal), 1.25 (s, 3H, $-CH_3$ ketal);

$^3J_{1',2'} = 8.1$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 2.0$, $^3J_{5',6b'} = 5.6$, $^2J_{6a',6b'} = 11.7$, $^3J_{1'',2''} = 7.6$, $^3J_{2'',3''} = 9.7$, $^3J_{3'',4''} = 9.7$, $^3J_{4'',5''} = 9.7$, $^3J_{5'',6a''} = 4.1$, $^3J_{5'',6b''} = 2.1$, $^2J_{6a'',6b''} = 12.6$, $^3J_{1a,2} = 4.1$, $^3J_{1b,2} = 6.1$, $^2J_{1a,1b} = 10.7$ Hz.

^{13}C -NMR (100 MHz, C_6D_6): δ = 170.23, 170.18, 169.73, 169.52, 169.28, 169.08, (C=O, OAc), 109.60 (C-ketal), 101.73 (C-1'), 101.41 (C-1''), 77.58 (C-4'), 74.88 (C-2), 73.76 (C-3'), 73.37 (C-3''), 73.12 (C-5'), 72.58 (C-2'', C-5''), 72.43 (C-2'), 69.86 (C-1), 68.39 (C-4'), 66.76 (C-3), 62.60 (C-6'), 61.67 (C-6''), 27.15, 25.64 ($-CH_3$ ketal), 20.76, 20.69, 20.62, 20.53, 20.48, 20.45, 20.39 ($-CH_3$, OAc).

3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-[4'''-methoxybenzyl]- β -D-glucopyranosyl)-2',3',6'-tri-*O*-[4'''-methoxybenzyl]- β -D-glucopyranosyl]-*sn*-glycerol **97**



3.75 g (5.00 mmol) **94** were deprotected using *General procedure 3*. The thus obtained compound **95** was dissolved under nitrogen in 40 ml dry *N,N*-dimethylformamide. The solution was cooled to 0°C and 1.66 g (69.17 mmol) NaH were added portionwise. After the addition of NaH was complete the mixture was brought to ambient temperature, 9.94 ml (73.12 mmol) *p*-methoxybenzyl chloride were added dropwise and the resulting mixture was stirred at ambient temperature overnight. Methanol was added carefully to destroy excess

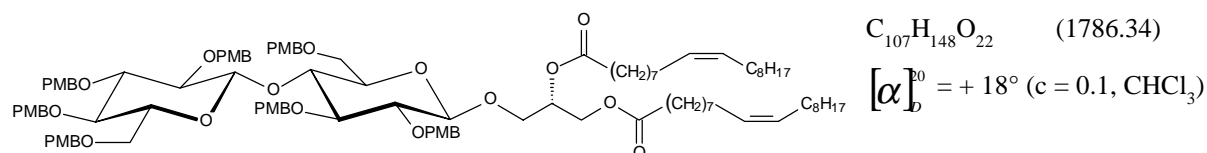
NaH and the solvent was evaporated *in vacuo*. The residue was dissolved in 150 ml ethyl acetate, washed twice with 50 ml of a saturated solution of NaHCO₃ and once with 50 ml water. The organic layer was dried (MgSO₄) and evaporated to dryness. The residue was purified by column chromatography (light petroleum (b.p. 50-70 °C)-ethyl acetate 7:5) to obtain compound **96**. This was added to 40 ml 70 % acetic acid and stirred for 4 hours at 50 °C. The solvent was evaporated under reduced pressure and the resulting oil was co-evaporated twice with toluene and chromatographed on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 1:2). Yield: 1.29 g (20 %).

¹H-NMR (500 MHz, C₆D₆): δ = 7.64 (d, 2H, H-aromatic), 7.42 (d, 2H, H-aromatic), 7.40 (d, 2H, H-aromatic), 7.38 (d, 2H, H-aromatic), 7.32 (d, 2H, H-aromatic), 7.31 (d, 2H, H-aromatic), 7.23 (d, 2H, H-aromatic), 6.93 (d, 2H, H-aromatic), 6.86-6.91 (m, 8H, H-aromatic), 6.83 (d, 2H, H-aromatic), 6.82 (d, 2H, H-aromatic), 5.41, 5.09, 4.98, 4.97, 4.93 (each d, 1H, CH₂-benzylic), 4.94 (d, 2H, CH₂-benzylic), 4.85, 4.83, 4.65 (each d, 1H, CH₂-benzylic), 4.66 (d, 1H, H-1''), 4.55, 4.54, 4.47 (each d, 1H, CH₂-benzylic), 4.42 (d, 1H, H-1'), 4.34 (d, 1H, CH₂-benzylic), 4.29 (dd, 1H, H-4'), 3.96 (dd, 1H, H-6a*), 3.80-3.87 (m, 4H, H-2, H-4'', H-6a*, H-6b*), 3.74-3.80 (m, 3H, H-3a, H-3b, H-3'), 3.72 (dd, 1H, H-6b*), 3.68 (dd, 1H, H-3''), 3.57-3.64 (m, 3H, H-1a, H-2', H-2''), 3.50-3.55 (dd, 1H, H-1b), 3.45-3.50 (m, 2H, H-5', H-5''), 3.40, 3.37, 3.36, 3.35, 3.34 (each s, 3H, OCH₃), 3.36 (s, 6H, OCH₃);

³J_{1,2'} = 7.6, ³J_{3',4'} = 9.5, ³J_{4',5'} = 9.5, ³J_{1'',2''} = 7.9, ³J_{2'',3''} = 9.2, ³J_{3'',4''} = 9.2 Hz.

¹³C-NMR (100 MHz, C₆D₆): δ = 160.17, 160.13, 160.04, 160.01, 159.98, 159.94, 159.92, 132.54, 132.11, 131.73, 131.61, 131.59, 131.45 (C_{quaternary} aromatic), 130.48, 130.38, 130.20, 130.15, 130.03, 129.74, 129.71, 114.54, 114.42, 114.39, 114.35, 114.30, 114.26, 114.20 (C-aromatic), 104.77 (C-1'), 103.32 (C-1''), 85.52 (C-3'), 83.26 (C-3''), 83.05 (C-2''), 81.95 (C-2'), 78.45 (C-2), 77.38 (C-4'), 76.06, 75.62 (C-5', C-5''), 75.66, 75.38, 75.17, 75.09, 74.94, 73.59, 73.56, 73.52 (C-3, C-benzylic), 71.63 (C-4''), 69.37, 68.58 (C-6', C-6''), 63.95 (C-1), 55.03 (C methoxy).

1,2-di-*O*-oleoyl-3-*O*-[4'-*O*-(2'',3'',4'',6''-tetra-*O*-{4'''-methoxybenzyl}-β-D-glucopyranosyl)-2',3',6'-tri-*O*-{4'''-methoxybenzyl}-β-D-glucopyranosyl]-*sn*-glycerol **98**



1.07 g (0.85 mmol) **97** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 4:1 →3:1). Yield: 1.02 g (67 %).

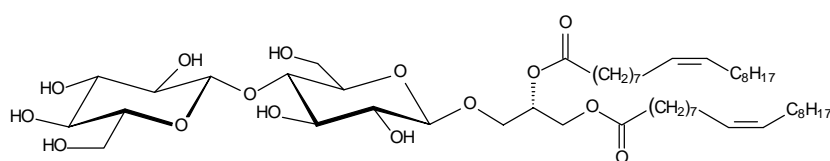
¹H-NMR (500 MHz, C₆D₆): δ = 7.63, 7.48, 7.41, 7.39, 7.32, 7.29, 7.21, 6.92, 6.91, 6.90, 6.88, 6.87, 6.81, 6.80 (each d, 2H, H-aromatic), 5.56-5.61 (m, 1H, H-2), 5.54 (m, 4H, H-olefinic), 5.42, 5.08, 5.06, 5.01, 4.97, 4.95, 4.92, 4.86, 4.83 (each d, 1H, CH₂-benzylic), 4.77 (d, 1H, H-1''), 4.65, 4.62 (each d, 1H, CH₂-benzylic), 4.59

(dd, 1H, H-1a), 4.54, 4.45 (each d, 1H, CH₂-benzylic), 4.44 (d, 1H, H-1'), 4.38-4.44 (m, 3H, H-1b, CH₂-benzylic, H-4'), 4.07-14 (m, 2H, H-3a, H-6a*), 3.78-3.88 (m, 4H, H-3', H-4'', H-6a*, H-6b*), 3.75 (dd, 1H, H-3b), 3.73 (dd, 1H, H-6b*), 3.68 (dd, 1H, H-3''), 3.65 (dd, 1H, H-2'), 3.61 (t, 1H, H-2''), 3.42-3.49 (m, 2H, H-5', H-5''), 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34 (each s, 3H, OCH₃), 2.27 (t, 2H, α-CH₂), 2.21 (t, 2H, α'-CH₂), 2.06-2.18 (m, 8H, CH₂-allylic), 1.64 (m, 4H, β'-CH₂, β-CH₂), 1.17-1.48 (m, 40H, -CH₂-), 0.95 (t, 6H, CH₃);

³J_{1,2'} = 8.2, ³J_{2,3'} = 8.2, ³J_{1'',2''} = 7.6, ³J_{2'',3''} = 8.8, ³J_{1a,2} = 2.8, ²J_{1a,1b} = 11.7, ³J_{3b,2} = 5.1, ²J_{3a,3b} = 11.8 Hz.

¹³C-NMR (100 MHz, C₆D₆): δ = 173.11, 172.96 (C=O, OAc), 160.11, 159.97, 159.95, 159.90, 159.88, 132.67, 132.17, 131.94, 131.69, 131.49, 131.04 (C_{quaternary} aromatic), 130.50, 130.43, 130.22, 130.18, 130.13, 130.01, 129.75, 129.69, 114.56, 114.39, 114.36, 114.33, 114.27, 114.24, 114.16 (C-aromatic), 104.71 (C-1'), 103.20 (C-1''), 85.55 (C-3'), 83.30 (C-2'), 83.07 (C-3''), 81.86 (C-2'), 78.50 (C-4'), 77.05 (C-4''), 76.12, 76.05 (C-5', C-5''), 75.64, 75.35, 75.14, 74.99, 74.92, 73.55 (C-benzylic), 70.92 (C-2), 69.32, 68.48 (C-6', C-6''), 68.36 (C-3), 63.46 (C-1), 55.07, 55.02 (C methoxy), 34.76, 34.48 (C-α, C-α'), 32.57, 30.51, 30.45, 30.26, 30.02, 29.90, 29.84, 29.82, 29.72 (C-alkyl), 27.97 (C-allylic), 25.57, 25.51 (C-β, C-β), 23.36 (C-alkyl), 14.63 (C-methyl).

1,2-di-*O*-oleoyl-3-*O*-[4'-*O*-(β-D-glucopyranosyl)-β-D-glucopyranosyl]-*sn*-glycerol **99**



C₅₁H₉₂O₁₅ (944.6436)

FAB: m/z = 967.8 (M+Na)

[α]_D²⁰ = -17° (c = 0.7, CHCl₃)

864 mg (0.48 mmol) **98** and 4.08 g (7.45 mmol) ceric ammonium nitrate were dissolved in a mixture of 22 ml acetonitrile and 1.2 ml water and stirred at ambient temperature. After completion, the precipitate was filtered off and dissolved in chloroform, washed with 50 ml water, 50 ml sodium hydrogen sulfite, 50 ml sodium hydrogen carbonate and again with water. The organic layer was dried (MgSO₄) and evaporated to dryness. The crude material was purified by silica gel chromatography (chloroform-methanol 95:5) and a subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 175 mg (39 %).

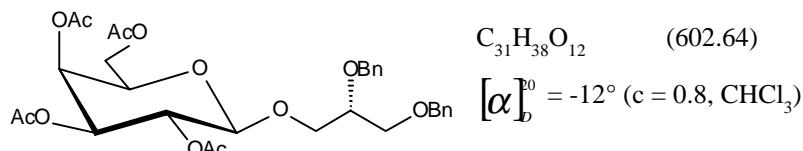
¹H-NMR (400 MHz, d₄-MeOH + TMS): δ = 5.22-5.43 (m, 5H, H-olefinic, H-2), 4.45 (dd, 1H, H-1a), 4.41 (d, 1H, H-1'), 4.31 (d, 1H, H-1''), 4.21 (dd, 1H, H-1b), 3.97 (dd, 1H, H-3a), 3.83-3.93 (m, 3H, H-6a', H-6b', H-6a''), 3.74 (dd, 1H, H-3b), 3.67 (dd, 1H, H-6b''), 3.58 (dd, 1H, H-4'), 3.52 (dd, 1H, H-3'), 3.30-3.44 (m, 4H, H-3'', H-4'', H-5', H-5''), 3.20-3.30 (m, 2H, H-2', H-2''), 2.33 (t, 2H, α-CH₂), 2.32 (t, 2H, α'-CH₂), 1.92-2.10 (m, 8H, CH₂-allylic), 1.55-1.67 (m, 4H, β-CH₂, β'-CH₂), 1.22-1.42 (m, 40H, -CH₂-), 0.90 (t, 6H, CH₃);

³J_{1,2'} = 7.6, ³J_{2,3'} = 9.1, ³J_{3,4'} = 9.1, ³J_{4',5'} = 9.1, ³J_{1'',2''} = 7.6, ³J_{5'',6b''} = 5.1, ²J_{6a'',6b''} = 11.7, ³J_{1a,2} = 2.5, ³J_{1b,2} = 6.6, ²J_{1a,1b} = 12.2, ³J_{3a,2} = 5.6, ³J_{3b,2} = 6.1, ²J_{3a,3b} = 11.7 Hz.

