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Synthesis and Liquid Crystalline Properties of Mono-, Di- and Tri-*O*-alkyl Pentaerythritol Derivatives Bearing Tri-, Di- or Monogalactosyl Heads: The Effects of Curvature of Molecular Packing on Mesophase Formation

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Abstract: Self-organisation and self-assembly are critical to the stability of synthetic and biological membranes. Of particular importance is consideration of the packing arrangements of the various molecular species. Both phospho- and glycolipids can pack in ways in which curvature can be introduced into self-organised or self-assembled systems. For instance, it is known that the degree of curvature can affect the structures of any condensed phases that are formed. In this article we report on a systematic study in which we have varied the shapes of glycolipids and examined the condensed phases that they form. In doing so, we have also unified the shape dependency of lyotropic liquid crystals with those of thermotropic liquid crystals. In order to undertake this systematic study a range of different pentaerythritol derivatives was synthesized, which covers combinations of one to three alkyl chains of different lengths (6,7,9,10,11,12,14,16 carbon atoms) and three to one galactosyl heads. Mono- and di-*O*-galactosyl derivatives were prepared directly by glycosylation of the corresponding alcohols using 2,3,4,6-tetra-*O*-benzoyl or acetyl-α-D-galactopyranosyl trichloroacetimidate or bromide as the donors; the tri-*O*-galactosyl derivatives were synthesized from *O*-alkyl-*O*-benzyl di-*O*-galactosyl pentaerythritol intermediates, followed by de-*O*-benzylation and glycosylation steps. All of the fully deprotected products were obtained by standard methods, and their self-organising and self-assembling properties examined.

Keywords: glycosylation · lipids · liquid crystals · pentaerythritol

Introduction

Biological membranes contain components of varying complexity and functionality; for example, functionality may involve the extremes of specific recognition processes to mechanical/pressure self-regulation. In terms of specific recognition processes, interactions between the carbohydrate parts of glycoconjugates and proteins are essential to cell function. In such interactions the terminal carbohydrate head groups are generally responsible for binding to ligands (e.g., proteins).[1–3] Although important in protein–carbohydrate recognition, this interaction appears to be relatively weak when examined experimentally. It has been shown that proteins have a greater affinity for glycolipids bearing multivalent carbohydrate ligands than for corresponding monovalent glycolipids.[4,5] This phenomenon is known as the "cluster glycoside effect".

Over the last ten years, the synthesis and study of various novel neoglycoconjugates has increased in respect to the demand for substances with higher affinities and increased specificity.[6,7] In particular, attention has been given to sialic acid and sialyloligosaccharides, together with mannosides and galactosides since such carbohydrate residues represent immuno-dominant structural elements.

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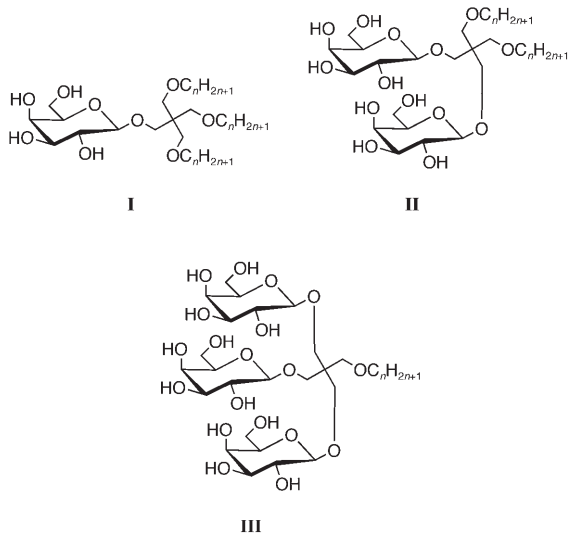
Other substances which are able to mimic glycolipid assemblies at cell surfaces include synthetically hydrophobised carbohydrates, because they are able to spontaneously self-organize in water, either in the presence or absence of other lipids. Carbohydrate recognition of such organized systems (mono- or bilayers) is somewhat different to recognition in isotropic media. Furthermore, the conformation and motion of the carbohydrate moiety of glycolipids embedded at interfaces are strongly affected by the nature of the lipid anchor and that of the surrounding lipid components. Through various related studies, it has been possible to rationalize and model the structural self-organization of amphiphilic carbohydrates by considering the structural geometries and functional features of the individual molecules. For example, the formation of micelles, liquid crystals, monolayers, or vesicles has been found to be dependent on the cross-sectional and surface area of the polar head relative to the length and volume of the apolar tail.[8]

The relationship between the cross-sectional areas and volumes of the head groups and tails is connected to the induction of curvature upon packing of the molecules together, which in turn determines the nature and structure of any self-organised mesophase that is formed. In biological cell membranes the effects of curvature are tightly controlled by integral and surface proteins which selectively introduce certain lipids into the outer membrane leaflets.[9–11] Furthermore, there are some indications that by affecting the degree of curvature in membranes cubic phases can be introduced locally. The incorporation of such phases effectively opens up a passageway into the inner parts of the cell.[12]

It appears that the selectivity of interactions and the bulk organisation of lipid systems in the liquid crystal environment are of considerable importance to cell function. Thus as a part of our work devoted understanding these processes, particularly in neoglycolipids,[13–16] we now report the preparation and systematic study of the liquid crystal properties of a range of pentaerythritol derivatives which are substituted by one to three alkyl chains of different lengths, **I**, **II** and **III**, with the remaining hydroxyl positions being galactosylated in each case.

In addition to systematically examining the self-organising properties of glycolipids as a function of the number of galactose units in the head groups, we also sought to investigate the effects of curvature associated with the packing of the molecules on mesophase formation. It is generally known for lyotropic liquid crystal phases that, as the "curvature" is varied from negative to positive, it can be possible for a passage through all of the mesophases, that is, from cubic–hexagonal–cubic–lamellar–cubic–hexagonal–cubic phases (see Figure 1). In some cases, however, it is possible to miss out certain of the phases in the sequence, which can be the case for galactosides. However, for thermotropic liquid crystal phases, the effects of curvature of packing on mesophase formation have not been examined fully. Indeed the phases formed by mesogens of unconventional structure (phasmidic and banana materials, dendrimers, Janus materials etc.[17–26]) are exciting topics of current interest. Thus we also proposed to examine the variation of phase type as a function of curvature in dry, thermotropic systems.



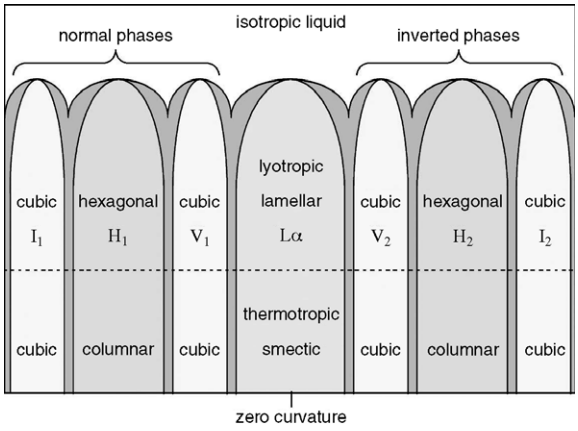


Figure 1. Effects of curvature of molecular packing on mesophase formation in lyotropic systems, and potentially in thermotropic liquid crystals.

Results

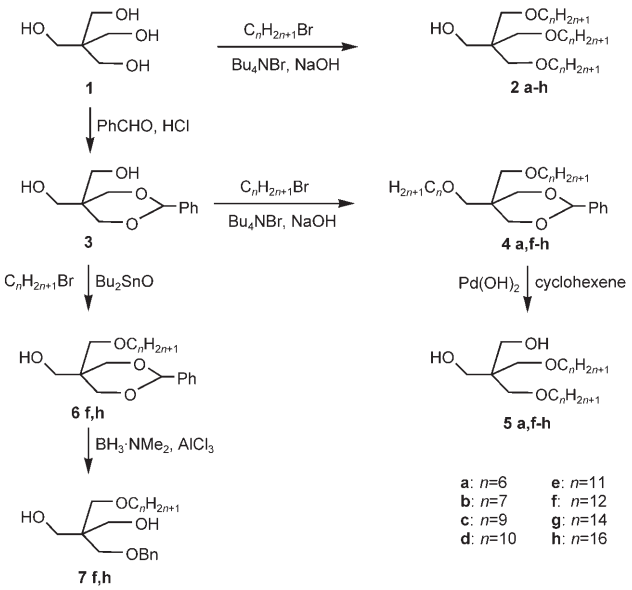
Synthetic rationale: Pentaerythritol has been used in the last ten years as a core component for the syntheses of glycoside clusters of glycolipids. In most cases a spacer has been introduced between the hydroxyl(s) group(s) of the pentaerythritol core and the glycosyl moieties. For example, Hanessian et al. prepared clustered α-D-GalNAc-Ser (Tn) and β-D-Gal-(1→3)-α-D-GalNAc-Ser antigenic motifs, by condensation of the corresponding glycopeptides with alkyl tris(aminoethyl) pentaerythritol.[27] A similar pentaerythritol derivative was used to obtain clusters of α-D-Gal-(1→3)-β-D-Gal glycosides of quinic acid.[28] Recently, glycotope biosteres bearing β-D-galactose moieties have been synthesized by the Sonogashira reaction of tetra-*O*-iodobenzyl pentaerythritol and 2-propinyl galactosides.[29] Two other routes to mannoside

clusters using pentaerythritol as scaffold have been described by Lindhorst et al.:[30] in the first, pentaerythritol tetrabromide was etherified by 2-hydroxyethyl mannosides; in the second, hydroboration of tetra-*O*-allyl pentaerythritol and subsequent mannosylation of the tetraol afforded the expected tetramannoside which was tested as an inhibitor of mannose-specific bacterial adhesion.

In the synthesis of some highly hydrophobic Lewis X glycolipids,[31] pentaerythritol was first condensed with triethylene glycol. The hydroxyl groups of the latter were then etherified by phytyl chains and the subsequent product was glycosylated with Lewis X donors. There are only a few examples in the literature of direct glycosylation of partly protected pentaerythritols. One such example was conducted in our laboratory, which involved glycosylation of di-*O*-hexadecyl pentaerythritol to give, the gemini glycoside, bis(*N*-acetyl-β-D-glucosaminyl)glycosides which were used to study the interfacial behaviour.[32] More recently, M. Schmidt et al.[33] described the synthesis of mannose clusters having a pentaerythritol core, in which the mannosyl residues were either attached directly to the pentaerythritol moiety or separated from the later by oligoethylene spacers of varying lengths.

The first part of our synthetic work was the preparation of the alcohol acceptors as depicted in Scheme 1. The tri-*O*-alkyl pentaerythritols **2a–h** (chain lengths $n = 6$, 7, 9–12, 14 and 16) were obtained by direct treatment of pentaerythritol (**1**) with an excess of alkyl bromide under phase transfer conditions, in the presence of 50% aqueous sodium hydroxide and tetrabutylammonium bromide, as described in the literature for tri-*O*-heptyl pentaerythritol.[34] The low yields were due to the simultaneous formation of mono-, di- and tetra-*O*-alkyl derivatives. The di-*O*-alkyl pentaerythritols **5a,f–h** were obtained from *O*-benzylidene pentaerythritol **3**,[35] by alkylation under similar conditions to afford **4a,f–h** and subsequent cleavage of the benzylidene group, in each case, by hydrogen transfer (cyclohexene, palladium hydroxide, ethanol, 80°C). Treatment of the *O*-benzylidene pentaerythritol **3** with dibutyltin oxide in methanol, followed by reaction with alkyl bromide in the presence of caesium fluoride, afforded the mono-*O*-alkyl derivatives **6f,h**, which were always contaminated by 5–10% of the alkyl alcohol. Reductive cleavage of the benzylidene group gave the *O*-alkyl-*O*-benzyl pentaerythritols **7f,h** in 40% yield over the two steps. Compounds **6h** and **7h** have been reported recently in the literature.[36]

Galactosylation reactions were performed using 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**8**),[14,37] 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**9**)[38] or 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**10**)[39] as glycosyl donors (Scheme 2). In a first attempt, we studied the galactosylation of diol **5h** with the donors **9** [$Hg(CN)_2$, HgO, $CaSO_4$, CH_2Cl_2] and **10** [cat. trimethylsilyl trifluoromethanesulfonate (TMSOTf), CH_2Cl_2, −20°C]. The yields remained low due to the formation of mixtures of mono- and di-*O*-galactosyl products, which both showed very similar behaviour by TLC. Donor **8** was then