¹³C-NMR (100 MHz, d₄-MeOH + TMS): δ = 175.52, 175.19 (C=O, OAc), 131.39, 131.21 (C-olefinic), 105.04 (C-1', C-1''), 81.06 (C-4'), 78.50, 78.25 (C-3'', C-5''), 76.96 (C-5'), 76.68 (C-3'), 75.28, 75.05 (C-2', C-2''),

72.10 (C-2), 71.73 (C-4''), 69.31 (C-3), 64.46 (C-1), 62.84 (C-6''), 62.30 (C-6'), 35.62, 35.47 (C- α , C- α'), 33.52, 31.31, 31.08, 30.91, 30.82, 30.79, 30.67 (C-alkyl), 26.47 (C-allylic), 24.21 (C- β ,C- β'), 15.04 (C-methyl).

1,2-di-O-benzyl-3-O-(2',3',4',6'-tetra-O-acetyl- β -D-galactopyranosyl)-sn-glycerol **103**



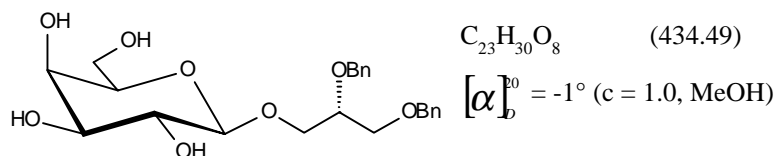
4.11 g (10 mmol) of acetobromo galactose and 2.5 g (9.17 mmol) 1,2-di-O-benzyl-*sn*-glycerol were reacted using *General procedure 4*. Yield: 4.81 g (87 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): δ = 7.26-7.38 (m, 10H, H-aromatic), 5.38 (dd, 1H, H-4'), 5.20 (dd, 1H, H-2'), 4.99 (dd, 1H, H-3'), 4.67, 4.64, 4.57, 4.52 (each d, 1H, CH_2 -benzylic), 4.49 (d, 1H, H-1'), 4.16 (dd, 1H, H-6a'), 4.12 (dd, 1H, H-6b'), 3.98 (dd, 1H, H-3a), 3.86 (ddd, 1H, H-5'), 3.68-3.79 (m, 2H, H-2, H-3b), 3.61 (dd, 1H, H-1a), 3.57 (dd, 1H, H-1b), 2.15, 2.04, 1.98, 1.95 (each s, 3H, OAc);

$^3J_{1,2'} = 7.6$, $^3J_{2',3'} = 10.5$, $^3J_{3',4'} = 3.6$, $^3J_{4',5'} = 1.0$, $^3J_{5',6a'} = 6.6$, $^3J_{5',6b'} = 6.6$, $^2J_{6a',6b'} = 11.2$, $^3J_{1a,2} = 4.1$, $^3J_{1b,2} = 5.1$, $^2J_{1a,1b} = 10.2$, $^3J_{3a,2} = 4.1$, $^3J_{3b,2} = 5.6$, $^2J_{3a,3b} = 9.8$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): δ = 170.39, 170.28, 170.16, 169.41 (C=O, OAc), 138.49, 138.24 ($C_{\text{quaternary}}$ aromatic), 128.42, 128.37, 127.65, 127.62 (C-aromatic), 101.63 (C-1'), 73.50, 72.17 (C-benzylic), 70.89, 70.68 (C-3', C-5'), 69.80 (C-1), 69.19 (C-3), 68.90 (C-2'), 67.06 (C-4'), 61.27 (C-6'), 20.68, 20.59 (CH_3 , OAc).

1,2-di-O-benzyl-3-O-(β -D-galactopyranosyl)-sn-glycerol **104**



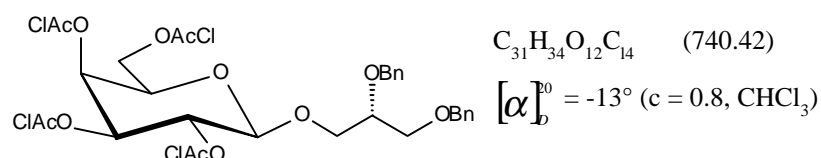
4.52 g (7.51 mmol) **103** were deprotected using *General procedure 3*. Yield: 3.10 g (95 %).

1H -NMR (400 MHz, d_4 -MeOH): δ = 7.07-7.24 (m, 10H, H-aromatic), 4.54 (d, 1H, CH_2 -benzylic), 4.50 (d, 1H, CH_2 -benzylic), 4.38 (s, 2H, CH_2 -benzylic), 4.06 (d, 1H, H-1'), 3.84 (dd, 1H, H-3a), 3.71 (m_c, 1H, H-2), 3.66 (dd, 1H, H-4'), 3.52-3.62 (m, 4H, H-1a, H-3b, H-6a', H-6b'), 3.49 (dd, 1H, H-1b), 3.36 (dd, 1H, H-2'), 3.33 (m_c, 1H, H-5'), 3.29 (dd, 1H, H-3');

$^3J_{1,2'} = 7.6$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 3.6$, $^3J_{4',5'} = 1.0$, $^3J_{1b,2} = 6.1$, $^2J_{1a,1b} = 10.7$, $^3J_{3a,2} = 4.6$, $^2J_{3a,3b} = 10.7$ Hz.

^{13}C -NMR (400 MHz, d_4 -MeOH): δ = 140.23, 140.12 ($\text{C}_{\text{quaternary}}$ aromatic), 129.78, 129.75, 129.58, 129.28, 129.13, 129.06 (C-aromatic), 105.77 (C-1'), 79.19 (C-2), 77.13 (C-5'), 75.31 (C-3'), 74.77, 73.72 (C-benzylic), 72.95 (C-2'), 71.87 (C-1), 70.70 (C-4'), 70.44 (C-3), 62.90 (C-6').

1,2-di-*O*-benzyl-3-*O*-(2',3',4',6'-tetra-*O*-chloroacetyl- β -D-galactopyranosyl)-*sn*-glycerol **105**



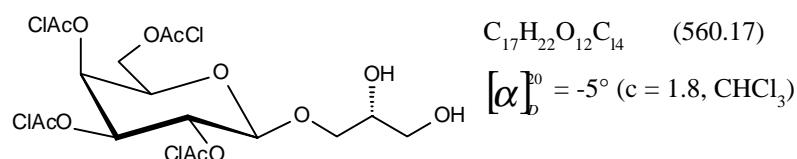
1.37 g (16.42 mmol) sodium hydrogen carbonate were added under nitrogen to a solution of 3.0 g (6.90 mmol) **104** and 9.44 g (55.23 mmol) chloroacetic acid anhydride in 35 ml dry N,N-dimethylformamide and the suspension was stirred for 3.5 hours at ambient temperature. After t.l.c. showed the reaction to be complete, the suspension was diluted with 80 ml ethyl acetate, poured into 150 ml of ice-water and stirred for an additional 30 minutes. The phases were separated and the aqueous layer was extracted twice with 80 ml ethyl acetate and the combined organic phases were washed twice with a saturated solution of sodium hydrogen carbonate and once with water. After drying (MgSO_4) the solvent was removed *in vacuo* and the resulting residue submitted to purification by column (light petroleum (b.p. 50-70 °C)-diethyl ether 25:20). Yield: 4.15 g (81 %).

^1H -NMR (500 MHz, CDCl_3 + TMS): δ = 7.27-7.40 (m, 10H, H-aromatic), 5.44 (dd, 1H, H-4'), 5.24 (dd, 1H, H-2'), 5.14 (dd, 1H, H-3'), 4.67, 4.61, 4.57 (d, 1H, CH_2 -benzylic), 4.56 (d, 1H, H-1'), 4.52 (d, 1H, CH_2 -benzylic), 4.31 (dd, 1H, H-6a'), 4.25 (dd, 1H, H-6b'), 4.16, 4.04, 3.98, 3.88 (each s, 2H, ClAcO), 3.93-4.02 (m, 2H, H-3a, H-5'), 3.69-3.77 (m, 2H, H-2, H-3b), 3.57 (m, 2H, H-1a, H-1b);

$^3\text{J}_{1',2'} = 8.1$, $^3\text{J}_{2',3'} = 10.4$, $^3\text{J}_{3',4'} = 3.3$, $^3\text{J}_{4',5'} = 1.0$, $^3\text{J}_{5',6a'} = 6.6$, $^3\text{J}_{5',6b'} = 6.6$, $^2\text{J}_{6a',6b'} = 11.2$ Hz.

^{13}C -NMR (125 MHz, CDCl_3 + TMS): δ = 167.19, 166.78, 166.53, 166.03 (C=O, OAcCl), 138.31, 138.15 ($\text{C}_{\text{quaternary}}$ aromatic), 128.45, 127.78, 127.76, 127.68 (C-aromatic), 101.24 (C-1'), 76.81 (C-2), 73.54, 72.25 (C-benzylic), 71.90 (C-3'), 70.13 (C-5'), 70.09 (C-2'), 69.69, 69.49 (C-1, C-3), 68.61 (C-4'), 62.19 (C-6'), 40.38, 40.33, 40.22 (CH_2 , OAcCl).

3-*O*-(2',3',4',6'-tetra-*O*-chloroacetyl- β -D-galactopyranosyl)-*sn*-glycerol **106**



A mixture of 3.65 g (4.93 mmol) **105** and 0.4 g Pd/C (10%) in 120 ml ethyl acetate was stirred under one

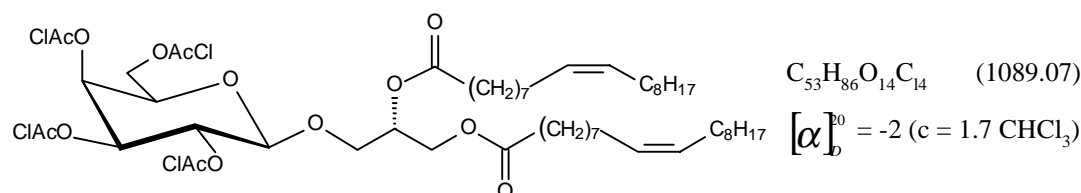
atmosphere of hydrogen until t.l.c. showed the reaction to be complete. After one day, the catalyst was filtered off and the solvent evaporated to dryness. Yield: 2.68 g (97 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 5.48 (dd, 1H, H-4'), 5.27 (dd, 1H, H-2'), 5.20 (dd, 1H, H-3'), 4.62 (d, 1H, H-1'), 4.35 (dd, 1H, H-6a'), 4.29 (dd, 1H, H-6b'), 4.19 (s, 2H, ClAcO), 4.05-4.11 (m, 5H, ClAcO, H-5'), 3.99 (s, 2H, ClAcO), 3.85-3.91 (m, 2H, H-2, H-3a), 3.79 (dd, 1H, H-3b), 3.71 (dd, 1H, H-1a), 3.62 (dd, 1H, H-1b), 1.93 (bs, 2H, -OH);

$^3\text{J}_{1',2'} = 7.6$, $^3\text{J}_{2',3'} = 10.4$, $^3\text{J}_{3',4'} = 3.5$, $^3\text{J}_{4',5'} = 1.0$, $^3\text{J}_{5',6a'} = 7.0$, $^3\text{J}_{5',6b'} = 6.3$, $^2\text{J}_{6a',6b'} = 11.4$, $^3\text{J}_{1a,2} = 3.5$, $^3\text{J}_{1b,2} = 4.4$, $^2\text{J}_{1a,1b} = 11.4$, $^3\text{J}_{3b,2} = 6.3$, $^2\text{J}_{3a,3b} = 12.9$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 167.18, 166.88, 166.52, 166.27 (C=O, OAcCl), 101.37 (C-1'), 72.63 (C-3), 71.80 (C-3'), 70.45, 70.30 (C-2, C-5'), 70.07 (C-2'), 68.60 (C-4'), 63.35 (C-1), 62.37 (C-6'), 40.42, 40.37, 40.20 (-H₂, ClAcO).

1,2-di-O-oleoyl-3-O-(2',3',4',6'-tetra-O-chloroacetyl- β -D-galactopyranosyl)-sn-glycerol 107

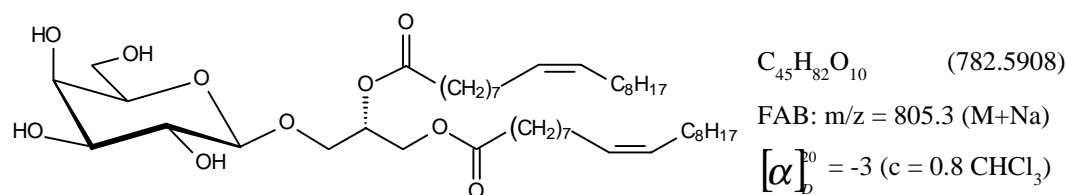


2.57 g (4.59 mmol) **106** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 4:1). Yield: 3.88 g (78 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 5.47 (dd, 1H, H-4'), 5.29-5.40 (m, 4H, H-olefinic), 5.24 (dd, 1H, H-2'), 5.18-5.23 (m, 1H, H-2), 5.17 (dd, 1H, H-3'), 4.57 (d, 1H, H-1'), 4.34 (dd, 1H, H-6a'), 4.28 (dd, 1H, H-1a), 4.26 (dd, 1H, H-6b'), 4.18 (s, 2H, ClAcO), 4.13-4.19 (m, 1H, H-1b), 4.08 (s, 4H, ClAcO), 4.04 (m, 1H, H-5'), 3.99 (s, 2H, ClAcO), 3.93 (dd, 1H, H-3a), 3.69 (dd, 1H, H-3b), 2.30 (t, 4H, α -CH₂, α' -CH₂), 1.94-2.06 (m, 8H, CH₂-allylic), 1.53-1.65 (m, 4H, β -CH₂, β' -CH₂), 1.22-1.37 (m, 40H, -CH₂-), 0.88 (t, 3H, -CH₃);

$^3\text{J}_{1',2'} = 7.6$, $^3\text{J}_{2',3'} = 10.7$, $^3\text{J}_{3',4'} = 3.1$, $^3\text{J}_{5',6a'} = 6.6$, $^3\text{J}_{5',6b'} = 6.6$, $^2\text{J}_{6a',6b'} = 11.2$, $^3\text{J}_{1a,2} = 3.6$, $^2\text{J}_{1a,1b} = 11.7$, $^3\text{J}_{3a,2} = 5.1$, $^3\text{J}_{3b,2} = 6.1$, $^2\text{J}_{3a,3b} = 11.2$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 173.33, 172.93 (C=O, oleoyl), 167.17, 166.84, 166.52, 166.00 (C=O, ClAcO), 130.06, 129.69 (C-olefinic), 101.038 (C-1'), 71.86 (C-3'), 70.35 (C-5'), 69.81 (C-2'), 69.49 (C-2), 68.56 (C-4'), 68.06 (C-3), 62.25, 62.14 (C-1, C-6'), 40.39, 40.37, 40.19 (CH₂, ClAcO), 34.92, 34.06 (C- α , C- α'), 31.92, 29.78, 29.73, 29.54, 29.35, 29.33, 29.22, 29.15, 29.12, 29.09 (C-alkyl), 27.24, 27.19 (C-allylic), 25.25 (C- β , C- β'), 22.69 (C-alkyl), 14.12 (C-methyl).

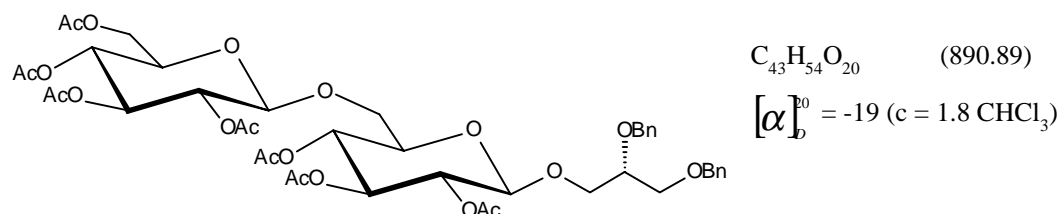
1,2-di-O-oleoyl-3-O-(β -D-galactopyranosyl)-sn-glycerol 108

A solution of 0.866 g (11.37 mmol) thiourea in 15 ml methanol was added to a solution of 2.44 g (2.24 mmol) **107** in 60 ml chloroform/methanol 3:1, and the mixture was stirred for 18 hours at ambient temperature followed by 3 hours at 50 °C. The solvent was evaporated to dryness and the residue was dissolved in chloroform, filtered and the solution again evaporated to dryness. The residue was purified by column chromatography on silica gel (chloroform-methanol 95:5) and a subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.88 g (50 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS + d_4 -MeOH): $\delta = 5.26$ -5.41 (m, 5H, H-2, H-olefinic), 4.37 (dd, 1H, H-1a), 4.26 (d, 1H, H-1'), 4.22 (dd, 1H, H-1b), 3.98 (dd, 1H, H-4'), 3.94 (dd, 1H, H-6a'), 3.92 (dd, 1H, H-3a), 3.82 (dd, 1H, H-6b'), 3.72 (dd, 1H, H-3b), 3.62 (dd, 1H, H-2'), 3.52-3.59 (m, 2H, H-3', H-5'), 2.33 (t, 2H, α - CH_2), 2.31 (t, 2H, α' - CH_2), 1.95-2.07 (m, 8H, CH_2 -allylic), 1.55-1.67 (m, 4H, β - CH_2 , β' - CH_2), 1.20-1.38 (m, 40 H, - CH_2 -), 0.88 (t, 3H, - CH_3);

$^3J_{1,2'} = 7.1$, $^3J_{2,3'} = 9.7$, $^3J_{3,4'} = 3.1$, $^3J_{4,5'} = 1.0$, $^3J_{5,6a'} = 6.6$, $^3J_{5,6b'} = 4.6$, $^2J_{6a',6b'} = 12.2$, $^3J_{1a,2} = 3.6$, $^3J_{1b,2} = 6.6$, $^2J_{1a,1b} = 12.2$, $^3J_{3a,2} = 5.6$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 11.0$ Hz.

^{13}C -NMR (400 MHz, $CDCl_3$ + TMS + d_4 -MeOH): $\delta = 173.88$, 173.62 (C=O, oleoyl), 130.064, 129.72 (C-olefinic), 104.01 (C-1'), 74.70 (C-5'), 73.40 (C-3'), 71.53 (C-2'), 70.29 (C-2), 69.35 (C-4'), 68.24 (C-3), 62.75 (C-1), 62.54 (C-6'), 34.31, 34.15 (C- α , C- α'), 31.93, 29.79, 29.75, 29.55, 29.35, 29.22, 29.16, 29.13, 29.08, 27.25, 27.20, 24.9 (C-alkyl), 22.70 (C- β , C- β'), 14.12 (C-methyl).

1,2-di-O-benzyl-3-O-[6'-O-(2'',3'',4'',6''-tetra-O-acetyl- β -D-glucopyranosyl)-2',3',4'-tri-O-acetyl- β -D-glucopyranosyl]-sn-glycerol 111

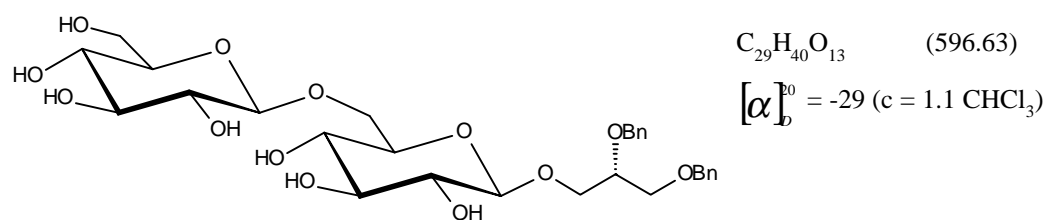
2.45 g (9.00 mmol) 1,2-di-O-benzyl-*sn*-glycerol were glycosylated with 6.10 g (9.00 mmol) gentiobiose peracetate using *General procedure 2*. The product was submitted to chromatographic purification (light petroleum (b.p. 50-70 °C)-ethyl acetate 1.5:1 \rightarrow 1.3:1). Yield: 5.69 g (71 %).

$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 7.26\text{--}7.38$ (m, 10H, H-aromatic), 5.18, 5.17 (each dd, 1H; H-3', H-3''), 5.05 (dd, 1H, H-4''), 4.98 (dd, 1H, H-2''), 4.96 (dd, 1H, H-2'), 4.90 (dd, 1H, H-4'), 4.66 (s, 2H, CH_2 -benzylic), 4.61 (d, 1H, H-1''), 4.53 (s, 2H, CH_2 -benzylic), 4.50 (d, 1H, H-1'), 4.22 (dd, 1H, H-6a''), 4.06 (dd, 1H, H-6b''), 3.99 (dd, 1H, H-3a), 3.85 (dd, 1H, H-6a'), 3.68-3.80 (m, 2H, H-2, H-3b), 3.56-3.68 (m, 4H, H-1a, H-1b, H-5', H-6b'), 3.56 (ddd, 1H, H-5''), 2.08, 2.03, 2.01, 1.95 (each s, 3H, OAc), 1.99 (s, 9H, OAc);

$^3\text{J}_{1',2'} = 8.1$, $^3\text{J}_{2',3'} = 9.7$, $^3\text{J}_{3',4'} = 9.7$, $^3\text{J}_{4',5'} = 9.7$, $^3\text{J}_{1'',2''} = 8.1$, $^3\text{J}_{2'',3''} = 9.7$, $^3\text{J}_{3'',4''} = 9.7$, $^3\text{J}_{4'',5''} = 9.7$, $^3\text{J}_{5'',6a''} = 4.6$, $^3\text{J}_{5'',6b''} = 2.5$, $^2\text{J}_{6a'',6b''} = 12.2$, $^3\text{J}_{3a,2} = 5.1$, $^3\text{J}_{3a,3b} = 9.7$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 170.62$, 170.20, 170.13, 169.61, 169.39, 169.31, 169.29 (C=O, OAc), 138.60, 138.22 (C_{quaternary} aromatic), 128.41, 128.33, 127.67, 127.65, 127.57 (C-aromatic), 100.85, 100.73 (C-1', C-1''), 76.98 (C-2), 73.46 (C-benzylic), 73.41 (C-5'), 72.81 (C-3', C-3''), 72.26 (C-benzylic), 71.86 (C-5''), 71.42, 71.13 (C-2', C-2''), 69.73 (C-1), 69.59 (C-3), 69.19 (C-4'), 68.27 (C-4''), 68.11 (C-6'), 61.75 (C-6''), 20.72, 20.65, 20.61 ($-\text{CH}_3$, OAc).

1,2-di-*O*-benzyl-3-*O*-[6'-*O*-(β -D-glucopyranosyl)- β -D-glucopyranosyl]-*sn*-glycerol **112**



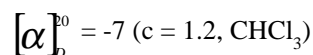
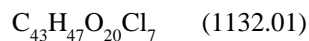
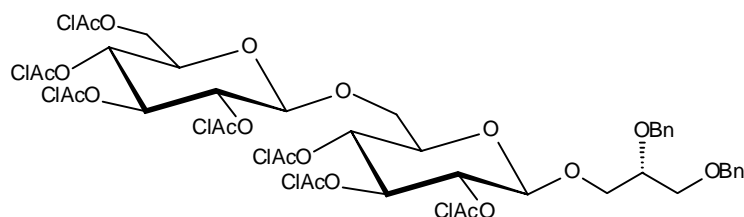
4.72 g (5.30 mmol) **111** were deprotected using *General procedure 3*. Yield: 3.09 g (98 %).

$^1\text{H-NMR}$ (400 MHz, MeOH): $\delta = 7.28\text{--}7.44$ (m, 10H, H-aromatic), 4.75, 4.71 (each d, 1H, CH_2 -benzylic), 4.59 (s, 2H, CH_2 -benzylic), 4.42, 4.32 (each d, 1H; H-1', H-1''), 4.19 (dd, 1H, H-6a'), 4.04 (dd, 1H, H-3a), 3.89-3.94 (m, 1H, H-2), 3.89 (dd, 1H, H-6a''), 3.82 (dd, 1H, H-6b'), 3.78 (dd, 1H, H-3b), 3.65-3.75 (m, 3H, H-1a, H-1b, H-6b'), 3.21-3.51 (m, 8H, H-2', H-3', H-4', H-5', H-2'', H-3'', H-4'', H-5'');

$^3\text{J}_{1',2'} = 7.6$, $^3\text{J}_{5',6a'} = 2.0$, $^3\text{J}_{5',6b'} = 5.6$, $^2\text{J}_{6a',6b'} = 11.7$, $^3\text{J}_{1'',2''} = 8.1$, $^3\text{J}_{5'',6a''} = 2.0$, $^2\text{J}_{6a'',6b''} = 12.2$, $^3\text{J}_{3a,2} = 4.6$, $^3\text{J}_{3b,2} = 5.1$, $^2\text{J}_{3a,3b} = 10.7$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, MeOH): $\delta = 139.86$, 139.72 (C_{quaternary} aromatic), 129.40, 129.37, 129.20, 128.91, 128.73, 128.68 (C-aromatic), 104.93, 104.76 (C-1', C-1''), 78.74 (C-2), 77.07 (C-5'), 75.13, 75.10 (C-2', C-2''), 74.37, 73.32 (C-benzylic), 71.38 (C-1), 70.22 (C-3), 69.90 (C-6'), 62.78 (C-6''), 78.05, 78.01, 77.84, 71.62, 71.50 (C-3', C-4', C-3'', C-4'', C-5'').