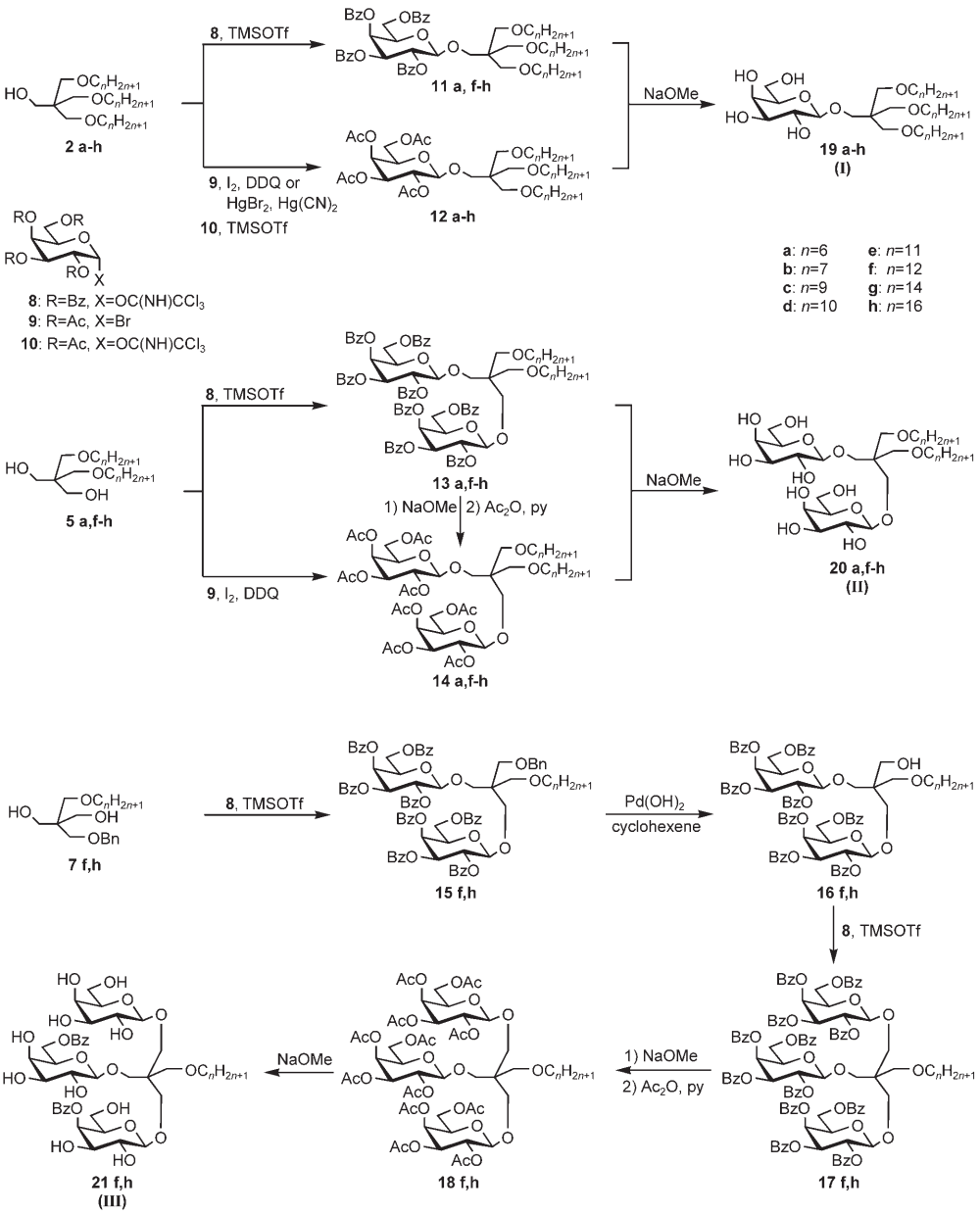
Scheme 1. Derivatisation of pentaerythritol.

reacted with the alcohol **5h** (cat. TMSOTf, CH_2Cl_2, 0°C) to afford the expected di-*O*-galactoside **13h** in 56% yield.

The per-*O*-benzoyl galactosides **11a,f–h** were obtained under the same conditions from donor **8** and acceptors **2a,f–h** (72–76%). The per-*O*-acetyl glycosides **12a,f–h** were also prepared in good yields (73–79%) from donor **9** (I_2, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, MeCN) and acceptors **2a,f–h**, using a method described in 1996 by Fields and coworkers.[40] In contrast, lower yields of galactosides **12a**, **f–h** (35–53%) were obtained from **2a,f–h** using per-*O*-acetyl imidate **10**. Alternative conditions of $Hg(CN)_2$, $HgBr_2$ in CH_2Cl_2 were employed to synthesize **12b–e** from donor **9** and acceptors **2b–e** in reasonable yields (53–66%).

The di-*O*-alkyl di-*O*-galactoside derivatives **13a,f–h** were synthesized from imidate **8** and the corresponding diols **5a,f–h** in acceptable yields (45 to 72%) using TMSOTf. Alternatively, compound **14g** was prepared in 40% yield from **5g** and bromide **9** using Fields' conditions.[27,40] For purification and identification purposes, the per-*O*-acetyl galactosides **14a,f–h** were prepared from their benzoyl counterparts **13a,f–h** by Zemplen de-*O*-benzoylation and re-*O*-acetylation.

The trigalactosylation of mono *O*-alkylpentaerythritol intermediates to compounds **17f,h** was unsuccessful, due to difficulties of separation from the mono- and di-*O*-glycosyl by-products. Therefore, **17f,h** were prepared via two glycosylation steps. In the first, acceptors **7f,h** were glycosylated with imidate **8**. The di-*O*-galactosyl derivatives **15f,h** thus obtained (68–72%) were then transformed by de-*O*-benzylation into acceptors **16f,h** (92%), respectively. The latter were subsequently glycosylated again under the same conditions affording the *O*-alkyl tris(per-*O*-benzoyl galactosyl) pentaerythritols **17f,h**. For purification and identification purposes, de-*O*-benzoylation was achieved under Zemplén conditions (catalytic amount of CH_3ONa in methanol), fol-



Scheme 2. Formation of series **I**, **II** and **III**.

lowed by re-*O*-acylation to obtain the derivatives **18 f**,**h** in good yields.

The fully deprotected derivatives **19 a**–**h**, **20 a**,**f**–**h** and **21 f**,**h** were prepared in high yields by Zemplen de-*O*-acetylation of the peracetylated derivatives **12 a**–**h**, **14 a**,**f**–**h** and **18 f**,**h**, respectively.

Transition temperatures: Phase identifications and determination of phase transition temperatures were carried out, concomitantly, by thermal polarized light microscopy (see Experimental Section for details). Differential scanning calorimetry was also used to confirm the phase transition temperatures determined by optical microscopy. Although it was possible to determine melting and clearing points by differential scanning calorimetry, determination of the associated enthalpies was not possible due to decomposition of the compounds in aluminium pans. The microscope data for the three homologous series of pentaerythritol derivatives taken by thermal polarized microscopy is compiled in Table 1.

O-β-D-*Galactopyranosyl-tri*-O-*alkyl pentaerythritols (I)*: All materials except **19 a**, the hexyl homologue, exhibited normal melting points determined by optical microscopy. Compound **19 a**, however, existed in its mesophase or soft crystal state at room temperature, and thus no melting point

Table 1. Transition temperatures *T* [°C] for series **I**–**III**.

				I				
Cpd.	*n*	Crystal	*T*	Columnar	*T*	Cubic	*T*	Isotropic liquid
19a	6	●	–[a]	●	62.3	–	–	●
19b	7	●	44.0	●	72.1	●	82.3	●
19c	9	●	36.0	●	59.4	●	76.2	●
19d	10	●	37.0	●	53.3	●	63.8	●
19e	11	●	30.0	●	38.3	●	43.4	●
19f	12	●	37.5	(●	32.0)	–	–	●
19g	14	●	52.7	–	–	–	–	●
19h	16	●	58.2	–	–	–	–	●

			II			
Cpd.	*n*	Crystal	*T*	Smectic A*	*T*	Isotropic liquid
20a	6	●	–[a]	●	156.2	●
20f	12	●	53.3	●	203.1	●
20g	14	●	46.9	●	202.2	●
20h	16	●	41.7	●	202.2	●

				III		
Cpd.	*n*	Crystal	*T*	Cubic	*T*	Isotropic liquid
21f	12	●	91.6	●	204.0	●
21h	16	●	150.0	●	>200.0 decomp	●

[a] Material in its condensed or amorphous phase at room temperature.

was recorded. Compounds **19g** and **19h** were found to be non-mesogenic.

A number of *O*-β-D-galactopyranosyl-tri-*O*-alkyl pentaerythritols (C_7 **19b** to C_{11} **19e**) were found to exhibit two liquid crystal phases; the columnar and cubic phases. The columnar phase gave textures typical of the hexagonal phase, whereas the cubic phase appeared optically extinct. The transition from the cubic phase to the isotropic liquid was observed via the insertion of a phase plate into the microscope above the objective and observing the Becker line between the two phases. The cooling cycle transition from the cubic phase to the columnar phase for compound **19e** (C_{11}) is shown in the photomicrograph in Figure 2. Fans typical of the hexagonal phase are formed, they have no elliptical or hyperbolic lines of optical discontinuity as found for lamellar phases, and indeed lines associated with rectilinear defects were observed.

The transition temperatures as a function of chain length are shown in Figure 3 for compounds **19a–f**. The graphical representation shows that all except for **19f** exhibit enantiotropic liquid crystal mesophases. Elongation of the three alkoxy chains attached to the pentaerythritol core results in a strong reduction of the transition temperatures. Conversely, the melting points first fall and then increase, thereby rendering the longer chain length homologues as being non-mesogenic. The phase range for the columnar mesophase is greatest for the heptyl compound (28.1 °C), but for longer chain length members the stability of this phases decreases markedly with increasing chain length. Conversely, the nonyl homologue, **19c**, is found to display the most stable cubic mesophase (16.8 °C). The compounds either side, **19b** and **d**, have a considerably reduced cubic phase range in

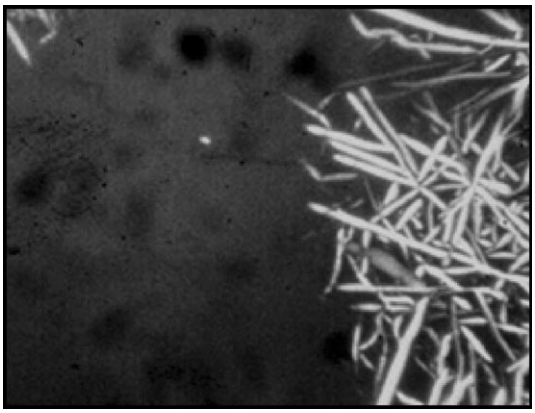


Figure 2. Transition from discontinuous cubic phase to columnar phase for *O*-β-D-galactopyranosyl-tri-*O*-undecanyl pentaerythritol (C_{11} **19b**) (×100).

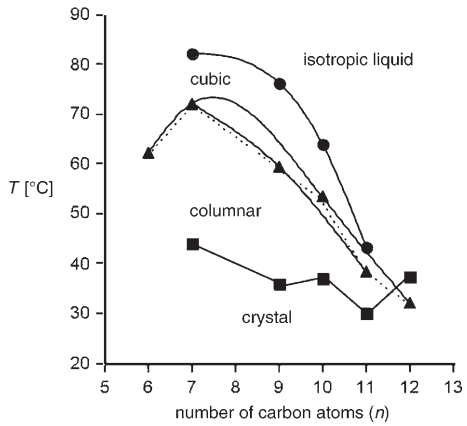


Figure 3. Comparison of the transition temperatures [°C] as a function of chain length (*n*) for the *O*-β-D-galactopyranosyl-tri-*O*-alkyl pentaerythritols (**I**) **19a–f**.

comparison. The dotted line in Figure 4 shows the odd/even effects of the chain length. Note, alternating clearing points reinforce the proof of purity of the samples.

Di*-O-β-D-*galactopyranosyl*-*di*-O-*alkyl* *pentaerythritols* *(II): The two aliphatic chain series of compounds, unlike the three chain analogues, were found to exhibit only one liquid crystal phase, the smectic A* phase. All of the materials exhibited enantiotropic phases which possessed temperature ranges in the region of 150 °C. The smectic A* phase was characterised by the formation of focal-conic domains where the elliptical and hyperbolic lines of optical discontinuity are diagnostic for the presence of the A phase. At the phase transition from the isotropic liquid decomposition occurred with the release of gas. The resulting texture showed large gas bubbles, with the mesophase sandwiched between the bubbles (see Figure 4). Differential scanning calorimetry also showed extensive decomposition at the clearing point with large fluctuations occurring with respect to the baseline.

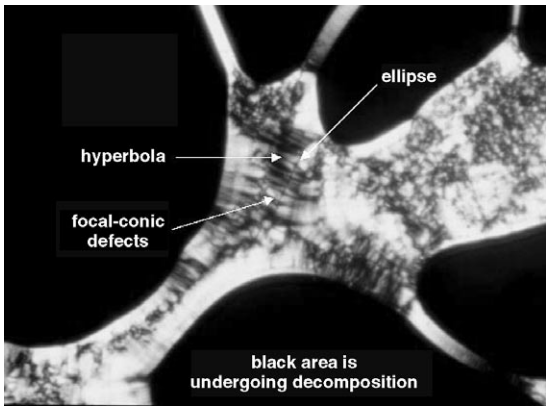


Figure 4. Transition from isotropic liquid to smectic A* phase for di-*O*-β-D-galactopyranosyl-di-*O*-hexadecyl pentaerythritol (C_{16} **20h**) (×100). Focal-conic domains are clearly seen as elliptical and hyperbolic lines of optical discontinuity.

In comparison to the three chain family of materials, **I**, the two chain-two sugar system, **II**, because of the increased degree of inter-molecular hydrogen bonding has much higher clearing temperatures, that is, in the range of 120 °C. However, the higher clearing points and the incorporation of an extra sugar unit leads to a increase susceptibility towards decomposition. Nevertheless, the clearing point transition temperatures lie on a smooth curve, with the smectic A* phase being introduced at the dihexyl homologue and quickly saturating at the didodecyl member.

O-*Alkyl-tri*-O-β-D-*galactopyranosyl pentaerythritols (III)*: Only two of this series were prepared: the dodecyl (**21f**) and hexadecyl (**21h**) homologues. Both exhibit enantiotropic cubic phases as predicted. However, the melting points are higher in comparison to those found for series **II**. However, these values probably reflect the higher degree of intramolecular hydrogen bonding. Interestingly, the clearing point temperatures are almost identical with respect to those obtained for series **II**. This suggests at such high temperatures the hydrogen bonding is possibly more dynamic and both intra- as well as intermolecular hydrogen bonding are of importance and as a consequence no increase is seen in the clearing temperatures. Furthermore, these materials exhibited strong decomposition, which made it difficult to ascertain their true clearing point values.

The two compounds were both found to exhibit an optically extinct phase formed upon cooling from the isotropic liquid. The transition from the isotropic liquid to the cubic phase was observed via the insertion of a phase plate into the microscope above the objective and observing the Becker line between the two phases. No birefringence was observed even around air bubbles, and the phase was found to be viscous when the sample was subjected to mechanic shearing. These observations are consistent with the phase being cubic. The detailed structure of the phase requires further studies by X-ray diffraction; however, this is beyond the scope of this study which is directed towards examining the effects of curvature of molecular packing on mesophase formation.