1,2-di-*O*-benzyl-3-*O*-[6'-*O*-(2'',3'',4'',6''-tetra-*O*-chloroacetyl- β -D-glucopyranosyl)-2',3',4'-tri-*O*-chloroacetyl- β -D-glucopyranosyl]-*sn*-glycerol 113



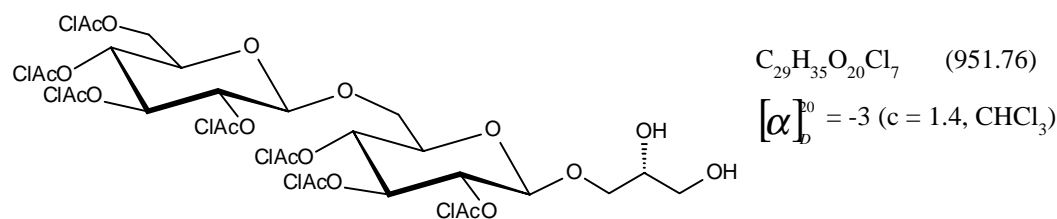
1.16 g (13.81 mmol) sodium hydrogen carbonate were added under nitrogen to a solution of 3.0 g (5.02 mmol) **112** and 8.07 g (47.18 mmol) chloroacetic acid anhydride in 30 ml dry N,N-dimethylformamide and the suspension was stirred for 4.5 hours at ambient temperature. After t.l.c. showed the reaction to be complete, the suspension was diluted with 100 ml ethyl acetate, poured into 150 ml of ice-water and stirred for an additional 30 minutes. The phases were separated and the aqueous layer was extracted twice with 100 ml ethyl acetate and the combined organic phases were washed twice with a saturated solution of sodium hydrogen carbonate and once with water. After drying (MgSO_4) the solvent was removed *in vacuo* and the resulting residue submitted to purification by column chromatography (light petroleum (b.p. 50-70 °C)-ethyl acetate 2:1). Yield: 4.71 g (83 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 7.27-7.39 (m, 10H, H-aromatic), 5.30 (dd, 1H, H-3''), 5.27 (dd, 1H, H-3'), 5.13 (dd, 1H, H-4''), 5.07 (dd, 1H, H-4'), 5.06 (dd, 1H, H-2''), 5.04 (dd, 1H, H-2'), 4.66 (d, 1H, CH_2 -benzylic), 4.64 (d, 1H, H-1''), 4.63 (d, 1H, CH_2 -benzylic), 4.56 (d, 1H, H-1'), 4.56, 4.52 (d, 1H, CH_2 -benzylic), 4.24-4.32 (m, 2H, H-6a'', H-6b''), 3.91-4.12 (m, 14H, ClAcO, H-3a, H-6a'), 3.88 (s, 2H, ClAcO), 3.72 (m, 2H, H-2, H-3b), 3.59-3.71 (m, H-5', H-5'', H-6b'), 3.53-3.59 (m, 2H, H1a, H-1b);

$^3\text{J}_{1',2'} = 7.9$, $^3\text{J}_{2',3'} = 9.5$, $^3\text{J}_{3',4'} = 9.5$, $^3\text{J}_{4',5'} = 9.5$, $^3\text{J}_{1'',2''} = 7.9$, $^3\text{J}_{2'',3''} = 9.5$, $^3\text{J}_{3'',4''} = 9.5$, $^3\text{J}_{4'',5''} = 9.5$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 166.98, 166.87, 166.21, 166.14, 166.02 (C=O, OAc), 138.43, 138.11 (C_{quaternary} aromatic), 128.47, 128.44, 127.80, 127.76, 127.73, 127.70 (C-aromatic), 100.60 (C-1'), 100.02 (C-1''), 77.00 (C-2), 73.97, 73.75 (C-3', C-3''), 73.52 (C-benzyl), 72.47 (C-2', C-2''), 72.37 (C-benzyl), 72.07, 71.35 (C-5', C-5''), 70.13 (C-4'), 70.03 (C-3), 69.43 (C-1, C-4''), 67.34 (C-6'), 62.74 (C-6''), 40.56, 40.41, 40.31, 40.26, 40.16 (C=O, ClAcO).

3-*O*-[6'-*O*-(2'',3'',4'',6''-tetra-*O*-chloroacetyl- β -D-glucopyranosyl)-2',3',4'-tri-*O*-chloroacetyl- β -D-glucopyranosyl]-*sn*-glycerol **114**



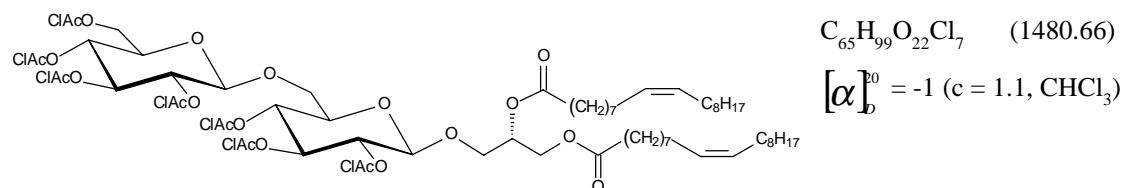
A mixture of 2.64 g (2.33 mmol) **113** and 0.15 g Pd/C (10%) in 40 ml ethyl acetate was stirred under one atmosphere of hydrogen until t.l.c. showed the reaction to be complete. After one day the catalyst was filtered off and the solvent evaporated to dryness. Yield: 2.20 g (99 %).

1H -NMR (500 MHz, $CDCl_3$ + TMS): δ = 5.36 (dd, 1H, H-3''), 5.33 (dd, 1H, H-3'), 5.19 (dd, 1H, H-4''), 5.10 (dd, 1H, H-2''), 5.08 (dd, 1H, H-2'), 5.07 (dd, 1H, H-4'), 4.71 (d, 1H, H-1''), 4.62 (d, 1H, H-1'), 4.41 (dd, 1H, H-6a''), 4.32 (dd, 1H, H-6b''), 3.97-4.16 (m, 14H, ClAcO), 3.94 (dd, 1H, H-6a'), 3.77-3.89 (m, 5H, H-2, H-3a, H-3b, H-5', H-5''), 3.72 (dd, 1H, H-1a), 3.68 (dd, 1H, H-6b'), 3.57 (dd, 1H, H-1b);

$^3J_{1,2'} = 7.9$, $^3J_{2',3'} = 9.5$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.5$, $^3J_{5',6a'} = 1.7$, $^3J_{5',6b'} = 3.6$, $^2J_{6a',6b'} = 11.0$, $^3J_{1'',2''} = 7.9$, $^3J_{2'',3''} = 9.5$, $^3J_{3'',4''} = 9.5$, $^3J_{4'',5''} = 9.5$, $^3J_{5'',6a''} = 1.9$, $^3J_{5'',6b''} = 4.4$, $^2J_{6a'',6b''} = 12.3$, $^3J_{1a,2} = 3.6$, $^3J_{1b,2} = 4.6$, $^2J_{1a,1b} = 11.5$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): δ = 167.06, 166.92, 166.46, 166.14 (C=O, OAc), 100.86 (C-1'), 99.66 (C-1''), 73.79, 73.77 (C-3', C-3''), 73.30 (C-3), 72.68 (C-5'), 72.39, 72.11 (C-2', C-2''), 71.49 (C-5''), 70.64 (C-2), 69.93 (C-4'), 69.43 (C-4''), 66.94 (C-6'), 63.19 (C-1), 62.78 (C-6''), 40.62, 40.58, 40.36, 40.27, 40.28, 40.26, 40.12 (C=O, ClAcO).

1,2-di-*O*-oleoyl-3-*O*-[6'-*O*-(2'',3'',4'',6''-tetra-*O*-chloroacetyl- β -D-glucopyranosyl)-2',3',4'-tri-*O*-chloroacetyl- β -D-glucopyranosyl]-*sn*-glycerol **115**



2.11 g (2.21 mmol) **114** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 4:1). Yield: 2.16 g (66 %).

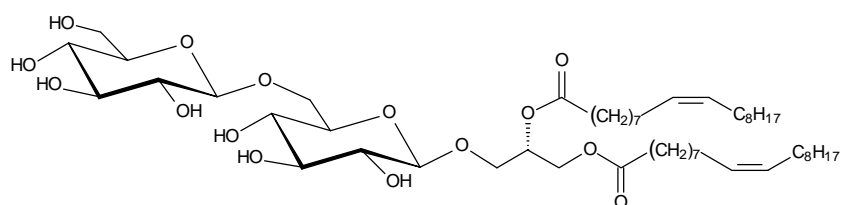
1H -NMR (500 MHz, $CDCl_3$ + TMS): δ = 5.30-5.40 (m, 5H, H-3'', H-olefinic), 5.30 (dd, 1H, H-3'), 5.18 (dd, 1H, H-4''), 5.15-5.22 (m, 1H, H-2), 5.09 (dd, 1H, H-4'), 5.08 (dd, 1H, H-2''), 5.02 (dd, 1H, H-2'), 4.64 (d, 1H, H-1''), 4.57 (d, 1H, H-1'), 4.39 (dd, 1H, H-6a''), 4.35 (dd, 1H, H-6b''), 4.27 (dd, 1H, H-1a), 3.92-4.18 (m, 17H, ClAcO, H-1b, H-3a, H-6a'), 3.84 (ddd, 1H, H-5''), 3.74 (ddd, 1H, H-5'), 3.66 (dd, 1H, H-3b), 3.65 (dd,

1H, H-6b'), 2.31 (t, 2H, α -CH₂), 2.30 (t, 2H, α' -CH₂), 1.98-2.05 (m, 8H, CH₂-allylic), 1.57-1.64 (m, 4H, β -CH₂, β' -CH₂), 1.25-1.36 (m, 40 H, -CH₂-), 0.88 (t, 6H, -CH₃);

³J_{1,2'} = 7.9, ³J_{2,3'} = 9.5, ³J_{3,4'} = 9.5, ³J_{4,5'} = 9.5, ³J_{5,6a'} = 2.0, ³J_{5,6b'} = 5.4, ²J_{6a',6b'} = 11.0, ³J_{1'',2''} = 7.9, ³J_{2'',3''} = 9.5, ³J_{3'',4''} = 9.5, ³J_{4'',5''} = 9.5, ³J_{5'',6a''} = 2.1, ³J_{5'',6b''} = 4.1, ²J_{6a'',6b''} = 12.3, ³J_{1a,2} = 3.2, ²J_{1a,1b} = 12.0, ³J_{3b,2} = 5.7, ²J_{3a,3b} = 11.0 Hz.

¹³C-NMR (125 MHz, CDCl₃ + TMS): δ = 173.37, 173.03 (C=O, oleoyl), 166.63, 166.60, 166.52, 165.88, 165.85, 165.82 (C=O, OAc), 130.05, 129.71 (C-olefinic), 100.84 (C-1'), 100.37 (C-1''), 73.86 (C-3'), 73.72 (C-3''), 72.44 (C-5'), 72.24 (C-2'), 72.12 (C-2''), 71.49 (C-5''), 69.98 (C-4'), 69.55, 69.46 (C-2, C-4''), 67.92 (C-3), 67.29 (C-6'), 62.79 (C-6''), 62.16 (C-1), 40.59, 40.44, 40.37, 40.32, 40.30, 40.26, 40.17 (ClAcO), 34.22, 34.05 (C- α , C- α'), 31.91, 29.78, 29.75, 29.54, 29.33, 29.24, 29.18, 29.13, 29.11 (C-alkyl), 27.25, 27.20 (C-allylic), 24.89 (C- β , C- β'), 22.68 (C-alkyl), 14.12 (C-methyl).

1,2-di-O-oleoyl-3-O-[6'-O-(β -D-glucopyranosyl)- β -D-glucopyranosyl]-sn-glycerol **116**



C₅₁H₉₂O₁₅ (944.6436)

FAB: m/z = 967.2 (M+Na)

$[\alpha]_D^{20} = -21$ (c = 1.1, CHCl₃)

A solution of 0.62 g (8.17 mmol) thiourea in 12 ml methanol was added to a solution of 1.24 g (0.84 mmol) **115** in 40 ml chloroform/methanol 3:1, and the mixture was stirred for 20 hours at ambient temperature and finally for 3.5 hours at 50 °C. The solvent was evaporated to dryness and the residue was extracted with chloroform, filtered and the solution again evaporated to dryness. The residue was purified by column chromatography on silica gel (chloroform-methanol 88:12) and a subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.55 g (69 %).