Discussion

In the introduction it was described how previously the curvature of packing can affect the self-organising and self-assembling properties of thermotropic, as well as lyotropic, liquid crystals.[8c,d] In order to examine the effects of curvature it is first instructive to examine the molecular structures of the materials under investigation. The relative shapes of the molecules were investigated via computer simulations using an Apple Macintosh G5 computer and ChemDraw3D as part of a ChemDraw Ultra 6.0 program. This programme assumes that the molecules are in the gas phase at absolute zero. For the purposes of comparison, Figure 5 shows the minimised structures for the dodecyl homologues of series, **I**, **II** and **III**.

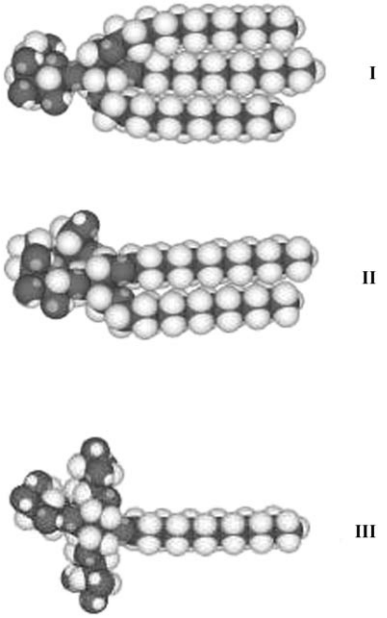


Figure 5. Minimised structures of the dodecyl homologues of series **I**, **II** and **III**.

As for all amphiphilic systems, the driving force for the liquid crystal phase formation in these three cases is the generation of a hydrogen-bonding network between adjacent galactose units, thereby, giving rise to the segregation of the aliphatic chains from the carbohydrate head groups. For series **I**, the compounds are composed of three chains and one carbohydrate unit, and have wedge-like shapes with the sugar units at the apices of the wedges. Consequently these materials would be expected to exhibit cubic and columnar mesophases that have inverted structures. Thus we propose that the type of columnar phase exhibited by series **I** is a hexagonal columnar phase with the individual mole-

cules disordered up and down the column axis as shown in Figure 6. However, as noted above X-ray diffraction studies would be necessary to clarify the detailed structure and to determine the inter-columnar distances.

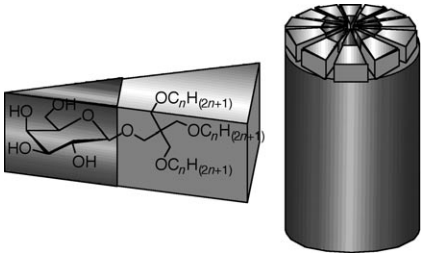


Figure 6. Columnar structure of the hexagonal columnar phase formed by series **I**.

In the columnar phase the materials probably adopt a relatively flat conformation to enable them to self-organise into a cylindrical columnar arrangement. However, at higher temperatures where the molecules are in increased dynamical motion, several of the compounds were also found to exhibit cubic mesophases. As the three aliphatic chains are attached to a tetrahedral shaped pentaerythritol core via very flexible ether linkages, it can be assumed that alternative molecular geometries are also possible. For example, the dynamical motion might induce the molecules to assume a conical shape, rather than a wedge. For this conformational volume, the best packing arrangement is spherical with the cones pointing towards the centre as shown in Figure 7.

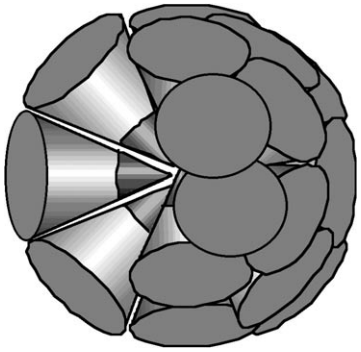


Figure 7. Packing of cone-shaped conformational volumes of the molecules for series **I** compounds.

From the analysis of the liquid crystal properties of systems that have similar shapes to series **I**,[41] it can be deduced that the isotropic mesophase observed is a discontinuous cubic phase. The curvature introduced into the system through the splay of the three chains for the compounds in series **I** is thought to be sufficient to support the formation of this type of mesophase. The structure of the discontinuous cubic mesophase in this case consists of a cubic arrangement of closed spherical or non-spherical micelle units. In lyotropic systems, for example, the micellar units are found to adopt a number of different conformations such as spherical, oblate and prolate. However, from the diffraction studies of other amphiphilic systems displaying thermotropic discontinuous cubic phases there appears to be two potential micellar structures, spherical and oblate, as shown in Figures 7 and 8.[41–43]

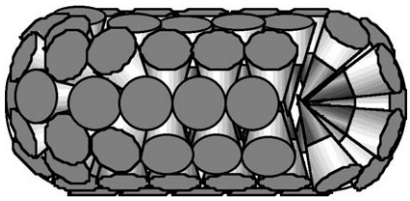


Figure 8. Oblate micellar structure found in cubic phases.

For materials of type **III**, the structures of the cubic mesophases are essentially the inverse of those of type **I** compounds. The galactose units are this time located towards the exterior of the micelle and the aliphatic chains are towards the centre, as shown in Figure 9.

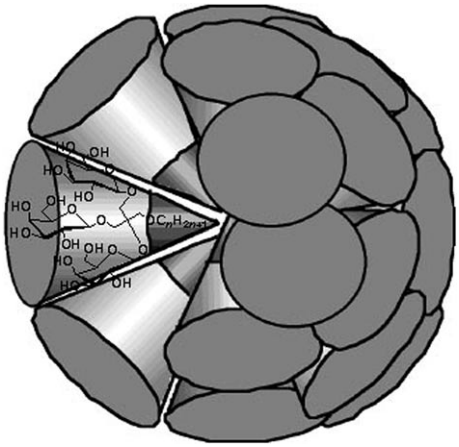


Figure 9. Packing of cone-shaped conformational volumes of the molecules for the cubic phases of series **III** compounds.

For series **II**, with structures half way between series **I** and **III**, not surprisingly the head groups are of a similar cross-sectional size to those of the aliphatic chains. Thus when the molecules pack together they will form a lamellar smectic A* phase as predicted. Figure 10 shows the packing structure of the molecules into a lamellar phase for the didodecyl homologue. It can be seen from this Figure that the degree of curvature in the packing is minimal.

From these studies and those made previously by ourselves and others[44–46] we can see that molecular shape and the related curvature of packing has a similar impact on thermotropic phases as it does for lyotropic systems. We can place some of the molecular architectures into the phase diagram shown in Figure 1, and thereby relate the molecular

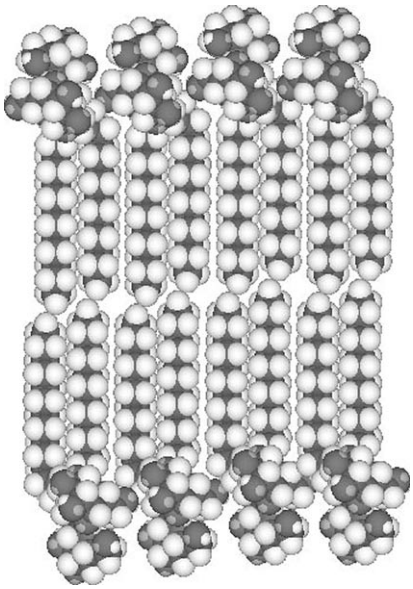


Figure 10. Packing structure of the molecules into a lamellar phase for the didodecyl homologue of series **II**.

shapes of rods, wedges and cones to mesophase formation and stability (see Figure 11). Although the results apply to a strongly microphase segregating amphiphilic system, they should also apply to other microphase segregating systems such as fluorocarbons/hydrocarbons. Thus this work unifies lyotropic and thermotropic systems for all forms of amphiphiles.

We can test this hypothesis via mixing of material designs derived from certain parts of the phase diagram, for example, if we mix compounds from series **I** with examples from series **III**, then a lamellar phase should be obtained in the 50/50 region of the phase diagram. Indeed this is the case, when a contact preparation is made between compounds **19 f** and **21 f**, both possessing dodecyl aliphatic chains, a lamellar phase appears in the centre of the defect texture (characterised by ellipse and hyperbolic lines of optical discontinuities, result not shown). Unfortunately, because of the large differences in transition temperatures between these two materials it was not possible to create a full phase diagram due to the effects of recrystallisation. However, through the use of contact preparations it was possible to observe a lamellar phase at the centre of the sample preparation which was characterised by hyperbolic and elliptical lines of optical discontinuity. To either sides of the contact preparation isotropic cubic phases were present, characterised by the presence of rectilinear lines with no elliptical or hyperbolic optical discontinuities.

A full phase diagram between glycolipids possessing two head groups and one chain and two chains and one head group was reported by us previously,[45] and, as predicted by the relationship described above, a full range of mesophase types was produced from one columnar phase to the other columnar phase across the phase diagram as shown in Figure 12.

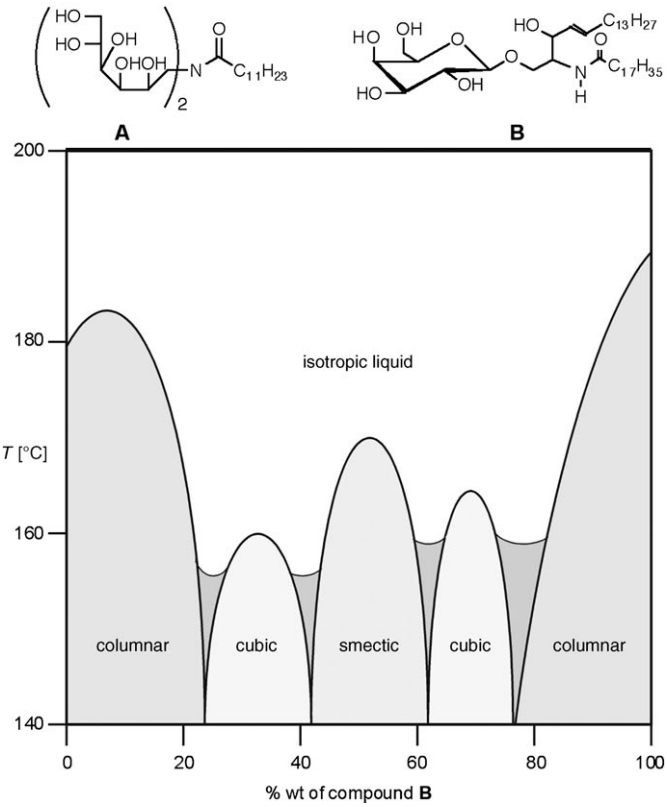


Figure 12. Miscibility phase diagram [wt %] as a function of temperature [°C] between compounds **A** and **B**.

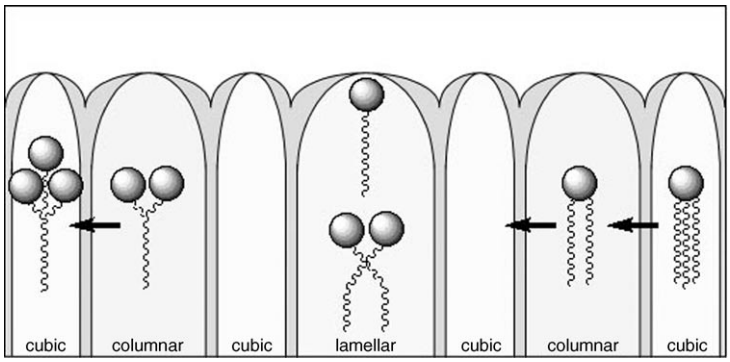


Figure 11. Effect of molecular shape and curvature of packing on mesophase formation in thermotropic liquid crystals.

Conclusion

In this study we have successfully demonstrated that the effects of molecular shape and curvature of packing in lyotropic systems is transferable to thermotropic liquid crystals. The results of this work are generally applicable to all forms of amphiphiles that exhibit liquid crystallinity. However, it is not clear whether or not this work will be applicable to shape dependency without amphiphilicity which takes the form of microphase segregation.

Experimental Section

Materials and methods: Pyridine was dried by boiling with CaH_2 prior to distillation. Dichloromethane was washed twice with water, dried with $CaCl_2$ and distilled over P_2O_5. Methanol was distilled from magnesium. Tetrahydrofuran was distilled over sodium/benzophenone. Pyridine, THF and CH_2Cl_2 were stored over 4 Å molecular sieves and MeOH over 3 Å molecular sieves. Melting points were determined on a Büchi apparatus and were uncorrected. Thin layer chromatography was performed on aluminium sheets coated with Silica gel 60 F_{254} (E. Merck). Compounds were visualized by spraying the TLC plates with dilute 15% aq H_2SO_4, followed by charring at 150°C for a few min. Column chromatography was performed on silica gel Geduran Si 60 (Merck). Optical rotations were recorded on a Perkin Elmer 241 polarimeter in a 1 dm^3 cell at 21°C. ^1H and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer (working at 200 and 50 MHz) or a JEOL JNM-LA400 spectrometer (working at 400 and 100 MHz), respectively, with Me_4Si as internal standard. Elemental analyses were performed by the "Laboratoire Central d'Analyses du CNRS" (Vernaison, France). Mass spectra were recorded on a Finnigan-MAT 1020 automated GC/MS spectrometer or a Shimatzu GC/MS-QP5050 A Gas Chromatograph spectrometer with electron impact. Phase identifications and determination of phase transition temperatures were carried out, concomitantly, by thermal polarized light microscopy using either a Zeiss Universal polarizing transmitted light microscope equipped with a Mettler FP52 microfurnace in conjunction with an FP50 Central Processor. Photomicrographs were obtained using a Zeiss polarizing light microscope equipped with a Nikon AFM camera. Differential scanning calorimetry was also used to confirm the phase transition temperatures determined by optical microscopy. Differential scanning thermograms (scan rate 10°C min^{-1}) were obtained using a Perkin Elmer DSC 7 PC system operating on DOS software.

General procedure for the preparation of tri-*O*-alkyl pentaerythritol derivatives 2a–h: Pentaerythritol (**1**) (3.0 g, 22.0 mmol) was added to a freshly prepared aq. NaOH solution (35.2 g NaOH and 30 mL water) and the resulting mixture was heated at 80°C with stirring, for 1 h. Alkyl bromide (66.0 mmol) and tetrabutylammonium bromide (0.88 g, 2.75 mmol) were then added and heating was maintained for a further 5 h. After cooling, the mixture was partitioned between CH_2Cl_2 (100 mL) and water (100 mL) and the organic phase was washed with water (3×50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography affording the pure tri-*O*-alkyl products.

Tri-*O*-hexyl pentaerythritol (2a): Obtained as described above after purification by column chromatography (EtOAc/petroleum ether 1:15) as an oily material (1.45 g, 17%); homogeneous by TLC, $R_f=0.40$; ^1H NMR (200 MHz, $CDCl_3$): $\delta=3.71$ (d, 2H, $J=6.0$ Hz, CH_2OH), 3.44 (s, 6H, $3CH_2OAlk)_3$), 3.39 (t, 6H, $J=6.2$ Hz, $3OCH_2Alk$), 3.16 (t, 1H, CH_2OH), 1.54 (m, 6H, $3OCH_2CH_2Alk$), 1.30 (m, 18H, $9CH_2$ alkyl chains), 0.89 ppm (t, 9H, $3CH_3$ alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=71.67$, 71.39 (CH_2OCH_2Alk), 66.37 (CH_2OH), 44.76 ($C(CH_2)_4$), 31.64, 29.53, 25.82, 22.60 (CH_2 alkyl chains), 14.13 ppm (CH_3); elemental analysis calcd (%) for $C_{23}H_{48}O_4$ (388.61): C 71.08, H 12.45; found: C 70.68, H 12.64.

Tri-*O*-heptyl pentaerythritol (2b): Obtained as described above, after purification by column chromatography (EtOAc/hexane 1:9) as a yellow oil (2.8 g, 30%); homogeneous by TLC, $R_f=0.35$; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2a**, except for ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.29$ ppm (m, 24H, $12CH_2$ alkyl chains) and ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=31.87$, 29.61, 29.16, 26.16, 22.66 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3539 (OH), 1108 (CO), 2935, 2863, 1466, 1376, 1051 cm^{-1} (C-H, C-C); MS (ES): *m*/*z*: calcd for: 430; found: 431 $[M+H]^+$, 382, 333, 295, 269, 243, 219, 198, 181, 169, 156, 145, 112, 98, 71.

Tri-*O*-nonyl pentaerythritol (2c): Obtained as described above, after purification by column chromatography (EtOAc/hexane 1:9) as a yellow oil (1.5 g, 20%); homogeneous by TLC, $R_f=0.35$; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2a**, except for ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.27$ ppm (m, 36H, $18CH_2$ alkyl chains) and ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=31.89$, 29.74, 29.58, 29.46, 29.37, 29.29, 26.17, 22.48 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3543 (OH), 1108 (CO), 2934, 2861, 1465, 1375, 1051, 723 cm^{-1} (C-H, C-C); MS (ES): *m*/*z*: calcd for: 514; found: 516 $[M+2]^+$, 352, 299, 247, 226, 210, 197, 173, 155, 141, 127, 115, 100, 95, 71.

Tri-*O*-decyl pentaerythritol (2d): Obtained as described above, after purification by column chromatography (EtOAc/hexane 1:9) as a yellow oil (3.2 g, 33%); homogeneous by TLC, $R_f=0.36$; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2a**, except for ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.26$ ppm (m, 42H, $21CH_2$ alkyl chains) and ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=31.87$, 29.60, 29.55, 29.54, 29.43, 29.30, 26.13, 22.64 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3543 (OH), 1109 (CO), 2932, 2861, 1466, 1376 cm^{-1} (C-H, C-C); MS (ES): *m*/*z*: calcd for: 556; found: 558 $[M+2]^+$, 539, 513, 490, 453, 430, 400, 380, 353, 327, 288, 261, 240, 223, 210, 196, 187, 155, 140, 108, 98, 91, 84, 70.

Tri-*O*-undecyl pentaerythritol (2e): Obtained as described above, after purification by column chromatography (EtOAc/hexane 1:9) as a yellow oil (3.4 g, 26%); homogeneous by TLC, $R_f=0.38$; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2a**, except for ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.26$ ppm (m, 48H, $24CH_2$ alkyl chains) and ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=31.88$, 29.60, 29.54, 29.44, 29.32, 26.13, 22.64 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3543 (OH), 1109 (CO), 2931, 2861, 1466, 1376, 723 cm^{-1} (C-H, C-C); MS (ES): *m*/*z*: calcd for: 598; found: 600 $[M+2]^+$, 570, 539, 510, 469, 445, 408, 380, 355, 327, 271, 253, 242, 224, 201, 167, 154, 141, 112, 98, 85, 69.

Tri-*O*-dodecyl pentaerythritol (2f): Obtained as described above, after purification by column chromatography (EtOAc/petroleum ether 1:20) as an oily material (3.2 g, 23%); homogeneous by TLC, $R_f=0.44$; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2a**, except for ^1H NMR (200 MHz, $CDCl_3$): $\delta=1.27$ ppm (m, 54H, $27CH_2$ alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=1.96$, 29.73, 29.69, 29.62, 29.50, 29.40, 26.21, 22.70 ppm (CH_2 alkyl chains); MS (ES): *m*/*z*: calcd for: 641; found: 642 $[M+H]^+$; elemental analysis calcd (%) for $C_{41}H_{84}O_4$ (641.08): C 76.81, H 13.21; found: C 76.87, H 13.37.

Tri-*O*-tetradecyl pentaerythritol (2g): Obtained as described above, after purification by column chromatography (EtOAc/petroleum ether 1:20) as a white solid (2.3 g, 15%); homogeneous by TLC, $R_f=0.44$; m.p. 35–36°C; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2f**, except for ^1H NMR (200 MHz, $CDCl_3$): $\delta=1.27$ ppm (m, 66H, $33CH_2$ alkyl chains); elemental analysis calcd (%) for $C_{47}H_{96}O_4$ (725.24): C 77.83, H 13.34; found: C 77.57, H 13.27.

Tri-*O*-hexadecyl pentaerythritol (2h): Obtained as described above, after purification by column chromatography (EtOAc/petroleum ether 1:20) as a white solid (1.9 g, 11%); homogeneous by TLC, $R_f=0.45$; m.p. 44–45°C; ^1H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound; they were similar to those recorded for **2f**, except for ^1H NMR (200 MHz, $CDCl_3$): $\delta=1.27$ ppm (m, 78H, $39CH_2$ alkyl chains); elemental analysis calcd (%) for $C_{53}H_{108}O_4$ (809.39): C 78.64, H 13.45; found: C 78.62, H 13.55.

General procedure for the preparation of *O*-benzylidene-di-*O*-alkyl pentaerythritol derivatives 4a,f–h: *O*-Benzylidene pentaerythritol (**3**)[35] (1.35 g, 6.02 mmol) was added to a freshly prepared 50% aq. NaOH solution (7 mL) and the mixture was heated at 80°C for 30 min under stirring. Alkyl bromide (24.0 mmol) and tetrabutylammonium bromide (0.77 g, 2.4 mmol) were successively added and heating was maintained for 8 h. After cooling to RT, water was added (100 mL) and the mixture was extracted with $CHCl_3$ (3×40 mL); the combined organic phases were washed with water (2×25 mL), dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography.

***O*-Benzylidene-di-*O*-hexyl pentaerythritol (4a)**: Prepared as described above using hexyl bromide (3.4 mL, 24.0 mmol). The crude product was purified by column chromatography (EtOAc/petroleum ether 1:15) affording the pure product **4a** as an oily material (1.95 g, 83%). $R_f=0.50$;

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52–7.27 (m, 5H, C_6H_5), 5.44 (s, 1H, CHC_6H_5), 4.11 (d, 2H, $J_{a,e}$ = 11.2 Hz, 2H-eq), 3.90 (d, 2H, 2H-ax), 3.73 (s, 2H, CH_2OAlk), 3.48 (t, 2H, J = 6.5 Hz, OCH_2Alk), 3.38 (t, 2H, J = 6.5 Hz, OCH_2Alk), 3.25 (s, 2H, CH_2OAlk), 1.59 (m, 4H, 2OCH$_2$$CH_2$Alk), 1.31 (m, 12H, 6$CH_2$ alkyl chains), 0.91 ppm (t, 6H, 2CH_3 alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.63, 128.90, 128.31, 126.20 (C_6H_5), 101.79 (CHC_6H_5), 71.82, 71.69, 70.85, 70.30, 69.40 (CH_2OAlk, OCH$_2$Alk, $CH_2OCHC_6H_5$), 38.97 ($C(CH_2)_4$), 31.80, 31.75, 29.70, 29.56, 25.92, 22.72 (CH_2 alkyl chains), 14.13 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{24}H_{40}O_4$ (392.56): C 73.42, H 10.27; found: C 73.29, H 9.87.

***O*-Benzylidene-di-*O*-dodecyl pentaerythritol (4f)**: Prepared as described above for **4a**, using dodecyl bromide (5.7 mL, 24.0 mmol). The pure product **4f** was recovered after purification by column chromatography (EtOAc/petroleum ether 1:20) as a white solid (2.45 g, 75%). R_f = 0.39; m.p. 40–41 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **4a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.28 ppm (m, 36H, 18CH_2 alkyl chains); elemental analysis calcd (%) for $C_{36}H_{64}O_4$ (560.87): C 77.08, H 11.50; found: C 76.65, H 11.27.

***O*-Benzylidene-di-*O*-tetradecyl pentaerythritol (4g)**: Prepared as described above for **4a**, using tetradecyl bromide (7.15 mL, 24.0 mmol). The pure product **4g** was recovered after purification by column chromatography (EtOAc/petroleum ether 1:15) as a white solid (3.12 g, 84%). R_f = 0.44; m.p. 45 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **4a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 44H, 22CH_2 alkyl chains); elemental analysis calcd (%) for $C_{40}H_{72}O_4$ (616.98): C 77.86, H 11.76; found: C 77.66, H 12.15.

***O*-Benzylidene-di-*O*-hexadecyl pentaerythritol (4h)**: Prepared as described above for **4a**, using hexadecyl bromide (7.3 mL, 24.0 mmol). The pure product **4h** was recovered after purification by column chromatography (EtOAc/petroleum ether 1:15) as a white solid (3.25 g, 80%); R_f = 0.46; m.p. 58–59 °C (lit.:[32] m.p. 59–60 °C); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **4a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 52H, 26CH_2 alkyl chains).

General procedure for the preparation of di-*O*-alkyl pentaerythritols 5a,f–h: Compounds **4a**,**f–h** (5.0 mmol) were dissolved in a mixture of dry EtOH (8 mL) and freshly distilled cyclohexene (4 mL). Pd(OH)$_2$/C (200 mg) was then added and the suspension was heated under reflux for 6 h under argon. After cooling, filtration through Celite and concentration, the residue was purified on a short column of silica gel.

Di-*O*-hexyl pentaerythritol (5a): Prepared in 88% yield as described above from **4a**. Purification of the crude product by column chromatography (EtOAc/petroleum 1:1 ether) afforded the pure compound **5a** as an oily material. R_f = 0.67; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.64 (d, 4H, 2CH_2OH), 3.50 (s, 4H, 2CH_2OAlk), 3.42 (m, 4H, 2OCH_2Alk), 2.93 (s, 2H, 2O*H*), 1.55 (m, 4H, 2OCH$_2$$CH_2$Alk), 1.29 (m, 12H, 6$CH_2$ alkyl chains), 0.90 ppm (t, 6H, 2CH_3 alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 72.13, 71.83 (CH_2OAlk, OCH_2Alk), 44.75 ($C(CH_2)_4$), 31.57, 29.43, 25.73, 22.52 (CH_2 alkyl chains), 14.02 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{17}H_{36}O_4 \times 0.25\,H_2O$ (308.96): C 66.09, H 11.91; found: C 66.10, H 11.82.

Di-*O*-dodecyl pentaerythritol (5f): Prepared in 95% yield as described above from **4f**. Purification of the crude product by column chromatography (EtOAc/petroleum ether 1:1) afforded the pure compound **5f** as a white solid. R_f = 0.70; m.p. 57–58 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **5a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 36H, 18CH_2 alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.96, 29.71, 29.67, 29.56, 29.48, 29.40, 26.18, 22.73 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{29}H_{60}O_4$ (472.77): C 73.67, H 12.79; found: C 73.29, H 12.44.

Di-*O*-tetradecyl pentaerythritol (5g): Prepared in 85% yield as described above from **4g**. Purification of the crude product by column chromatography (EtOAc/petroleum ether 1:1) afforded the pure compound **5g** as a white solid. R_f = 0.57 (EtOAc/petroleum ether 1:2); m.p. 62 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **5f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 44H, 22CH_2 alkyl chains): elemental analysis calcd (%) for $C_{33}H_{68}O_4$ (528.87): C 74.94, H 12.96; found: C 74.67, H 13.04.

Di-*O*-hexadecyl pentaerythritol (5h): Prepared in 88% yield as described above from **4h**. Purification of the crude product by column chromatography (EtOAc/petroleum ether 1:2) afforded the pure compound **5h** as a white solid. R_f = 0.74; m.p. 69–70 °C (lit.:[32] m.p. 70–71 °C); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **5f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 ppm (m, 52H, 26CH_2 alkyl chains).