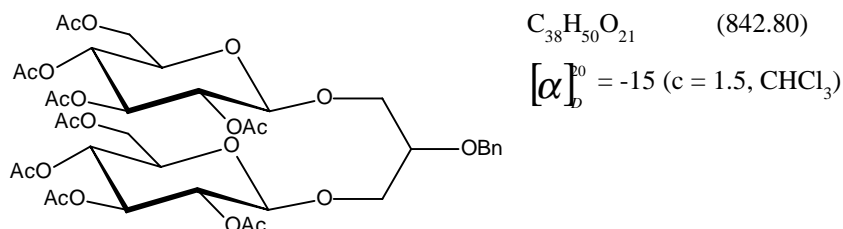
¹H-NMR (400 MHz, d₄-MeOH + TMS): δ = 5.30-5.40 (m, 4H, H-olefinic), 5.23-5.30 (m, 1H, H-2), 4.43 (dd, 1H, H-1a), 4.36 (d, 1H, H-1''), 4.28 (d, 1H, H-1'), 4.21 (dd, 1H, H-1b), 4.16 (dd, 1H, H-6a'), 3.98 (dd, 1H, H-3a), 3.87 (dd, 1H, H-6a''), 3.72-3.80 (m, 2H, H-3b, H-6b'), 3.67 (dd, 1H, H-6b''), 3.41-3.49 (m, 1H, H-5'), 3.25-3.49 (m, 5H, H-3', H-4', H-3'', H-4'', H-5''), 3.22, 3.18 (each dd, 1H; H-2', H-2''), 2.33 (t, 2H, α -CH₂), 2.32 (t, 2H, α' -CH₂), 1.97-2.09 (m, 8H, CH₂-allylic), 1.55-1.66 (m, 4H, β -CH₂, β' -CH₂), 1.24-1.39 (m, 40H, -CH₂-), 0.90 (t, 6H, -CH₃);

³J_{1,2'} = 7.6, ³J_{2,3'} = 9.2, ³J_{5,6a'} = 1.5, ²J_{6a',6b'} = 11.7, ³J_{1'',2''} = 7.6, ³J_{2'',3''} = 9.2, ³J_{5'',6a''} = 1.5, ³J_{15'',6b''} = 5.1, ²J_{6a'',6b''} = 11.7, ³J_{1a,2} = 3.1, ³J_{1b,2} = 6.6, ²J_{1a,1b} = 12.2, ³J_{3a,2} = 5.6, ²J_{3a,3b} = 11.2 Hz.

¹³C-NMR (100 MHz, d₄-MeOH + TMS): δ = 175.06, 174.84 (C=O, oleoyl), 130.95, 130.81 (C-olefinic), 104.99 (C-1'), 104.71 (C-1''), 78.05, 77.88, 71.81, 71.65, 71.50 (C-2, C-3', C-4', C-3'', C-4'', C-5''), 77.16 (C-5'), 75.14, 74.97 (C-2', C-2''), 70.03 (C-6'), 68.98 (C-1), 64.06 (C-3), 62.82 (C-6''), 35.23, 35.01 (C- α , C- α'), 33.10, 30.90, 30.66, 30.50, 30.41, 30.29, 30.26, 30.24, 30.22 (C-alkyl), 28.20 (C-allylic), 26.09, 26.07 (C- β ,

C-β'), 23.78 (C-alkyl), 14.51 (C-methyl).

1,3-di-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-2-*O*-benzyl-*sn*-glycerol **117**



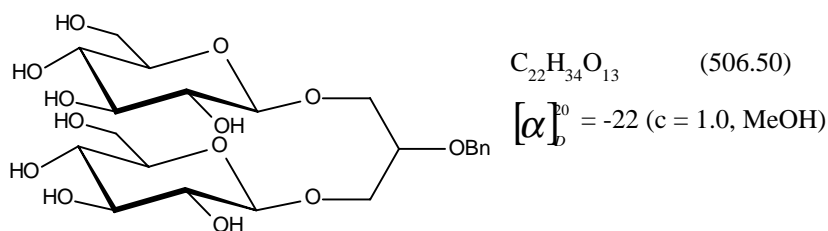
2.00 g (10.97 mmol) 2-benzyloxy-1,3-propanediol were glycosylated with 9.84 g (23.94 mmol) acetobromoglucose using *General procedure 4*. The product was purified by silica gel chromatography (light petroleum (b.p. 50-70 °C)-ethyl acetate 1:1). Yield: 4.23 g (46%).

1H -NMR (500 MHz, $CDCl_3$ + TMS): $\delta = 7.27$ -7.38 (m, 5H, H-aromatic), 5.20, 5.197 (each dd, 1H; H-3', H-3''), 5.09, 5.08 (each dd, 1H; H-4' H-4''), 5.02, 4.99 (each dd, 1H; H-2', H-2''), 4.63, 4.59 (each d, 1H; CH_2 -benzylic), 4.56, 4.51 (each d, 1H; H-1', H-1''), 4.27, 4.25 (each dd, 1H; H-6a', H-6a''), 4.11, 4.13 (each dd, 1H; H-6b', H-6b''), 3.96, 3.88 (each dd, 1H; H-1a, H-3a), 3.75 (m, 1H, H-2), 3.59-3.71 (m, 4H, H-1b, H-3b, H-5', H-5''), 2.08, 2.07 (each 2, 3H; OAc), 2.03 (s, 6H, OAc), 2.01 (s, 9H, OAc), 1.95 (s, 3H, OAc);

$^3J_{1',2'} = 8.1$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4',5'} = 9.7$, $^3J_{5',6a'} = 4.6$, $^3J_{5',6b'} = 2.6$, $^2J_{6a',6b'} = 12.2$, $^3J_{1'',2''} = 8.1$, $^3J_{2'',3''} = 9.7$, $^3J_{3'',4''} = 9.7$, $^3J_{4'',5''} = 9.7$, $^3J_{5'',6a''} = 4.6$, $^3J_{5'',6b''} = 2.6$, $^2J_{6a'',6b''} = 12.2$, $^3J_{1a,2} = 3.1$, $^2J_{1a,1b} = 10.7$, $^3J_{3a,2} = 3.1$, $^2J_{3a,3b} = 10.7$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): $\delta = 170.66$, 170.26, 170.24, 169.42, 169.31, 169.28 (C=O, OAc), 138.31 ($C_{\text{quaternary}}$ aromatic), 128.43, 127.74, 127.59 (C-aromatic), 101.20, 101.12 (C-1', C-1''), 77.28 (C-2), 72.86, 72.70 (C-3', C-3''), 72.42 (C-benzylic), 71.87 (C-5', C-5''), 71.37, 71.29 (C-2', C-2''), 70.34, 69.21 (C-1, C-3), 68.38 (C-4', C-4''), 61.88 (C-6', C-6''), 20.74 20.60 (- CH_3 , OAc).

1,3-di-*O*-(β-*D*-glucopyranosyl)-2-*O*-benzyl-*sn*-glycerol **118**



4.07 g (4.83 mmol) **117** were deprotected using *General procedure 3*. Yield: 2.27 g (93 %).

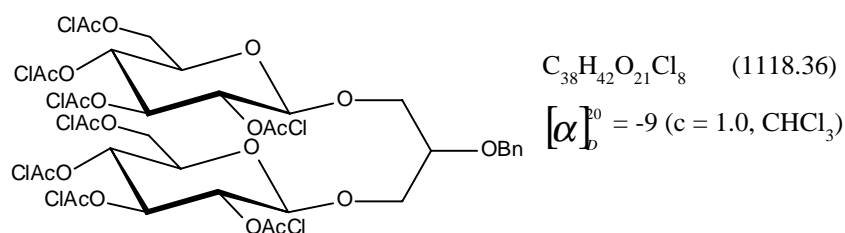
1H -NMR (400 MHz, MeOH): $\delta = 7.28$ -7.48 (m, 5H, H-aromatic), 4.77, 4.73 (each d, 1H; CH_2 -benzylic), 4.38, 4.35 (each d, 1H; H-1', H-1''), 4.13, 4.05 (each dd, 1H; H-1a, H-3a), 3.86-3.98 (m, 3H, H-2, H-6a', H-6a''),

3.82, 3.81 (each dd, 1H; H-1b, H-3b), 3.66-3.73 (m, 2H, H-6b', H-6b''), 3.28-3.43 (m, 6H, H-3', H-4', H-5', H-3'', H-4'', H-5''), 3.23, 3.25 (each dd, 1H; H-2', H-2'');

$^3J_{1,2'} = 7.6$, $^3J_{2,3'} = 9.2$, $^3J_{1'',2''} = 7.6$, $^3J_{2'',3''} = 9.2$ Hz.

^{13}C -NMR (400 MHz, MeOH): $\delta = 139.76$ (C_{quaternary} aromatic), 129.39, 128.82 (C-aromatic), 104.84, 104.71 (C-1', C-1''), 78.79 (C-2), 78.08, 78.02, 71.70 (C-3', C-4', C-5', C-3'', C-4'', C-5''), 75.16 (C-2', C-2''), 73.32 (C-benzylic), 70.20, 69.64 (C-1, C-3), 62.83 (C-6', C-6'').

1,3-di-O-(2',3',4',6'-tetra-O-chloroacetyl- β -D-glucopyranosyl)-2-O-benzyl-*sn*-glycerol **119**

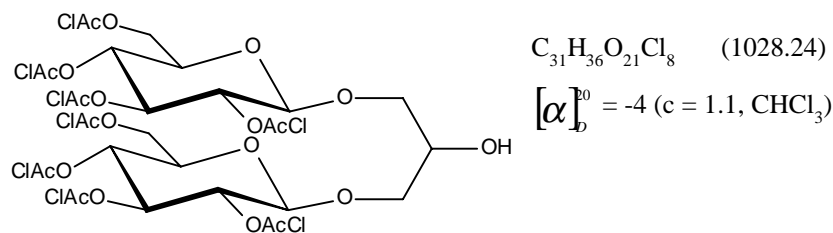


1.69 g (20.12 mmol) sodium hydrogen carbonate were added under nitrogen to a solution of 2.16 g (4.26 mmol) **118** and 11.65 g (68.14 mmol) chloroacetic acid anhydride in 45 ml dry N,N-dimethylformamide and the suspension was stirred for 5 hours at ambient temperature. After t.l.c. showed the reaction to be complete, the suspension was diluted with 100 ml ethyl acetate, poured into 150 ml of ice-water and stirred for an additional 30 minutes. The phases were separated and the aqueous layer was extracted twice with 100 ml ethyl acetate and the combined organic phases were washed twice with a saturated solution of sodium hydrogen carbonate and once with water. After drying (MgSO_4) the solvent was removed *in vacuo* and the resulting residue submitted to purification by column chromatography (light petroleum (b.p. 50-70 °C)-ethyl acetate 1.6:1). Yield: 2.20 g (46 %).

^1H -NMR (500 MHz, CDCl_3 + TMS): $\delta = 7.28$ -7.41 (m, 5H, H-aromatic), 5.33, 5.34 (each dd, 1H; H-3', H-3''), 5.17, 5.18 (each dd, 1H; H-4', H-4''), 5.05, 5.08 (each dd, 1H; H-2', H-2''), 4.63, 4.56 (each d, 1H; H-1', H-1''), 4.61, 4.56 (each d, 1H; CH_2 -benzylic), 4.29-4.38 (m, 4H, H-6a', H-6b', H-6a'', H-6b''), 4.11, 4.12 (each s, 2H; ClAcO), 3.88-4.03 (m, 14H, H-1a, H-3a, ClAcO), 3.76-3.85 (m, 2H, H-5', H-5''), 3.72 (m, 1H, H-2), 3.64, 3.65 (each dd, 1H; H-1b, H-3b);

$^3J_{1,2'} = 7.9$, $^3J_{2,3'} = 9.8$, $^3J_{3,4'} = 9.8$, $^3J_{4,5'} = 9.8$, $^3J_{1'',2''} = 7.9$, $^3J_{2'',3''} = 9.8$, $^3J_{3'',4''} = 9.8$, $^3J_{4'',5''} = 9.8$ Hz.

^{13}C -NMR (125 MHz, CDCl_3 + TMS): $\delta = 167.02$, 166.97, 166.92, 166.90, 166.29, 166.11, 166.05 (C=O, ClAcO), 137.98 (C_{quaternary} aromatic), 128.58, 128.02, 127.61 (C-aromatic), 101.01, 100.60 (C-1', C-1''), 76.64 (C-2), 73.85, 73.57 (C-3', C-3''), 72.51, 72.46 (C-2', C-2''), 72.48 (C-benzylic), 71.33, 71.29 (C-5', C-5''), 70.11, 69.39 (C-1, C-3), 69.61 (C-4', C-4''), 63.02, 62.99 (C-6', C-6''), 40.61, 40.56, 40.43, 40.30, 40.27, 40.20 (ClAcO).

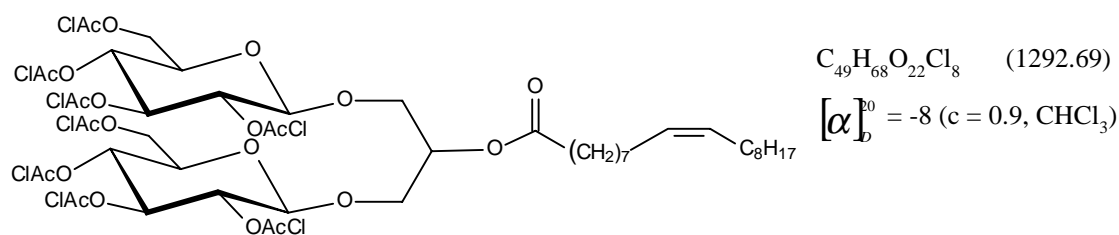
1,3-di-*O*-(2',3',4',6'-tetra-*O*-chloroacetyl- β -D-glucopyranosyl)-*sn*-glycerol 120

A mixture of 2.09 g (1.87 mmol) **119** and 0.15 g Pd/C (10%) in 40 ml ethyl acetate was stirred under one atmosphere of hydrogen until t.l.c. showed the reaction to be complete. After one day the catalyst was filtered off and the solvent evaporated to dryness. Yield: 1.83 g (95 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): δ = 5.36 (dd, 2H, H-3', H-3''), 5.17 (dd, 2H, H-4', H-4''), 5.08, 5.07 (each dd, 1H; H-2', H-2''), 4.64, 4.62 (each d, 1H; H-1', H-1''), 4.32-4.40 (m, 4H, H-6a', H-6b', H-6a'', H-6b''), 4.14 (m, 4H, ClAcO), 4.07 (m, 4H, ClAcO), 4.03 (m, 4H, ClAcO), 4.00 (s, 4H, ClAcO), 3.76-3.93 (m, 5H, H-1a, H-2, H-3a, H-5', H-5''), 3.65-3.75 (m, 2H, H-1b, H-3b);

$^3J_{1',2'} = 7.6$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.7$, $^3J_{4',5'} = 9.7$, $^3J_{1'',2''} = 8.1$, $^3J_{2'',3''} = 9.7$, $^3J_{3'',4''} = 9.7$, $^3J_{4'',5''} = 9.7$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): δ = 167.01, 166.89, 166.88, 166.28, 166.18, 166.13 (C=O, ClAcO), 100.95, 100.84 (C-1', C-1''), 73.63 (C-3', C-3''), 72.46, 72.44 (C-2', C-2''), 71.74, 71.29 (C-1, C-3), 71.39, 71.35 (C-5', C-5''), 69.59 (C-4', C-4''), 69.01 (C-2), 63.00 (C-6', C6''), 40.57, 40.47, 40.40, 40.26, 40.17 (- CH_3 , ClAcO).

1,3-di-*O*-(2',3',4',6'-tetra-*O*-chloroacetyl- β -D-glucopyranosyl)-2-*O*-oleoyl-*sn*-glycerol 121

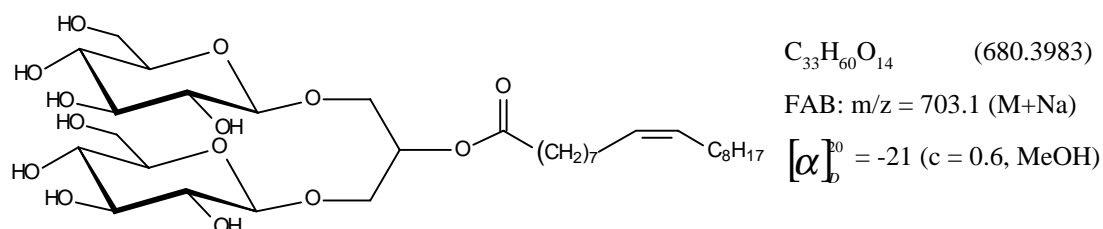
1.72 g (1.67 mmol) **120** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 2.1:1). Yield: 1.21 g (56 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): δ = 5.28-5.40 (m, 4H, H-olefinic, H-3', H-3''), 5.16, 5.18 (each dd, 1H; H-4', H-4''), 5.05, 5.07 (each dd, 1H, H-2', H-2''), 5.04-5.09 (m, 1H, H-2), 4.58, 4.60 (each d, 1H; H-1', H-1''), 4.30-4.41 (m, 4H, H-6a', H-6b', H-6a'', H-6b''), 4.15, 4.14, 4.02, 4.01 (each s, 2H; ClAcO), 4.04-4.08 (m, 4H, ClAcO), 3.99 (s, 4H, ClAcO), 3.92, 3.84 (each dd, 1H; H-1a, H-3a), 3.80-3.90 (m, 2H, H-5', H,5''), 3.72,

3.69 (each dd, 1H; H-1b, H-3b), 2.30 (t, 2H, α -CH₂), 1.97-2.05 (m, 4H, CH₂-allylic), 1.59 (m_c, 2H, β -CH₂), 1.23-1.38 (m, 20 H, -CH₂-), 0.88 (t, 3H, -CH₃);

¹³C-NMR (125 MHz, CDCl₃ + TMS): δ = 173.09 (C=O, oleoyl), 167.04, 167.01, 166.91, 166.88, 166.27, 166.08, 166.02 (C=O; ClAcO), 130.07, 129.72 (C-olefinic), 100.76, 100.44 (C-1', C-1''), 73.69, 73.61 (C-3', C-3''), 72.41, 72.37 (C-2', C-2''), 71.42, 71.37 (C-5', C-5''), 70.31 (C-2), 69.62, 69.59 (C-4', C-4''), 68.18, 67.82 (C-1, C-3), 63.03, 62.99 (C-6', C-6''), 40.59, 40.40, 40.38, 40.26, 40.17 (-CH₂, ClAcO), 34.16 (α -CH₂), 30.15, 29.78, 29.74, 29.54, 29.32, 29.22, 29.16, 29.12 (C-alkyl), 27.25, 27.20 (C-allylic), 24.84 (C- β), 22.69 (C-alkyl), 14.12 (C-methyl).

1,3-di-O-(β -D-glucopyranosyl)-2-O-oleoyl-*sn*-glycerol **122**



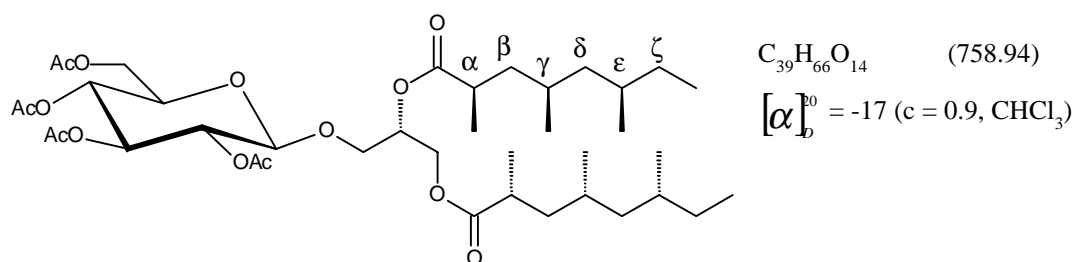
A solution of 0.687 g (9.03 mmol) thiourea in 12 ml methanol was added to a solution of 1.15 g (0.89 mmol) **121** in 40 ml chloroform/methanol 3:1, and the mixture was stirred for 24 hours at ambient temperature followed by 3 hours at 50 °C. The solvent was evaporated to dryness and the residue was purified by column chromatography on silica gel (chloroform-methanol 80:20) and a subsequent gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.23 g (38 %).

¹H-NMR (400 MHz, MeOD): δ = 5.33-5.44 (m, 2H, H-olefinic), 5.24 (H-2), 4.34, 4.35 (each d, 1H; H-1', H-1''), 4.10, 4.03 (each dd, 1H; H-1a, H-3a), 3.80, 3.93 (m, 4H, H-1b, H-3b, H-6a', H-6a''), 3.65-3.73 (m, 2H, H-6b', H-6b''), 3.26-3.41 (m, 6H, H-3', H-4', H-5', H-3'', H-4'', H-5''), 3.22, 3.20 (each dd, 1H; H-2', H-2''), 2.39 (t, 2H, α -CH₂), 2.03-2.12 (m, 4H, CH₂-allylic), 1.65 (m_c, 2H, β -CH₂), 1.30-1.42 (m, 20H, -CH₂-), 0.94 (t, 3H, -CH₃);

³J_{1',2'} = 7.6, ³J_{2',3'} = 9.2, ³J_{1'',2''} = 7.6, ³J_{2'',3''} = 9.2, ³J_{1a,2} = 4.1, ²J_{1a,1b} = 11.2, ³J_{3a,2} = 5.6, ²J_{3a,3b} = 10.7 Hz.

¹³C-NMR (100 MHz, MeOD): δ = 175.63 (C=O, oleoyl), 131.30, 131.22 (C-olefinic), 105.31, 105.10 (C-1', C-1''), 78.45, 78.42, 78.38, 72.03 (C-3', C-4', C-5', C-3'', C-4'', C-5''), 75.44 (C-2', C-2''), 73.51 (C-2), 69.69 (C-1), 69.18 (C-3), 63.22, 63.20 (C-6', C-6''), 35.58 (C- α), 33.47, 31.25, 31.02, 30.85, 30.76, 30.63, 30.61 (C-alkyl), 28.53, 26.38 (C-allylic), 24.15 (C- β), 14.86 (C-methyl).

1,2-di-*O*-[(2'*R*,4'*R*,6'*R*)-2',4',6'-trimethyloctanoyl]-3-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- β -D-glucopyranosyl)-*sn*-glycerol 123



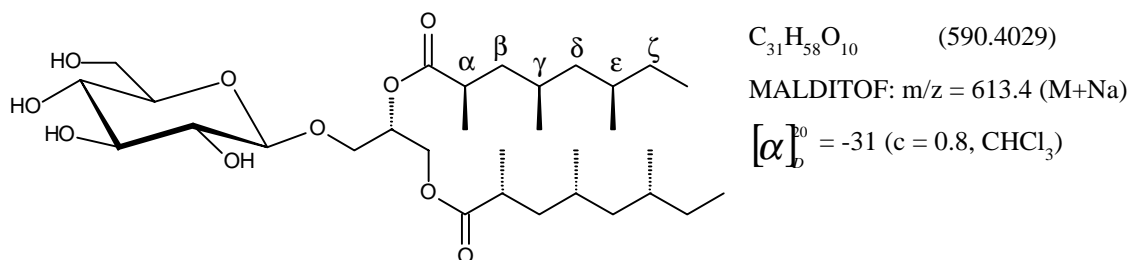
1.00 g (2.37 mmol) **62** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 3:1). Yield: 1.68 g (93 %).

1H -NMR (500 MHz, $CDCl_3$ + TMS): δ = 5.19 (dd, 1H, H-3'), 5.16-5.23 (m, 1H, H-2), 5.08 (dd, 1H, H-4'), 4.98 (dd, 1H, H-2'), 4.52 (d, 1H, H-1'), 4.32 (dd, 1H, H-1a), 4.26 (dd, 1H, H-6a'), 4.13 (dd, 1H, H-6b'), 4.12 (dd, 1H, H-1b), 3.96 (dd, 1H, H-3a), 3.68 (ddd, 1H, H-5'), 3.66 (dd, 1H, H-3b), 2.56 (m, 2H, H- α , H- α'), 2.09, 2.05, 2.02, 2.00 (s, 3H, OAc), 1.72 (ddd, 1H, H- β a), 1.70 (ddd, 1H, H- β a'), 1.38-1.54 (m, 4H, H- γ , H- γ' , H- ϵ , H- ϵ'), 1.28-1.38 (dd, 2H, H- ζ a, H- ζ a'), 1.16-1.23 (m, 2H, H- δ a, H- δ a'), 1.13, 1.14 (each d, 3H; - CH_3 - α , - CH_3 - α'), 1.02-1.11 (m, 4H, H- β b, H- β b', H- ζ b, H-b'), 0.88-0.96 (m, 2H, H- δ b, H- δ b'), 0.81-0.88 (m, 18H, - CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ' , - CH_3 - ζ , - CH_3 - ζ');

$^3J_{1',2'} = 7.9$, $^3J_{2',3'} = 9.5$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.6$, $^3J_{5',6a'} = 4.7$, $^3J_{5',6b'} = 2.2$, $^2J_{6a',6b'} = 12.3$, $^3J_{1a,2} = 3.5$, $^3J_{1b,2} = 6.0$, $^2J_{1a,1b} = 12.0$, $^3J_{3a,2} = 5.0$, $^3J_{3b,2} = 5.7$, $^2J_{3a,3b} = 11.0$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): δ = 176.42, 175.93 (C=O, oleoyl), 170.65, 170.25, 169.37, 169.19 (C=O, OAc), 101.13 (C-1'), 72.74 (C-3'), 71.96 (C-5'), 71.13 (C-2'), 69.64 (C-2), 68.33 (C-4'), 67.79 (C-3), 62.15 (C-1), 61.86 (C-6'), 44.74, 44.70 (C- δ , C- δ'), 41.24, 41.16 (C- β , C- β'), 37.30, 37.20 (C- α , C- α'), 31.44, 31.42 (C- ϵ , C- ϵ'), 29.23, 29.16 (C- ζ , C- ζ'), 28.16, 28.14 (C- γ , C- γ'), 20.70, 20.59, 20.27, 20.25, 19.65, 19.61 (- CH_3 , OAc, - CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ'), 18.08 (- CH_3 - α , - CH_3 - α'), 11.22, 11.20 (- CH_3 - ζ , - CH_3 - ζ').