General procedure for the preparation of *O*-benzylidene-*O*-alkyl pentaerythritol derivatives 6f,h: A suspension of *O*-benzylidene pentaerythritol **3**[35] (2.24 g, 10.00 mmol) and dibutyltin oxide (2.96 g, 11.89 mmol) was heated under reflux in dry MeOH (30 mL) at 80 °C for 6 h. The solvent was removed by evaporation and the residue was carefully dried under high vacuum. The product was dissolved in DMF (60 mL), alkyl bromide (16 mmol) and caesium fluoride (4.03 g, 26.5 mmol) were added and the mixture was stirred for 24 h at RT. Ethyl acetate (50 mL) and water (1.5 mL) were then added and the mixture was stirred for 1 h. After filtration and concentration, the residue was dissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with water (2 × 50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography to afford mixtures of *cis* and *trans* isomers.

***O*-Benzylidene-*O*-dodecyl pentaerythritol (6f)**: Prepared as described above in 63% yield after purification by column chromatography EtOAc/petroleum ether 2:5). The less polar isomer (R_f = 0.69) could be obtained as a solid. M.p. 46 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52–7.35 (m, 5H, C_6H_5), 5.44 (s, 1H, CHC_6H_5), 4.18 (2d, 2H, $J_{a,e}$ = 11.9 Hz, 2H-eq), 4.05 (d, 2H, J = 6.0 Hz, CH_2OH), 3.78 (2d, 2H, J = 11.9 Hz, 2H-ax), 3.40 (t, 2H, OCH_2Alk), 3.29 (s, 2H, CH_2OAlk), 2.46 (t, 1H, CH_2O*H*), 1.57 (m, 2H, OCH$_2$$CH_2$Alk), 1.27 (m, 18H, 9$CH_2$ alkyl chain), 0.89 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.33, 128.98, 128.30, 126.21 (C_6H_5), 101.96 (CHC_6H_5), 72.89, 72.16, 69.97, 69.97 (C(OCH_2)$_4$), 63.44 (CH_2OH), 38.80 ($C(OCH_2)_4$), 32.00, 29.72, 29.70, 29.50, 29.44, 26.16, 22.76 (CH_2 alkyl chain), 14.20 ppm (CH_3 alkyl chain).; elemental analysis calcd (%) for $C_{24}H_{40}O_4$ (392.56): C 73.42, H 10.27; found: C 73.43, H 10.33.

The more polar isomer (R_f = 0.59) was obtained as an oil, contaminated by dodecyl alcohol. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52–7.35 (m, 5H, C_6H_5), 5.45 (s, 1H, CHC_6H_5), 4.19 (2d, 2H, J = 11.9 Hz, 2H-eq), 3.94 (s, 2H, CH_2OAlk), 3.76 (2d, 2H, J = 11.9 Hz, 2H-ax), 3.57–3.50 (m, 4H, CH_2OH, OCH_2Alk), 2.89 (t, 1H, CH_2O*H*), 1.57 (m, 2H, OCH$_2$$CH_2$Alk), 1.27 (m, 18H, 9$CH_2$ alkyl chain), 0.89 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.25, 129.05, 128.36, 126.12 (C_6H_5), 102.12 (CHC_6H_5), 73.24, 72.22, 70.60, 70.60 (C(OCH_2)$_4$), 66.61 (CH_2OH), 38.40 ($C(OCH_2)_4$), 31.97, 29.71, 29.70, 29.50, 29.41, 26.20, 22.74 (CH_2 alkyl chain), 14.17 ppm (CH_3 alkyl chain).

***O*-Benzylidene-*O*-hexadecyl pentaerythritol (6h)**: Prepared as described above in 68% yield after purification by column chromatography (EtOAc/petroleum ether 2:5). A pure fraction of the less polar isomer (R_f = 0.63 in EtOAc/petroleum ether 1:3) could be obtained as a solid. M.p. 52 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **6f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{30}H_{48}O_4$ (448.66): C 74.95, H 10.78; found: C 74.65, H 10.98.

The more polar isomer (R_f = 0.63 in EtOAc/petroleum ether 1:3) was obtained as an oil, contaminated by hexadecyl alcohol; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **6f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 26H, 13CH_2 alkyl chain).

General procedure for the preparation of *O*-alkyl-*O*-benzyl pentaerythritol derivatives 7f,h: A mixture of *O*-benzylidene-*O*-alkyl pentaerythritols **6f,h** (6.00 mmol), borane trimethylamine complex (1.824 g, 25.00 mmol) and crushed activated 4 Å molecular sieves (4 g) in dry THF (40 mml) was cooled to 0 °C. Aluminium trichloride (3.35 g, 25.05 mmol) was then added over 30 min; the mixture was allowed to reach RT and stirring was maintained for 16 h. After filtration, the solution was concentrated and the residue was dissolved in ethyl acetate (100 mL) and washed with saturated aq. $NaHCO_3$ (3 × 50 mL). The organic phase was concentrated and the residue was treated overnight with stirring in 1 M aq. HCl (50 mL). The product was extracted with CH_2Cl_2 (100 mL) and the organic phase was dried. After concentration, the crude residue was purified by column chromatography.

***O*-Benzyl-*O*-dodecyl pentaerythritol (7f)**: Obtained in 65% yield, as described above from **6f**, after purification by column chromatography (EtOAc/petroleum ether 1:1) as an oily material. $R_f = 0.40$; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.39$–7.29 (m, 5H, C_6H_5), 4.52 (s, 2H, $CH_2C_6H_5$), 3.68 (s, 4H, $2CH_2OH$), 3.56, 3.52 (2s, 4H, CH_2OAlk, CH_2OBn), 3.41 (t, 2H, $J = 6.5$ Hz, OCH_2Alk), 2.75 (m, 2H, $2CH_2OH$), 1.55 (m, 2H, OCH_2CH_2Alk), 1.27 (m, 18H, $9CH_2$ alkyl chain), 0.89 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 138.18$, 128.43, 127.69, 126.51 (C_6H_5), 73.68 ($CH_2C_6H_5$), 72.54, 72.00, 71.52 (CH_2OCH_2Alk, CH_2OBn), 64.66 (CH_2OH), 44.98 ($C(OCH_2)_4$), 31.98, 29.73, 29.70, 29.67, 29.59, 29.42, 26.19, 22.74 (CH_2 alkyl chain), 14.17 ppm (CH_3 alkyl chain); elemental analysis calcd (%) for $C_{24}H_{42}O_4$ (394.58): C 73.05, H 10.73; found: C 73.19, H 10.66.

***O*-Benzyl-*O*-hexadecyl pentaerythritol (7h)**: Obtained as described above from **6h**, in 54% yield after purification by column chromatography (EtOAc/petroleum ether 2:3) as a white solid. $R_f = 0.48$; m.p. 47 °C; ^{1}H and ^{13}C NMR spectra were similar to those recorded for **7f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ ppm (m, 26H, $13CH_2$ alkyl chain); elemental analysis calcd (%) for $C_{28}H_{50}O_4$ (450.68): C 74.62, H 11.18; found: C 74.41, H 11.16.

General procedure for the preparation of tri-*O*-alkyl-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) pentaerythritol derivatives (11a,f–h): Compounds **2a**,**f**–**h** (0.75 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (**8**)[14,36] (0.584 g, 0.79 mmol) were dissolved in dry CH_2Cl_2 (4.5 mL) in the presence of crushed activated 4 Å molecular sieves (0.4 g) and the suspension was cooled to 0 °C with stirring. A solution of TMSOTf (15 μL, 0.083 mmol) in CH_2Cl_2 (0.5 mL) was added over 1 h and the mixture was stirred overnight at 0 °C. After filtration through Celite, and addition of CH_2Cl_2 (50 mL), the organic phase was washed with saturated aq $NaHCO_3$, dried and concentrated to afford the crude product which was purified by column chromatography.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-tri-*O*-hexyl pentaerythritol (11a)**: Prepared as described above in 74% yield from tri-*O*-hexyl pentaerythritol **2a**. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:6) to yield an oily material. $R_f = 0.53$; $[\alpha]_D = +52.9°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.12$–7.21 (m, 20H, $4C_6H_5CO$), 6.01 (dd, 1H, $J_{3,4} = 3.4$, $J_{4,5} = 0.5$ Hz, H-4), 5.80 (dd, 1H, $J_{1,2} = 7.8$, $J_{2,3} = 10.4$ Hz, H-2), 5.63 (dd, 1H, H-3), 4.79 (d, 1H, H-1), 4.70 (dd, 1H, $J_{5,6a} = 6.0$, $J_{6a,6b} = 10.9$ Hz, H-6a), 4.41 (dd, 1H, $J_{5,6b} = 7.2$ Hz, H-6b), 4.29 (ddd, 1H, H-5), 4.01, 3.59 (2d, 2H, $J = 9.4$ Hz, CH_2OC-1), 3.33–3.18 (m, 12H, $3CH_2OCH_2Alk$), 1.44 (m, 6H, $3OCH_2CH_2Alk$), 1.27 (m, 18H, $9CH_2$ alkyl chains), 0.89 ppm (t, 9H, $3CH_3$ alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 166.00$, 165.66, 165.60, 165.18 (COC_6H_5), 133.55, 133.24, 130.08–128.31 (C_6H_5), 102.45 (C-1), 71.76 (OCH_2Alk), 71.21 (C-3), 71.21 (C-5), 70.18 (C-2), 69.76 (CH_2OC-1), 69.33 (CH_2OAlk), 68.28 (C-4), 61.96 (C-6), 45.43 ($C(CH_2O)_4$), 31.73, 29.63, 25.82, 22.72 (CH_2 alkyl chains), 14.13 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{57}H_{74}O_{13}$ (967.16): C 70.78, H 7.71; found: C 70.85, H 8.01.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-tri-*O*-dodecyl pentaerythritol (11f)**: Prepared as described above in 73% yield from tri-*O*-dodecyl pentaerythritol **2f**. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:5) to yield an oily material. $R_f = 0.73$; $[\alpha]_D = +43.7°$ ($c = 1.0$, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **11a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ ppm (m, 54H, $27CH_2$ alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.01$, 29.78–29.46, 26.30, 22.76 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{75}H_{110}O_{13}$ (1219.63): C 73.86, H 9.09; found: C 73.97, H 9.35.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-tri-*O*-tetradecyl pentaerythritol (11g)**: Prepared as described above in 72% yield from tri-*O*-tetradecyl pentaerythritol **2g**. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:9) to yield an oily material. $R_f = 0.50$; $[\alpha]_D = +40.3°$ ($c = 1.0$, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **11f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ ppm (m, 66H, $33CH_2$ alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 32.02$, 29.81, 29.71, 29.63, 29.46, 26.30, 22.77 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{81}H_{122}O_{13}$ (1303.79): C 74.61, H 9.43; found: C 74.67, H, 9.57.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-tri-*O*-hexadecyl pentaerythritol (11h)**: Prepared as described above in 76% yield from tri-*O*-hexadecyl pentaerythritol **2h**. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:9) to yield an oily material. $R_f = 0.50$; $[\alpha]_D = +37.8°$ ($c = 1.0$, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **11f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ ppm (m, 78H, $39CH_2$ alkyl chains); elemental analysis calcd (%) for $C_{87}H_{134}O_{13}$ (1387.94): C 75.28, H 9.73; found: C 75.25, H, 9.73.

General procedure for the preparation of *O*-(2,3,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-alkyl pentaerythritol derivatives (12a–h)

Method A: A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**9**)[38] (0.411 g, 1.00 mmol), alcohol, **2a**,**f**–**h** (0.5 mmol) and crushed activated 4 Å molecular sieves (0.4 g) in freshly distilled acetonitrile (4 mL) was stirred for 10 min under argon. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.110 g, 0.50 mmol) and iodine (0.252 g, 1.0 mmol) were then added and the solution was stirred for 6 h at RT. After filtration and concentration, the residue was dissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with saturated aq $Na_2S_2O_3$ (2×25 mL), dried (Na_2SO_4) and concentrated. The product was purified by column chromatography.

Method B: Compounds **2a**,**f**–**h** (0.75 mmol) and 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**10**)[39] (0.406 g, 0.83 mmol) were dissolved in dry CH_2Cl_2 (4 mL) in the presence of crushed activated 4 Å molecular sieves (0.4 g) and the suspension was cooled to −20 °C with stirring. A solution of TMSOTf (15 μL, 0.083 mmol) in CH_2Cl_2 (0.5 mL) was added over 1 h and the mixture was stirred overnight at −20 °C. The mixture was neutralized by addition of triethylamine (20 μL, 0.14 mmol), then allowed to reach RT; after filtration through Celite, and concentration, the crude product was purified by column chromatography.

Method C: A mixture of the respective alcohol, **2b**–**e** (2.3 mmol), mercury cyanide (0.88 g, 3.5 mmol) mercury bromide (1.26 g, 3.50 mmol) and anhydrous CH_2Cl_2 (100 mL) was stirred under nitrogen. To this was added galactosyl bromide **9**[38] (2.47 g, 6.90 mmol) in anhydrous CH_2Cl_2 (50 mL) dropwise over 30 min, after which the mixture was stirred overnight. The resulting suspension was diluted with CH_2Cl_2 (200 mL) was washed with 1 M potassium bromide (5×100 mL) and water (5×100 mL). The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo to yield a pale yellow oil which was purified by column chromatography (CH_2Cl_2/diethyl ether 4:1) to yield a clear oil which was homogeneous on TLC.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-hexyl pentaerythritol (12a)**: Prepared from the alcohol **2a** in 76% yield (Method A) or 40% yield (Method B) after purification by column chromatography (EtOAc/petroleum ether 1:3) as an oily material. $R_f = 0.54$; $[\alpha]_D = -11.0°$ ($c = 1.0$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.38$ (dd, 1H, $J_{3,4} = 3.4$, $J_{4,5} = 0.5$ Hz, H-4), 5.20 (dd, 1H, $J_{1,2} = 7.8$, $J_{2,3} = 10.5$ Hz, H-2), 4.99 (dd, 1H, H-3), 4.42 (d, 1H, H-1), 4.18 (dd, 1H, $J_{5,6a} = 6.9$, $J_{6a,6b} = 11.1$ Hz, H-6a), 4.12 (dd, 1H, $J_{5,6b} = 7.0$ Hz, H-6b), 3.90, 3.49 (2 d, 2H, $J = 9.7$ Hz, CH_2OC-1), 3.86 (ddd, 1H, H-5), 3.38–3.28 (m, 12H, $3CH_2OCH_2Alk$), 2.15, 2.06, 2.05, 1.99 (4s, 12H, $4CH_3COO$), 1.52 (m, 6H, $3OCH_2CH_2Alk$), 1.29 (m, 18H, $9CH_2$ alkyl chains), 0.89 ppm (t, 9H, $3CH_3$ alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.17$, 170.17, 170.00, 169.04 ($COCH_3$), 101.98 (C-1), 71.40 (OCH_2Alk), 70.93 (C-3), 70.39 (C-5), 69.54 (CH_2OC-1), 69.33 (CH_2OAlk), 69.07 (C-2), 67.02 (C-4), 61.07 (C-6), 45.28 ($C(CH_2O)_4$), 31.62, 29.56, 25.85, 22.60 (CH_2 alkyl chains), 13.98 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{37}H_{66}O_{13}$ (718.90): C 61.81, H 9.25; found: C 61.61, H 9.27.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-heptyl pentaerythritol (12b)**: Prepared from the alcohol **2b** in 66% yield (Method C) after purification by column chromatography. Oil; homogeneous by TLC, $R_f = 0.54$; $[\alpha]_D = -9.0°$ ($c = 1.0$, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **12a**, except for ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$ ppm (m, 24H, $12CH_2$ alkyl chains) and ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.87$, 29.65, 26.17, 22.63 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu} = 1759$ (C=O), 2936, 2865, 1466, 1373, 1225, 1081, 758 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 760; found: 761

$[M+H]^+$, 731, 702, 666, 601, 566, 514, 514, 486, 460, 427, 395, 370, 330, 313, 296, 271, 243, 210, 197, 168, 144, 126, 97, 69.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-nonyl pentaerythritol (12c)**: Prepared from the alcohol **2c** in 62% yield (Method C) after purification by column chromatography. Oil; homogeneous by TLC, R_f = 0.56; $[\alpha]_D = -7.0°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12a**, except for ^1H NMR (400 MHz, $CDCl_3$): δ = 1.27 ppm (m, 36H, 18CH_2 alkyl chains) and ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.92, 29.69, 29.65, 29.54, 29.35, 26.25, 22.70 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 1758 (C=O), 2933, 2863, 1561, 1464, 1373, 1225, 1083 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 844; found: 846 $[M+2]^+$, 702, 610, 556, 528, 498, 468, 443, 413, 383, 369, 352, 331, 325, 299, 289, 268, 250, 229, 225, 210, 197, 173, 169, 152, 139, 127, 109, 99, 85, 71.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-decyl pentaerythritol (12d)**: Prepared from the alcohol **2d** in 53% yield (Method C) after purification by column chromatography. Oil; homogeneous by TLC, R_f = 0.59; $[\alpha]_D = -8.0°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12a**, except for ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 ppm (m, 42H, 21CH_2 alkyl chains) and ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.92, 29.69, 29.63, 29.53, 29.36, 26.24, 22.69 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 1759 (C=O), 2932, 2861, 1466, 1373, 1225, 1081, 758 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 909; found: 912, 911, 910 $[M+Na+H^+]$, 908, 844, 804, 784, 726, 698, 674, 596, 533, 504, 436, 392, 364, 334, 278.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-undecyl pentaerythritol (12e)**: Prepared from the alcohol **2e** in 61% yield (Method C) after purification by column chromatography. Oil; homogeneous by TLC, R_f = 0.62; $[\alpha]_D = -7.0°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12a**, except for ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 ppm (m, 48H, 24CH_2 alkyl chains) and ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.92, 29.69, 29.66, 29.54, 29.37, 26.25, 22.69 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 1759 (C=O), 2932, 2861, 1466, 1372, 1224, 1081 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 951; found: 952 $[M+Na+H^+]$, 911, 909, 805, 783, 765, 692, 670, 568, 510, 486, 436, 414, 351, 320, 243.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-dodecyl pentaerythritol (12f)**: Prepared from the alcohol **2f** in 75% yield (Method A) or 53% yield (Method B) after purification by column chromatography (ethyl acetate/petroleum ether 1:3) as an oily material. R_f = 0.78; $[\alpha]_D = -5.2°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12a**, except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.29 ppm (m, 54H, 27CH_2 alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.91, 29.66, 29.50, 29.35, 26.24, 22.66 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{55}H_{102}O_{13}$ (971.37): C 68.00, H 10.58; found: C 68.12, H 10.72.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-tetradecyl pentaerythritol (12g)**: Prepared from the alcohol **2g** in 82% yield (method A) after purification by column chromatography (EtOAc/petroleum ether 1:4) as an oily material; R_f = 0.72; $[\alpha]_D = -7.6°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12f**, except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 66H, 33CH_2 alkyl chains); elemental analysis calcd (%) for $C_{61}H_{114}O_{13}$ (1055.52): C 69.41, H 10.88; found: C 69.43, H 11.10.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-tri-*O*-hexadecyl pentaerythritol (12h)**: Prepared from the alcohol **2h** in 79% yield (method A) or 35% yield (Method B) after purification by column chromatography (EtOAc/petroleum ether 1:3) as an oily material; R_f = 0.84 (ethyl acetate/petroleum ether 1:3); $[\alpha]_D = -6.0°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **12f**, except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.27 ppm (m, 78H, 39CH_2 alkyl chains); elemental analysis calcd (%) for $C_{67}H_{126}O_{13}$ (1139.68): C 70.60, H 11.14; found: C 70.65, H 11.33.

General procedure for the preparation of di-*O*-alkyl-bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) pentaerythritol derivatives (13a,f–h): Compounds **5a**,**f**–**h** (1.00 mmol) and trichloroacetimidate (**8**)[14,37] (1.50 g, 2.20 mmol) were dissolved in dry CH_2Cl_2 (6.0 mL) in the presence of crushed activated 4 Å molecular sieves (0.5 g) and the suspension was cooled to 0°C with stirring. A solution of TMSOTf (30 μL, 0.166 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 1 h and the mixture was stirred overnight at 0°C. After filtration on Celite, and addition of CH_2Cl_2 (50 mL), the organic phase was washed with saturated aq $NaHCO_3$, dried and concentrated to afford the crude product which was purified by column chromatography.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-di-*O*-hexyl pentaerythritol (13a): Prepared in 72% yield from **5a**; the crude product was purified twice by column chromatography (CH_2Cl_2/EtOH 99:1, then EtOAc/petroleum ether 1:2). Oily material; R_f = 0.63 (EtOAc/petroleum ether 1:2); $[\alpha]_D = +46.7°$ (c = 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 8.20–7.09 (m, 40H, 8C_6H_5CO), 5.91 (br d, 2H, $J_{3,4}$ = 3.4, $J_{4,5}$ = 0.5 Hz, 2H-4), 5.68 (br d, 2H, $J_{1,2}$ = 7.8, $J_{2,3}$ = 10.4 Hz, 2H-2), 5.41 (dd, 2H, 2H-3), 4.54 (dd, 2H, $J_{5,6a}$ = 6.2, $J_{6a,6b}$ = 11.2 Hz, 2H-6a), 4.29 (dd, 2H, $J_{5,6b}$ = 7.1 Hz, 2H-6b), 4.06 (d, 2H, 2H-1), 3.93 (d, 2H, J = 9.4 Hz, 2CH_aOC-1), 3.54 (m, 2H, 2H-5), 3.42–3.22 (m, 10H, 2CH_2OCH_2Alk, 2CH_bOC-1), 1.64 (m, 4H, 2OCH$_2$CH_2Alk), 1.26 (m, 12H, 6CH_2 alkyl chains), 0.89 ppm (t, 6H, 2CH_3 alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.95, 165.66, 165.59, 164.94 (COC_6H_5), 133.62, 133.35, 130.07–128.37 (C_6H_5), 102.05 (C-1), 71.54 (OCH$_2$Alk), 71.25 (C-3), 70.92 (C-5), 70.15 (C-2), 69.17, 69.04 (CCH$_2$O), 68.06 (C-4), 61.71 (C-6), 45.24 (C(CH$_2$O)$_4$), 31.74, 29.64, 25.90, 22.72 ppm (CH_2 alkyl chains), 14.15 (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{85}H_{88}O_{22}$ (1461.55): C 69.85, H 6.07; found: C 69.46, H 6.00.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-di-*O*-dodecyl pentaerythritol (13f): Prepared in 45% yield from **5f**; the crude product was purified twice by column chromatography (CH_2Cl_2/EtOH 99:1, then EtOAc/petroleum ether 1:3). Oily material; R_f = 0.62 (EtOAc/petroleum ether 1:3); $[\alpha]_D = +54.0°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **13a** except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 ppm (m, 36H, 18CH_2 alkyl chains) and ^{13}C NMR (200 MHz, $CDCl_3$): δ = 32.00, 29.80, 29.64, 29.46, 26.32, 22.77 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{97}H_{112}O_{22}$ (1629.87): C 71.48, H 6.93; found: C 71.61, H 7.24.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-di-*O*-tetradecyl pentaerythritol (13g): Prepared in 62% yield from **5g**; the crude product was purified twice by column chromatography (CH_2Cl_2/EtOH 99:1, then EtOAc/petroleum ether 1:3). Oily material; R_f = 0.65 (EtOAc/petroleum ether 1:3); $[\alpha]_D = +46.4°$ (c = 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were similar to those recorded for **13f** except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 ppm (m, 44H, 22CH_2 alkyl chains); elemental analysis calcd (%) for $C_{101}H_{120}O_{22}$ (1685.97): C 71.95, H 7.17; found: C 71.55, H 7.17.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-di-*O*-hexadecyl pentaerythritol (13h): Prepared in 56% yield from **5h**; the crude product was purified twice by column chromatography (CH_2Cl_2/EtOH 99:1, then EtOAc/petroleum ether 1:3). Oily material; R_f = 0.67 (EtOAc/petroleum ether 1:3); $[\alpha]_D = +52.4°$ (c = 1.0, $CHCl_3$);^1H and ^{13}C NMR spectra were similar to those recorded for **13f** except for ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 (m, 52H, 26CH_2 alkyl chains); elemental analysis calcd (%) for $C_{105}H_{128}O_{22}$ (1742.07): C 72.38, H 7.40; found: C 72.13, H 7.28.

General procedure for the preparation of bis-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-di-*O*-alkyl pentaerythritol derivatives (14a,f–h)

Method A: Benzoyl derivative **13a**,**f**–**h** (0.50 mmol) was treated overnight in MeOH containing a catalytic amount of sodium methylate (1—5 μmol). After neutralization with Amberlyst IR 120 (H^+), the solution was concentrated and the residue was acetylated for 16 h in pyridine/Ac_2O 2:1 (15 mL). After concentration the product was purified by column chromatography affording compounds **14a**,**f**–**h** in good yields.

Method B: A mixture of galactosyl bromide **9** (0.822 g, 2.00 mmol), acceptor alcohol (0.5 mmol) and crushed activated 4 Å molecular sieves (0.8 g) in freshly distilled acetonitrile (8 mL) was stirred for 10 min under argon. DDQ (0.220 g, 1.00 mmol) and iodine (0.504 g, 2.00 mmol) were then added and the solution was stirred for 6 h at RT. After filtration and concentration, the residue was dissolved in CH_2Cl_2 (100 mL) and the organic phase was washed with saturated aq $Na_2S_2O_3$ (2×25 mL), dried (Na_2SO_4) and concentrated. The product was purified by column chromatography.

Bis-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-di-*O*-hexyl pentaerythritol (14a): Obtained in 83% yield (method A) from **13a** after purification by column chromatography (EtOAc/petroleum ether 1:1) as an oily material; $R_f = 0.30$ (EtOAc/petroleum ether 2:3); $[\alpha]_D = -13.1°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.39$ (br d, 2H, $J_{3,4} = 3.2$, $J_{4,5} = 0.5$ Hz, 2H-4), 5.19 (br d, 2H, $J_{1,2} = 7.8$, $J_{2,3} = 10.3$ Hz, 2H-2), 4.99 (dd, 2H, 2H-3), 4.40 (d, 2H, 2H-1), 4.15 (m, 4H, 2H-6a, 2H-6b), 3.86 (dd, 2H, $J_{5,6a} = 6.1$, $J_{5,6b} = 7.1$ Hz, 2H-5), 3.85 (d, 2H, $J = 9.4$ Hz, 2CH_aOC-1), 3.43 (d, 2H, $J = 9.4$ Hz, 2CH_bOC-1), 3.37–3.22 (m, 8H, 2CH_2OCH_2Alk), 2.14, 2.05, 2.03, 1.97 (4s, 24H, 8CH_3CO), 1.47 (m, 4H, 2OCH$_2$CH_2Alk), 1.28 (m, 12H, 6CH_2 alkyl chains), 0.88 ppm (t, 6H, 2CH_3 alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.29$, 170.24, 170.07, 169.13 (CH_3CO), 101.85 (C-1), 71.53 (OCH_2Alk), 70.85 (C-3), 70.47 (C-5), 69.18 (CCH$_2$O), 69.13 (C-2), 68.78 (CCH$_2$O), 67.02 (C-4), 61.09 (C-6), 45.19 (C(CH$_2$O)$_4$), 31.63, 29.57, 25.85, 22.60 (CH_2 alkyl chains), 14.02 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{45}H_{72}O_{22}$ (965.03): C 56.00, H 7.52; found: C 56.22, H 7.49.

Bis-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-di-*O*-dodecyl pentaerythritol (14f): Obtained in 84% yield (method A) from **13f** after purification by column chromatography (EtOAc/petroleum ether 1:1). Oily material; $R_f = 0.45$ (EtOAc/petroleum ether 2:3); $[\alpha]_D = -12.7$ (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **14a** except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.28$ ppm (m, 36H, 18CH_2 alkyl chains); elemental analysis calcd (%) for $C_{57}H_{96}O_{22}$ (1133.34): C 60.40, H 8.54; found: C 60.61, H 8.83.