1,2-di-*O*-[(2'*R*,4'*R*,6'*R*)-2',4',6'-trimethyloctanoyl]-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol 124



1.60 g (2.10 mmol) **123** were dissolved in a mixture of 30 ml dry methanol and 10 ml dry dichloromethane.

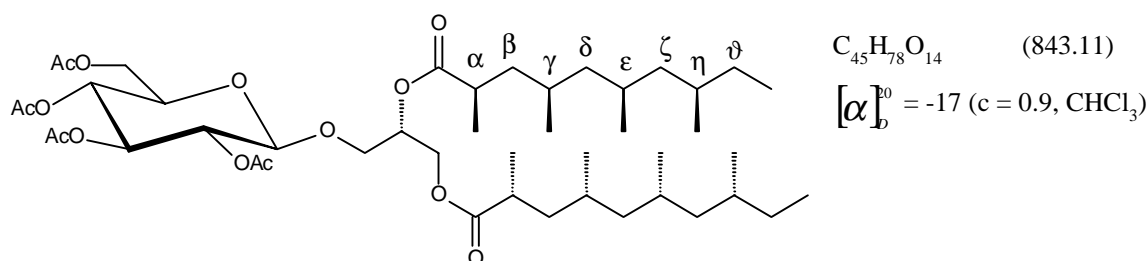
0.82 ml (16.8 mmol) hydrazine hydrate (100%) were added to this solution and the mixture was heated at the temperature of reflux for 8 hours. The solution was cooled in an ice-bath, neutralised with formic acid and the solvent removed *in vacuo*. The residue was submitted to chromatographic purification on silica gel (chloroform-methanol 30:1) and gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.61 g (49 %).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 + TMS): δ = 5.27 (m, 1H, H-2), 4.40 (dd, 1H, H1a), 4.30 (d, 1H, H-1'), 4.19 (dd, 1H, H-1b), 3.90 (dd, 1H, H-3a), 3.87 (dd, 1H, H-6a'), 3.80 (dd, 1H, H-6b'), 3.70 (dd, 1H, H-3b), 3.45-3.56 (m, 2H, H-3', H-4'), 3.25-3.36 (m, 2H, H-2', H-5'), 2.51-2.64 (m, 2H, H- α , H- α'), 1.64-1.76 (m, 2H, H- β a, H- β a'), 1.36-1.54 (m, 4H, H- γ , H- γ' , H- ϵ , H- ϵ'), 1.27-1.37 (m, 2H, H- ζ a, H- ζ a'), 1.00-1.22 (m, 12H, H- β b, H- β b', H- δ a, H- δ a', H- ζ b, H- ζ b', - CH_3 - α , - CH_3 - α'), 0.76-0.97 (m, 20H, H- δ b, H- δ b', - CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ' , - CH_3 - ζ , - CH_3 - ζ');

$^3J_{1',2'} = 7.6$, $^3J_{5',6a'} = 2.5$, $^3J_{5',6b'} = 4.6$, $^2J_{6a',6b'} = 12.2$, $^3J_{1a,2} = 3.1$, $^3J_{1b,2} = 6.1$, $^2J_{1a,1b} = 11.7$, $^3J_{3a,2} = 5.6$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 11.2$ Hz.

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 + TMS): δ = 177.06, 176.81 (C=O, oleoyl), 103.59 (C-1'), 76.21, 69.94 (C-3', C-4'), 75.85, 73.57 (C-2', C-5'), 70.20 (C-2), 68.19 (C-3), 62.34 (C-1), 61.99 (C-6'), 44.70 (C- δ , C- δ'), 41.23, 41.18 (C- β , C- β'), 37.36, 37.29 (C- α , C- α'), 31.44 (C- ϵ , C- ϵ'), 29.21, 29.16 (C- ζ , C- ζ'), 28.17, 28.15 (C- γ , C- γ'), 20.28, 20.22, 19.65, 19.61 (- CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ'), 18.12, 18.05 (- CH_3 - α , - CH_3 - α'), 11.21 (- CH_3 - ζ , - CH_3 - ζ').

1,2-di-*O*-[(2'*R*,4'*R*,6'*R*,8'*R*)-2',4',6',8'-tetramethyldecanoyl]-3-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- β -D-glucopyranosyl)-*sn*-glycerol 125



1.00 g (2.37 mmol) **62** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 3:1). Yield: 1.55 g (76 %).

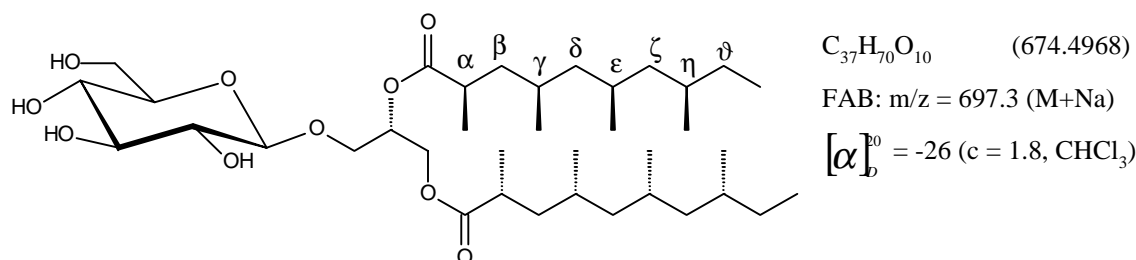
$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 5.19 (dd, 1H, H-3'), 5.16-5.23 (m, 1H, H-2), 5.08 (dd, 1H, H-4'), 4.98 (dd, 1H, H-2'), 4.52 (d, 1H, H-1'), 4.32 (dd, 1H, H-1a), 4.26 (dd, 1H, H-6a'), 4.13 (dd, 1H, H-1b), 4.12 (dd, 1H, H-6b'), 3.96 (dd, 1H, H-3a), 3.68 (ddd, 1H, H-5'), 3.66 (dd, 1H, H-3b), 2.56 (m, 2H, H- α , H- α'), 2.09, 2.05, 2.02, 2.00 (s, 3H, OAc), 1.74 (ddd, 1H, H- β a), 1.72 (ddd, 1H, H- β a'), 1.54-1.64 (m, 2H, H- ϵ , H- ϵ'), 1.46-1.54 (m, 2H, H- γ , H- γ'), 1.31-1.46 (m, 4H, H- η , H- η' , H- θ a, H- θ a'), 1.11-1.22 (m, 10H, H- δ a, H- δ a', H- ζ a, H- ζ a', - CH_3 - α , - CH_3 - α'), 0.99-1.09 (m 4H, H- β b, H- β b', H- θ b, H- θ b'), 0.80-0.93 (m, 28H, H- δ b, H- δ b', H- ζ b, H- ζ b',

$-\text{CH}_3-\gamma, -\text{CH}_3-\gamma', -\text{CH}_3-\varepsilon, -\text{CH}_3-\varepsilon', -\text{CH}_3-\eta, -\text{CH}_3-\eta', -\text{CH}_3-\vartheta, -\text{CH}_3-\vartheta'$);

$^3J_{1,2'} = 7.9, ^3J_{2,3'} = 9.5, ^3J_{3,4'} = 9.7, ^3J_{4,5'} = 9.9, ^3J_{5,6a'} = 4.7, ^3J_{5,6b'} = 2.5, ^2J_{6a',6b'} = 12.3, ^3J_{1a,2} = 3.5, ^3J_{1b,2} = 6.0, ^2J_{1a,1b} = 12.0, ^3J_{3a,2} = 4.7, ^3J_{3b,2} = 6.0, ^2J_{3a,3b} = 11.0$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 176.40, 175.93$ (C=O, oleoyl), 170.65, 170.25, 169.37, 169.18 (C=O, OAc), 101.15 (C-1'), 72.75 (C-3'), 71.96 (C-5'), 71.13 (C-2'), 69.65 (C-2), 68.33 (C-4'), 67.80 (C-3), 62.14 (C-1), 61.85 (C-6'), 45.34, 44.86, 44.82 (C- δ , C- δ' , C- ζ , C- ζ'), 40.91, 40.81 (C- β , C- β'), 37.26, 37.17 (C- α , C- α'), 31.53 (C- η , C- η'), 28.98, 28.96 (C- ϑ , C- ϑ'), 28.09, 28.06 (C- γ , C- γ'), 27.25 (C- ε , C- ε'), 20.70, 20.68, 20.64, 20.59, 20.48, 20.45, 19.92, 19.90 ($-\text{CH}_3$ OAc, $-\text{CH}_3-\gamma, -\text{CH}_3-\gamma', -\text{CH}_3-\varepsilon, -\text{CH}_3-\varepsilon', -\text{CH}_3-\eta, -\text{CH}_3-\eta'$), 18.15 ($-\text{CH}_3-\alpha, -\text{CH}_3-\alpha'$), 11.20 ($-\text{CH}_3-\vartheta, -\text{CH}_3-\vartheta'$).

1,2-di-*O*-[(2'*R*,4'*R*,6'*R*,8'*R*)-2',4',6',8'-tetramethyldecanoyl]-3-*O*-(β -D-glucopyranosyl)-*sn*-glycerol **126**



1.39 g (1.65 mmol) **125** were dissolved in a mixture of 25 ml dry methanol and 8 ml dry dichloromethane. 0.64 ml (13.11 mmol) hydrazine hydrate (100%) were added to this solution and the mixture was heated at the temperature of reflux for 8 hours. The solution was cooled in an ice-bath, neutralised with formic acid and the solvent removed *in vacuo*. The residue was submitted to chromatographic purification on silica gel (chloroform-methanol 40:1→30:1) and gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.71 g (64 %).

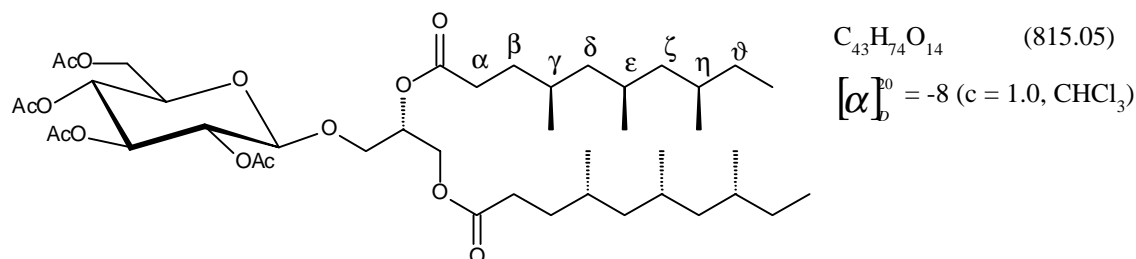
$^1\text{H-NMR}$ (400 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 5.27$ (m, 1H, H-2), 4.40 (dd, 1H, H1a), 4.30 (d, 1H, H-1'), 4.20 (dd, 1H, H-1b), 3.90 (dd, 1H, H-3a), 3.87 (dd, 1H, H-6a'), 3.80 (dd, 1H, H-6b'), 3.70 (dd, 1H, H-3b), 3.45-3.56 (m, 2H, H-3', H-4'), 3.25-3.36 (m, 2H, H-2', H-5'), 2.53-2.64 (m, 2H, H- α , H- α'), 1.68-1.78 (m, 2H, H- β a, H- β a'), 1.46-1.64 (m, 4H, H- γ , H- γ' , H- ε , H- ε'), 1.30-1.46 (m, 4H, H- η , H- η' , H- ϑ a, H- ϑ a'), 1.10-1.22 (m, 10H, H- δ a, H- δ a', H- ζ a, H- ζ a'), $-\text{CH}_3-\alpha, -\text{CH}_3-\alpha'$), 0.99-1.10 (m, 4H, H- β b, H- β b', H- ϑ b, H- ϑ b'), 0.79-0.94 (m, 28H, H- δ b, H- δ b', H- ζ b, H- ζ b'), $-\text{CH}_3-\gamma, -\text{CH}_3-\gamma', -\text{CH}_3-\varepsilon, -\text{CH}_3-\varepsilon', -\text{CH}_3-\eta, -\text{CH}_3-\eta', -\text{CH}_3-\vartheta, -\text{CH}_3-\vartheta'$);

$^3J_{1,2'} = 7.6, ^3J_{5,6a'} = 3.1, ^3J_{5,6b'} = 4.6, ^2J_{6a',6b'} = 12.2, ^3J_{1a,2} = 3.1, ^3J_{1b,2} = 6.1, ^2J_{1a,1b} = 12.2, ^3J_{3a,2} = 5.6, ^3J_{3b,2} = 6.1, ^2J_{3a,3b} = 11.2$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, $\text{CDCl}_3 + \text{TMS}$): $\delta = 177.03, 176.78$ (C=O, oleoyl), 103.57 (C-1'), 76.19, 69.93 (C-3', C-4'), 75.83, 73.57 (C-2', C-5'), 70.20 (C-2), 68.21 (C-3), 62.61 (C-1), 62.01 (C-6'), 45.31, 44.85 (C- δ , C- δ' , C- ζ , C- ζ'), 40.89, 40.82 (C- β , C- β'), 37.32, 37.27 (C- α , C- α'), 31.52 (C- η , C- η'), 28.98 (C- ϑ , C- ϑ'), 28.09 (C- γ , C- γ'), 27.24 (C- ε , C- ε'), 20.60, 20.64, 20.48, 20.46, 19.91 ($-\text{CH}_3-\gamma, -\text{CH}_3-\gamma', -\text{CH}_3-\varepsilon, -\text{CH}_3-\varepsilon', -\text{CH}_3-\eta$,

$-\text{CH}_3-\eta'$), 18.19, 18.14 ($-\text{CH}_3-\alpha$, $-\text{CH}_3-\alpha'$), 11.20 ($-\text{CH}_3-\vartheta$, $-\text{CH}_3-\vartheta'$).