Bis-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-di-*O*-tetradecyl pentaerythritol (14g): Obtained from **13g** in 85% yield (method A) or from **5g** in 40% yield (method B), after purification by column chromatography (EtOAc/petroleum ether 3:4). Oily material; $R_f = 0.67$; $[\alpha]_D = -11.0$ (c = 1.0, $CHCl_3$; ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **14f** except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ ppm (m, 44H, 22CH_2 alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.84, 29.61, 29.44, 29.28, 26.18, 22.60 ppm (CH_2 alkyl chains); elemental analysis calcd (%) for $C_{61}H_{104}O_{22}$ (1189.44): C 61.59, H 8.81; found: C 61.54, H 8.92.

Bis-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-di-*O*-hexadecyl pentaerythritol (14h): Obtained from **13h** in 86% yield (method A) after purification by column chromatography (EtOAc/petroleum ether 1:2). Oily material; $R_f = 0.69$; $[\alpha]_D = -11.5°$ (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **14f** except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ ppm (m, 52H, 26CH_2 alkyl chains); elemental analysis calcd (%) for $C_{65}H_{112}O_{22}$ (1245.55): C 62.67, H 9.06; found: C 62.36, H 9.25.

General procedure for the preparation of *O*-alkyl-bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-benzyl pentaerythritol derivatives (15f,h): Compounds **7f,h** (1.00 mmol) and trichloroacetimidate **8** (1.50 g, 2.20 mmol) were dissolved in dry CH_2Cl_2 (6.0 mL) in the presence of crushed activated 4 Å molecular sieves (0.8 g) and the suspension was cooled to 0°C with stirring. A solution of TMSOTf (30 μL, 0.166 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 1 h and the mixture was stirred overnight at 0°C. After filtration on Celite, and addition of CH_2Cl_2 (50 mL), the organic phase was washed with saturated aq $NaHCO_3$, dried and concentrated to afford the crude product which was purified twice by column chromatography, first with MeOH/$CHCl_3$ 1:300, then with different mixtures EtOAc/petroleum ether.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-benzyl-*O*-dodecyl pentaerythritol (15f): Prepared as described above and purified by column chromatography (EtOAc/petroleum ether 2:5). Product **15f** was obtained in 72% yield as an oily material; $R_f = 0.54$ (EtOAc/petroleum ether 1:3); $[\alpha]_D = +50.5°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.08$–7.21 (m, 45H, 9C$_6H_5$), 5.80 (br d, 2H, $J_{3,4} = 3.4$, $J_{4,5} = 0.5$ Hz, 2H-4), 5.64 (dd, 2H, $J_{1,2} = 7.8$, $J_{2,3} = 10.3$ Hz, 2H-2), 5.39 (dd, 2H, 2H-3), 4.54, 4.53 (2dd, $J_{5,6a} = 6.3$, $J_{6a,6b} = 11.2$ Hz, 2 H-6a), 4.39 (d, 2H, CH_2C$_6H_5$), 4.29 (d, 2H, $J_{5,6b} = 7.1$ Hz, 2H-6b), 4.05 (d, 2H, 2H-1), 3.97, 3.96 (2d, 2H, 2CH_aOC-1), 3.53 (m, 4H, 2H-5, 2CH_bOC-1), 3.43, 3.39 (2d, 2H, J= 5.9 Hz, CH_2OCH$_2$C$_6H_5$), 3.34–3.20 (m, 4H, CH_2OCH_2Alk), 1.43 (m, 2H, OCH$_2$CH_2Alk), 1.26 (m, 18H, 9CH_2 alkyl chain), 0.88 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 165.97$, 165.68, 165.61, 165.03 (C_6H_5CO), 138.91, 133.64, 133.38, 131.09–127.31 (C_6H_5), 102.03 (C-1), 73.30 ($CH_2C_6H_5$), 71.65 (OCH$_2$Alk), 71.27 (C-3), 70.99 (C-5), 70.18 (C-2), 69.97 (C(CH$_2$O)$_4$), 68.10 (C-4), 61.77 (C-6), 45.37 (C(CH$_2$O)$_4$), 31.99, 29.78, 29.64, 29.44, 26.28, 22.70 (CH_2 alkyl chain), 14.28 ppm (CH_3 alkyl chain); elemental analysis calcd (%) for $C_{92}H_{94}O_{22}$ (1551.67): C 71.21, H 6.11; found: C 70.77, H 6.25.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-benzyl-*O*-hexadecyl pentaerythritol (15h): Prepared as described above and purified by column chroamtography (EtOAc/petroleum ether 2:5). Product **15h** was obtained in 70% yield. Oily material; $R_f = 0.58$ (EtOAc/petroleum ether 1:3); $[\alpha]_D = +48.0°$ (c = 1.0, $CHCl_3$). ^{1}H NMR and ^{13}C NMR spectra were similar to those obtained for **15f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{96}H_{102}O_{22}$ (1607.78): C 71.71, H 6.39; found: C 71.65, H 6.42.

General procedure for the preparation of *O*-alkyl-bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) pentaerythritol derivatives (16f,h): 20% Pd(OH)$_2$/C (100 mg) was added to compounds **15f,h** (0.65 mmol) in EtOH (8 mL) and freshly distilled cyclohexene (4 mL, 39 mmol) and the suspension was refluxed for 6 h. After filtration over Celite and concentration, the residue was purified by column chromatography (EtOAc/petroleum ether 1:2).

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-dodecyl pentaerythritol (16f): Prepared in 92% yield from **15f**. Oily material; $R_f = 0.66$ (EtOAc/petroleum ether 1:2); $[\alpha]_D = +58.7°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.09$–7.21 (m, 40H, 8C$_6H_5$), 5.79 (m, 2H, 2H-4), 5.62 (dd, 2H, $J_{1,2} = 7.8$, $J_{2,3} = 10.2$ Hz, 2H-2), 5.39, 5.37 (2dd, 2H, $J_{3,4}$ = 3.4 Hz, 2H-3), 4.56, 4.50 (2 dd, $J_{5,6a} = 6.5$, $J_{6a,6b} = 11.1$ Hz, 2H-6a), 4.29 (dd, 2H, $J_{5,6b} = 6.5$ Hz, 2H-6b), 3.93 (d, 2H, 2H-1), 3.87 (d, 2H, J= 9.5 Hz, 2CH_aOC-1), 3.74, 3.66 (2dd, 2H, $J = 11.5$, $J_{H,OH} = 6.4$ Hz, CH_2OH), 3.50 (m, 2H, H-5), 3.45–3.26 (m, 6H, 2CH_bOC-1, CH_2OCH_2Alk), 2.66 (dd, 1H, CH$_2$OH), 1.44 (m, 2H, OCH$_2$CH_2Alk), 1.25 (m, 18H, 9CH_2 alkyl chain), 0.89 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (200 MHz, $CDCl_3$): $\delta = 165.96$, 165.65, 165.62, 165.54, 165.10, 165.05 (C_6H_5CO), 133.79, 133.67, 133.40, 130.05–128.38 (C_6H_5CO), 102.03 (C-1), 71.98 (OCH$_2$Alk), 71.08 (C-3), 70.95 (C-5), 70.07 (C-2), 69.64, 68.99 (CH$_2$OC-1, CH$_2$OAlk), 68.09, 67.94 (C-4), 65.31 (CH$_2$OH), 61.78 (C-6), 44.75 (C(CH$_2$O)$_4$), 31.96, 29.70, 29.54, 29.41, 26.15, 22.74 (CH_2 alkyl chain), 14.17 ppm (CH_3 alkyl chain); elemental analysis calcd (%) for $C_{85}H_{88}O_{22} \times H_2O$ (1479.57): C 69.00, H 6.13; found: C 69.00, H 6.15.

Bis-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-hexadecyl pentaerythritol (16h): Prepared in 92% yield from **15h**. Oily material; R_f= 0.70 (EtOAc/petroleum ether 1:2); $[\alpha]_D = +62.7°$ (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **16b** except for ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.25$ ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{89}H_{96}O_{22}$ (1517.66): C 70.43, H 6.38; found: C 70.25, H 6.61.

General procedure for the preparation of tris-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-alkyl pentaerythritol derivatives (17f,h): Compounds **16f,h** (0.50 mmol) and trichloroacetimidate **8** (0.407 g, 0.55 mmol) were dissolved in dry CH_2Cl_2 (5.0 mL) in the presence of crushed activated 4 Å molecular sieves (0.4 g) and the suspension was cooled to 0°C with stirring. A solution of TMSOTf (20 μL, 0.11 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise over 1 h and the mixture was stirred overnight at 0°C. After filtration on Celite, the solution was directly concentrated to afford the crude product which was purified by column chromatography.

Tris-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-dodecyl pentaerythritol (17f): Prepared as described above in 68% yield, after purification by column chromatography (MeOH/$CHCl_3$ 1:175, then EtOAc/petroleum ether 1:2). Amorphous solid; $R_f = 0.58$ (EtOAc/petroleum ether 1:2); $[\alpha]_D = +55.0°$ (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.09–7.21 (m, 60H, 12C$_6H_5$), 5.82 (br d, 3H, $J_{3,4} = 3.3$, $J_{4,5} = 0.5$ Hz, 3H-4), 5.65 (dd, 3H, $J_{1,2} = 7.8$, $J_{2,3} = 10.4$ Hz, 3H-2), 5.39 (dd, 3H, 3H-3), 4.52 (dd, $J_{5,6a} = 6.2$, $J_{6a,6b} = 11.1$ Hz, 3H-6a), 4.29 (dd, 3H, $J_{5,6b} = 6.4$ Hz, 3H-6b), 4.08 (d, 3H, 3H-1), 3.92 (d, 3H, $J = 9.5$ Hz, 3CH_aOC-1), 3.52 (m, 3H, 3H-5), 3.39–3.20 (m, 7H, 3CH_bOC-1, CH_2OCH_2Alk), 1.44 (m, 2H, OCH$_2$CH_2Alk), 1.22 (m, 18H, 9CH_2 alkyl chain), 0.87 ppm (t, 3H, CH_3

alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 165.92, 165.69, 165.60, 165.02 (C_6H_5CO), 133.96, 133.64, 133.43, 130.08–128.39 (C_6H_5), 101.94 (C-1), 71.71 (OCH_2Alk), 71.38 (C-3), 70.96 (C-5), 70.28 (C-2), 68.34 (C-(CH_2O)$_4$), 68.04 (C-4), 61.66 (C-6), 45.32 ($C(CH_2O)_4$), 31.98, 29.78, 29.75, 29.68, 29.44, 26.31, 22.76 (CH_2 alkyl chain), 14.22 ppm (CH_3 alkyl chain); elemental analysis calcd (%) for $C_{119}H_{114}O_{31}$ (2040.10): C 70.05, H 5.63; found: C 70.09, H 5.56.

Tris-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-*O*-hexadecyl pentaerythritol (17h): Prepared as described above in 73% yield, after purification by column chromatography (MeOH/$CHCl_3$ 1:300, then EtOAc/petroleum ether 1:2). Amorphous solid; R_f = 0.62 (EtOAc/petroleum ether 1:2); $[\alpha]_D$ = +44.3° (c = 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **17f** except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.23 ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{123}H_{122}O_{31}$ (2096.21): C 70.47, H 5.87; found: C 70.17, H 5.81.

General procedure for the preparation of tris-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-*O*-alkyl pentaerythritol derivatives (18f,h): Compounds **17f,h** (0.30 mmol) were treated overnight in MeOH (50 mL) containing a catalytic amount of sodium (1–3 μmol). After neutralization of the solution with Amberlyst IR 120 [H^+], filtration and concentration, the residue was washed with petroleum ether (2×20 mL); the supernatant was removed and the product was acetylated overnight in Ac_2O/pyridine 1:2 (15 mL). After a new concentration, the pure compound was recovered after purification by column chromatography.

Tris-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-*O*-dodecyl pentaerythritol (18f): Prepared as described above in 71% yield, after purification by column chromatography (EtOAc/petroleum ether 3:2). Oily material; R_f = 0.69; $[\alpha]_D$ = −15.7° (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.39 (br d, 3H, $J_{3,4}$ = 3.3, $J_{4,5}$ = 0.5 Hz, 3H-4), 5.17 (dd, 3H, $J_{1,2}$ = 7.8, $J_{2,3}$ = 10.4 Hz, 3H-2), 5.02 (dd, 3H, 3H-3), 4.39 (d, 3H, 3H-1), 4.16 (d, 6H, $J_{5,6a}$ = $J_{5,6b}$ = 6.7 Hz, 3H-6a, 3H-6b), 3.90 (br t, 3H, 3H-5), 3.83 (d, 3H, J = 9.8 Hz, 3CH_aOC-1), 3.42 (d, 3H, J = 9.8 Hz, 3CH_bOC-1), 3.40–3.20 (m, 4H, CH_2OCH_2Alk), 2.17, 2.07, 2.05, 1.99 (4s, 36H, 12CH_3CO), 1.52 (m, 2H, OCH_2CH_2Alk), 1.26 (m, 18H, 9CH_2 alkyl chain), 0.88 ppm (t, 3H, CH_3 alkyl chain); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.21, 170.18, 169.98, 169.09 (CH_3CO), 101.72 (C-1), 71.64 (OCH_2Alk), 70.73, 70.52 (C-3, C-5), 69.16 (C-2), 68.73 (CH_2OC-1), 68.33 (CH_2OAlk), 66.96 (C-4), 60.99 (C-6), 45.08 ($C(CH_2O)_4$), 31.94, 29.65, 29.48, 29.28, 26.19, 22.65 (CH_2 alkyl chain), 14.15 ppm (CH_3 alkyl chain); elemental analysis calcd (%) for $C_{59}H_{90}O_{31}$ (1295.31): C 54.70, H 7.00; found: C 54.27, H 6.88.