1,2-di-*O*-[(4'*R*,6'*R*,8'*R*)-4',6',8'-trimethyldecanoyl]-3-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- β -*D*-glucopyranosyl)-*sn*-glycerol 127

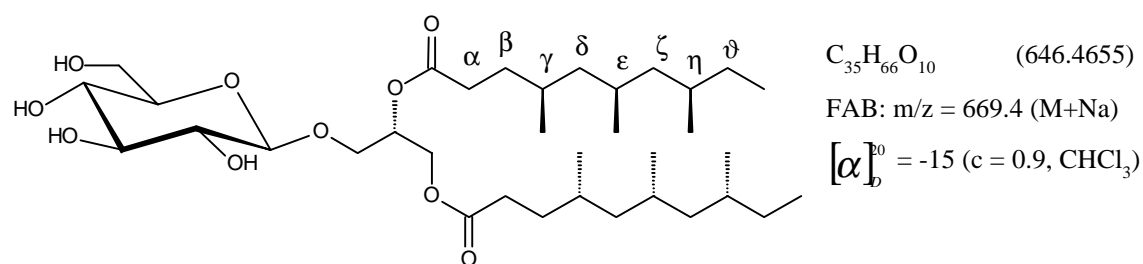


0.67 g (1.59 mmol) **62** were acylated using *General procedure 5*. The crude product was subjected to chromatographic purification on silica gel (light petroleum (b.p. 50-70 °C)-ethyl acetate 3:1). Yield: 1.10 g (85 %).

$^1\text{H-NMR}$ (500 MHz, CDCl_3 + TMS): δ = 5.20 (dd, 1H, H-3'), 5.16-5.22 (m, 1H, H-2), 5.08 (dd, 1H, H-4'), 4.98 (dd, 1H, H-2'), 4.52 (d, 1H, H-1'), 4.30 (dd, 1H, H-1a), 4.26 (dd, 1H, H-6a'), 4.13 (dd, 1H, H-1b), 4.12 (dd, 1H, H-6b'), 3.95 (dd, 1H, H-3a), 3.69 (ddd, 1H, H-5'), 3.67 (dd, 1H, H-3b), 2.22-2.38 (m, 4H, H- α a, H- α b, H- α a', H- α b'), 2.09, 2.05, 2.02, 2.00 (s, 3H, OAc), 1.65-1.73 (m, 2H, H- β a, H- β a'), 1.49-1.61 (m, 4H, H- γ , H- γ' , H- ϵ , H- ϵ'), 1.29-1.46 (m, 6H, H- β b, H- β b', H- η , H- η' , H- ϑ a, H- ϑ a'), 1.15-1.23 (m, 4H, H- δ a, H- δ a', H- ζ a, H- ζ a'), 1.00-1.10 (m, 2H, H- ϑ b, H- ϑ b'), 0.79-0.97 (m, 28H, H- δ b, H- δ b', H- ζ b, H- ζ b', $-\text{CH}_3-\gamma$, $-\text{CH}_3-\gamma'$, $-\text{CH}_3-\epsilon$, $-\text{CH}_3-\epsilon'$, $-\text{CH}_3-\eta$, $-\text{CH}_3-\eta'$, $-\text{CH}_3-\vartheta$, $-\text{CH}_3-\vartheta'$);

$^3J_{1',2'} = 7.9$, $^3J_{2',3'} = 9.7$, $^3J_{3',4'} = 9.5$, $^3J_{4',5'} = 9.5$, $^3J_{5',6a'} = 4.7$, $^3J_{5',6b'} = 2.4$, $^2J_{6a',6b'} = 12.3$, $^3J_{1a,2} = 3.5$, $^3J_{1b,2} = 6.0$, $^2J_{1a,1b} = 12.0$, $^3J_{3a,2} = 4.9$, $^3J_{3b,2} = 5.7$, $^2J_{3a,3b} = 10.7$ Hz.

$^{13}\text{C-NMR}$ (125 MHz, CDCl_3 + TMS): δ = 173.59, 173.14 (C=O, oleoyl), 170.65, 170.24, 169.37, 169.23 (C=O, OAc), 101.08 (C-1'), 72.68 (C-3'), 71.95 (C-5'), 71.12 (C-2'), 69.71 (C-2), 68.34 (C-4'), 67.74 (C-3), 62.28 (C-1), 61.86 (C-6'), 45.00 (C- δ , C- δ'), 44.80, 44.77 (C- ζ , C- ζ'), 31.87, 31.71, 31.42 (C- α , C- α' , C- β , C- β'), 31.53 (C- η , $-\eta'$), 29.71, 29.69 (C- γ , C- γ'), 28.93, 28.91 (C- ϑ , C- ϑ'), 27.41 (C- ϵ , C- ϵ'), 20.75, 20.73, 20.71, 20.59, 19.97, 19.94 ($-\text{CH}_3$ OAc, $-\text{CH}_3-\gamma$, $-\text{CH}_3-\gamma'$, $-\text{CH}_3-\epsilon$, $-\text{CH}_3-\epsilon'$, $-\text{CH}_3-\eta$, $-\text{CH}_3-\eta'$).

1,2-di-O-[(4'R,6'R,8'R)-4',6',8'-trimethyldecanoyl]-3-O-(β-D-glucopyranosyl)-sn-glycerol 128


0.91 g (1.12 mmol) **127** were dissolved in a mixture of 17 ml dry methanol and 6 ml dry dichloromethane. 0.43 ml (8.89 mmol) hydrazine hydrate (100%) were added to this solution and the mixture was heated at the temperature of reflux for 8 hours. The solution was cooled in an ice-bath, neutralised with formic acid and the solvent removed *in vacuo*. The residue was submitted to a chromatographic purification on silica gel (chloroform-methanol 20:1) and a gel filtration on a column of Serva LH-20 suspended in methanol. Yield: 0.32 g (42 %).

1H -NMR (400 MHz, $CDCl_3$ + TMS): $\delta = 5.27$ (m, 1H, H-2), 4.38 (dd, 1H, H1a), 4.30 (d, 1H, H-1'), 4.20 (dd, 1H, H-1b), 3.91 (dd, 1H, H-3a), 3.87 (dd, 1H, H-6a'), 3.78 (dd, 1H, H-6b'), 3.71 (dd, 1H, H-3b), 3.44-3.52 (m, 2H, H-3', H-4'), 3.26-3.36 (m, 2H, H-2', H-5'), 2.24-2.42 (m, 4H, H- α a, H- α b, H- α a', H- α b'), 1.64-1.74 (m, 2H, H- β a, H- β a'), 1.48-1.62 (m, 4H, H- γ , H- γ' , H- ϵ , H- ϵ'), 1.30-1.47 (m, 6H, H- β b, H- β b', H- η , H- η' , H- ϑ a, H- ϑ a'), 1.15-1.24 (m, 4H, H- δ a, H- δ a', H- ζ a, H- ζ a'), 0.99-1.10 (m, 2H, H- ϑ b, H- ϑ b'), 0.82-0.97 (m, 28H, H- δ b, H- δ b', H- ζ b, H- ζ b', - CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ' , - CH_3 - η , - CH_3 - η' , - CH_3 - ϑ , - CH_3 - ϑ');

$^3J_{1',2'} = 7.6$, $^3J_{5',6a'} = 3.1$, $^3J_{5',6b'} = 4.6$, $^2J_{6a',6b'} = 12.2$, $^3J_{1a,2} = 3.6$, $^3J_{1b,2} = 6.6$, $^2J_{1a,1b} = 12.2$, $^3J_{3a,2} = 5.6$, $^3J_{3b,2} = 6.1$, $^2J_{3a,3b} = 11.2$ Hz.

^{13}C -NMR (125 MHz, $CDCl_3$ + TMS): $\delta = 174.30$, 174.00 (C=O, oleoyl), 103.58 (C-1'), 76.28, 70.03 (C-3', C-4'), 76.03, 73.55 (C-2', C-5'), 70.36 (C-2), 68.15 (C-3), 62.86 (C-1), 61.94 (C-6'), 45.02, 44.80 (C- δ , C- δ' , C- ζ , C- ζ'), 31.98, 31.82 (C- α , C- α'), 31.56 (C- η , C- η'), 31.46 (C- β , C- β'), 29.73 (C- γ , C- γ'), 28.95 (C- ϑ , C- ϑ'), 27.43 (C- ϵ , C- ϵ'), 20.76, 19.95 (- CH_3 - γ , - CH_3 - γ' , - CH_3 - ϵ , - CH_3 - ϵ' , - CH_3 - η , - CH_3 - η'), 11.17 (- CH_3 - ϑ , - CH_3 - ϑ').

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9. Supplement – Safety information

The table below lists information about dangerous properties (R) of important chemicals used in this work, as well as advice for their secure handling (S), using the system of the R and S safety standards.

Name	R	S
Acetic acid, 100%	10-35	23-26-45
Acetic anhydride	10-34	26-45
Acetone	11	9-16-23-33
Acetonitrile	11-23/24/25	16-27-45
Acetobromo- α -D- cellobiose		
Acetobromo- α -D- galactose	36/37/38	26-36
Acetobromo- α -D- glucose	-	22-24/25
Acetobromo- α -D- maltose	23/24/25-36/37/38	45-26-36/37/39
Boron trifluoride diethyl etherate	14/15-34	26-28-36/37/39-45
2-Benzyloxy-1,3-propanediol	-	22-24/25
1-Butanol	10-20	16
Ceric ammonium nitrate	8-36/37/38	17-26-36
Chloroacetic anhydride	25-34-37	26-28-36/37/39-45
Chloroform	22-38-40-48/20/22	36/37
Dichloromethane	40	23-24/25-36/37
N,N-Dicyclohexylcarbodiimide	22-24-40-41-43	23-24/25-26-37/39-45
Diethyl ether	12-19	9-16-29-33
Diisopropyl ether	11-19	9-16-33
2,2-Dimethoxypropane	11-22-36/37/38	16-26-36
Dimethylaminopyridine	24/25-36/37/38	26-36/37/39-45
N,N-Dimethylformamide	61-20/21	53.1-45
1-Dodecanethiol	36/37/38-42/43	22-26-36/37
1-Dodecanol	36/37/38	26-36
Ethanol	11	7-16
Ethyl acetate	11	16-23-29-33
Formic acid	35	23-26-45
Hydrazine hydrate, 100%	45-23/24/25-34-43	53-26-36/37/39-45
Hydrogen	12	9-16-33
Light petroleum [50/70]	11-48/20-65	9-16-29-33-36-62
Magnesium sulphate	-	-

Mercury bromide	26/27/28-33	13-28-45
Mercury cyanide	26/27/28-32	7-28-29-45
Methanol	11-23/25	7-16-24-45
4-Methoxybenzylchloride	34-36/37	26-36/37/39-45
Octa-O-acetyl- β -D-cellobiose	no data available	no data available
Octa-O-acetyl- β -D-gentiobiose	no data available	no data available
Octa-O-acetyl- β -D-lactose	no data available	no data available
Octa-O-acetyl- β -D-maltobiose	no data available	no data available
Octa-O-acetyl- β -D-melibiose	no data available	no data available
Oleic acid	36/37/38	26-36
Oleyl alcohol	36/37/38	26-36
Penta-O-acetyl- β -D-galactose	-	22-24/25
Penta-O-acetyl- β -D-glucose	-	22-24/25
Potassium bromide	36/37/38	26-36
4-(1-Pyrrolidinyl)pyridine	34	26-36/37/39-45
Sodium acetate, anhydrous	-	22-24/25
Sodium disulfite	22-31-36/37/38	26-36
Sodium hydride	15	7/8-24/25-43.12
Sodium hydrogen carbonate	-	22-24/25
Sodium methoxide	11-14-34	8-16-26-43.11-45
Stearyl alcohol	36/37/38	26-36
Thiourea	22-40-51/53	22-24-36/37-51
Tin tetrachloride	34-37	7/8-26-45
4-Toluensulfonic acid	36/37/38	26-37
Tridecanethiol	36/37/38-42/43	22-26-36/37
Triethylamine	11-20/21/22-35	3-16-26-29-36/37/39-45

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