Tris-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-*O*-hexdecyl pentaerythritol (18h): Prepared as described above in 73% yield, after purification by column chromatography (EtOAc/petroleum ether 4:3). Oily material; R_f = 0.71 (EtOAc/petroleum ether 3:2); $[\alpha]_D$ = −19.2° (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR were similar to those recorded for **18f**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.25 ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{63}H_{98}O_{31}$ (1351.41): C 55.99, H 7.31; found: C 55.86, H 7.43.

General procedure for de-*O*-acetylation of the pentaerythritol derivatives 12a–h, 14a,f–h and 18f,h

Method A: Compounds **12a,f–h** (1.00 mmol), **14a,f–h** (0.50 mmol) or **18f,h** (0.20 mmol) were treated overnight in MeOH (50 mL) containing a catalytic amount of sodium (1 mol%). The pure product was directly obtained after neutralization of the solution with Amberlyst IR 120 [H^+], filtration and concentration.

Method B: A solution of 1M sodium methoxide in MeOH (1 mL) was added to a solution of the respective protected derivative **12b–e** (1.02 g, 1.3 mmol) in anhydrous MeOH (18 mL) and anhydrous CH_2Cl_2 (12 mL). The resulting mixture was stirred at room temperature for 15 min under nitrogen. The solvent was removed, water (20 mL) and methanol (5 mL) added and the subsequent solution stirred overnight at room temperature. The reaction mixture was neutralized with Amberlyst IR-120 [H^+] filtered and the resin washed with EtOH (20 mL). The solvent was removed to yield an off white solid which was partitioned between with butanol (60 mL) and water (40 mL). The organic layer was separated, ethanol added (150 mL) and the solvent concentrated to yield a white solid which was removed by filtration.

***O*-β-D-Galactopyranosyl-tri-*O*-hexyl pentaerythritol (19a)**: Prepared from **12a** in 93% yield as described in Method A. Oily material; $[\alpha]_D$ = −9.5° (c = 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.22 (dd, 1H, $J_{1,2}$ = 7.0 Hz, H-1), 3.99–3.35 (m, 20H, H-2, H-3, H-4, H-5, H-6a, H-6b, CH_2OC-1, 3CH_2OCH_2Alk), 1.53 (m, 6H, 3OCH_2CH_2Alk), 1.29 (m, 18H, 9CH_2 alkyl chains), 0.89 ppm (t, 9H, 3CH_3 alkyl chains); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 104.70 (C-1), 74.71 (C-5), 73.45 (C-3), 71.68 (OCH_2Alk), 71.31 (C-2), 70.33 (CH_2OC-1), 69.52 (CH_2OAlk), 68.55 (C-4), 60.92 (C-6), 45.47 ($C(CH_2O)_4$), 31.70, 29.55, 25.86, 22.65 (CH_2 alkyl chains), 14.03 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{29}H_{58}O_9 \times H_2O$ (568.77): C 61.26, H 10.63; found: C 61.36, H 10.50.

***O*-β-D-Galactopyranosyl-tri-*O*-heptyl pentaerythritol (19b)**: Prepared from **12b** in 40% yield as described Method B. Oil; $[\alpha]_D$ = −7.5° (c = 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **19c** (see below) except for ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.25 ppm (m, 24H, 12CH_2 alkyl chains) and ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.30, 29.07, 28.49, 25.66, 22.03 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3418 (OH), 2934, 2864, 1660, 1467, 1376, 1302, 1101 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 593; found: 593 [M]$^+$, 561, 472, 459, 446, 431, 413, 396, 394, 369, 360, 352, 333, 315, 299, 296, 243, 229, 217, 201, 197, 182, 169, 145, 133, 127, 113, 99, 83, 71.

***O*-β-D-Galactopyranosyl-tri-*O*-nonyl pentaerythritol (19c)**: Prepared from **12c** in 60% yield as described Method B. Oil; $[\alpha]_D$ = −6.5° (c = 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound. They are shown as Supporting Information in Figures S14 and S15, together with the COSY (Figure S16) and HMQC (Figure S17) 2-D spectra. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.72 (d, 1H, $J_{2,OH}$ = 4 Hz, OH-2), 4.66 (d, 1H, $J_{3,OH}$ = 5 Hz, OH-3), 4.53 (t, 1H, $J_{6,OH}$ = 5.0 Hz, OH-6), 4.33 (d, 1H, $J_{4,OH}$ = 4.0 Hz, OH-4), 3.96 (d, 1H, J = 7.0 Hz, H-1), 3.66 (d, 1H, J_{gem} = 10.0 Hz, CH_aOC-1), 3.61 (m, 1H, H-4), 3.52 (m, 1H, H-6a), 3.46 (m, 1H, H-6′), 3.34–3.18 (m, 16H, CH_bOC-1, 3CH_2OCH_2Alk, H-2, H-3, H-5), 1.45 (m, 6H, 3OCH_2CH_2Alk), 1.23 (m, 36H, 18CH_2 alkyl chains), 0.84 ppm (t, 9H, 3CH_3 alkyl chains); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 104.76 (C-1), 75.12 (C-5), 73.35 (C-3), 70.65 (C-2), 70.54 (OCH_2Alk), 68.73 (CH_2OAlk), 68.32 (CH_2OC-1), 68.02 (C-4), 60.24 (C-6), 45.05 (C-($CH_2O)_4$), 31.29, 29.04, 28.84, 28.67, 25.71, 22.08 (CH_2 alkyl chains), 13.91 ppm (CH_3 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3409 (OH), 2935, 2860, 1466, 1376, 1078 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 677; found: 677 [M]$^+$, 516, 299, 250, 237, 180, 164, 150, 137, 121, 91, 85, 71.

Tri-*O*-decyl-*O*-β-D-galactopyranosyl pentaerythritol (19d): Prepared from **12d** in 88% yield as described Method B. Oil; $[\alpha]_D$ = −6.0° (c = 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra were similar to those recorded for **19c** (see below) except for ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.23 ppm (m, 42H, 21CH_2 alkyl chains) and ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.30, 29.09, 29.05, 28.98, 28.83, 25.72, 25.70, 22.08 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3394 (OH), 2929, 1649, 1466, 1377, 1304, 1080, 915, 721 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 719; found: 719 [M]$^+$, 558, 516, 418, 402, 380, 352, 327, 299, 259, 254, 240, 224, 211, 187, 173, 163, 145, 141, 127, 110, 91, 85, 71.

***O*-β-D-Galactopyranosyl-tri-*O*-undecyl pentaerythritol (19e)**: Prepared from **12e** in 67% yield as described Method B. Oil; $[\alpha]_D$ = −5.5° (c = 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectra showed no peaks additional to those interpreted for the target compound. ^{1}H and ^{13}C NMR spectra were similar to those recorded for **19c** (see below) except for ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.23 ppm (m, 48H, 24CH_2 alkyl chains) and ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.27, 29.06, 29.00, 28.80, 28.70, 25.68, 22.06 ppm (CH_2 alkyl chains); IR (KBr disc): $\tilde{\nu}$ = 3422 (OH), 2929, 2859, 2336, 1619, 1464, 1068 cm^{-1} (C-O, C-H, C-C); MS (ES): m/z: calcd for: 761; found: 761 [M]$^+$, 600, 432, 416, 395, 355, 339, 315, 296, 269, 254, 225, 198, 182, 169, 145, 133, 119, 113, 99, 85, 71.

Tri-*O*-dodecyl-*O*-β-D-galactopyranosyl pentaerythritol (19f): Prepared from **12f** in 90% yield as described in Method A. Oily material; $[\alpha]_D$ = −5.2° (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **19a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ =

1.29 ppm (m, 54H, 27CH_2 alkyl chains) and ^{13}C NMR (50 MHz, $CDCl_3$): δ=31.97, 29.77, 29.73, 29.63, 29.60, 29.42, 26.24, 22.76 ppm (*C*H_2 alkyl chains); elemental analysis calcd (%) for $C_{47}H_{94}O_9\times2H_2O$ (839.34): C 67.25, H 11.77; found: C 67.48, H 11.43.

***O*-β-D-Galactopyranosyl-tri-*O*-tetradecyl pentaerythritol (19g)**: Prepared from **12g** in 95% yield as described in Method A. White solid; m.p. 77–78°C (MeOH); $[\alpha]_D=-4.6°$ (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **19a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 ppm (m, 66H, 33CH_2 alkyl chains); elemental analysis calcd (%) for $C_{53}H_{106}O_9\times2H_2O$ (923.41): C 68.93, H 12.00; found: C 68.76, H 11.61.

***O*-β-D-Galactopyranosyl-tri-*O*-hexadecyl pentaerythritol (19h)**: Prepared from **12h** in 93% yield as described in Method A. White solid; mp 87–88°C (MeOH); $[\alpha]_D=-5.0°$ (c = 1.0, $CHCl_3$); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **19a**, except for ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.26 ppm (m, 78H, 39CH_2 alkyl chains); elemental analysis calcd (%) for $C_{59}H_{118}O_9\times2H_2O$ (1007.57): C 70.33, H 12.21; found: C 70.22, H 12.36.

Di-*O*-β-D-galactopyranosyl-di-*O*-hexyl pentaerythritol (20a): Prepared from **14a** in 95% yield as described in Method A. Amorphous solid; $[\alpha]_D=-11.6°$ (c = 1.0, CH_3OH); ^{1}H NMR (200 MHz, CD_3OD): δ=4.25 (d, 2H, $J_{1,2}$=7.0 Hz, 2H-1), 3.93 (d, 2H, J=9.9 Hz, 2CH_aOC-1), 3.83 (d, 2H, $J_{3,4}$=3.4, $J_{4,5}$=0.6 Hz, 2H-4), 3.74 (m, 4H, 2H-6a, 2H-6b), 3.61 (d, 2H, J=9.9 Hz, 2CH_bOC-1), 3.52 (dd, 2H, $J_{2,3}$=9.9 Hz, 2H-2), 3.50–3.42 (m, 8H, 2H-3, 2H-5, 2CH_2OAlk), 3.40 (t, 4H, J=6.3 Hz, 2OCH_2CH$_2$), 1.54 (m, 4H, 2OCH$_2$CH_2Alk), 1.31 (m, 12H, 6CH_2 alkyl chains), 0.91 ppm (t, 6H, 2CH_3 alkyl chains); ^{13}C NMR (50 MHz, CD_3OD): δ=106.01 (C-1), 76.76 (C-5), 75.29 (C-3), 72.95 (C-2), 72.88 (OCH$_2$CH$_2$Alk), 70.85, 70.44 (OCH$_2$Alk, OCH$_2$C-1), 70.52 (C-4), 62.61 (C-6), 46.82 (*C*(CH$_2$O)$_4$), 33.14, 30.99, 27.34, 24.00 (*C*H$_2$ alkyl chains), 14.03 ppm (*C*H$_3$ alkyl chains); elemental analysis calcd (%) for $C_{29}H_{56}O_{14}\times H_2O$ (646.75): C 53.85, H 9.04; found: C 53.67, H 8.82.

Di-*O*-dodecyl-di-*O*-β-D-galactopyranosyl pentaerythritol (20f): Compound **20f** was prepared from **14f** in 91% yield as described in Method A. Amorphous solid; $[\alpha]_D=-7.2°$ (c = 1.0, CH_3OH); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **20a**, except for ^{1}H NMR (200 MHz, CD_3OD): δ=1.31 ppm (m, 36H, 18CH_2 alkyl chains) and ^{13}C NMR (50 MHz, CD_3OD): δ=33.38, 31.14, 31.09, 30.96, 30.79, 27.72, 24.03 ppm (*C*H$_2$ alkyl chains); elemental analysis calcd (%) for $C_{41}H_{80}O_{14}\times1.5H_2O$ (824.07): C 59.75, H 10.15; found: C 59.40, H 10.15.

Di-*O*-β-D-galactopyranosyl-di-*O*-tetradecyl pentaerythritol (20g): Compound **20g** was prepared from **14g** in 92% yield as described in Method A. Amorphous solid; $[\alpha]_D=-5.2°$ (c = 1.0, CH_3OH); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **20f**, except for ^{1}H NMR (200 MHz, CD_3OD): δ = 1.29 ppm (m, 44H, 22CH_2 alkyl chains); elemental analysis calcd (%) for $C_{45}H_{88}O_{14}\times2H_2O$ (889.19): C 60.78, H 10.42; found: C 60.79, H 10.13.

Di-*O*-β-D-galactopyranosyl-di-*O*-hexadecyl pentaerythritol (20h): Compound **20h** was prepared from **14h** in 92% yield as described in Method A. Amorphous solid; $[\alpha]_D=-8.4°$ (c = 1.0, MeOH); ^{1}H NMR and ^{13}C NMR spectra were similar to those recorded for **20f** except for ^{1}H NMR (200 MHz, CD_3OD): δ=1.30 ppm (m, 52H, 26CH_2 alkyl chains); elemental analysis calcd (%) for $C_{49}H_{96}O_{14}\times1.5H_2O$ (936.28): C 62.85, H 10.66; found: C 62.73, H 10.54.

***O*-Dodecyl-tri-*O*-β-D-galactopyranosyl pentaerythritol (21f)**: Prepared from **18f** in 92% yield as described in Method A. White solid; $[\alpha]_D=-10.6°$ (c = 1.0, MeOH); ^{1}H NMR (200 MHz, CD_3OD): δ=4.27 (d, 3H, $J_{1,2}$=7.1 Hz, 3H-1), 3.98 (d, 3H, J=9.9 Hz, 3CH_aOC-1), 3.83 (br d, 3H, $J_{3,4}$=3.2, $J_{4,5}$=0.6 Hz, 3H-4), 3.78–3.72 (m, 6H, 3H-6a, 3H-6b), 3.65 (d, 3H, J=9.9 Hz, 3CH_bOC-1), 3.57–3.37 (m, 13H, 3H-2, 3H-3, 3H-5, CH_2OCH_2Alk), 1.54 (m, 2H, OCH$_2$CH_2Alk), 1.30 (m, 18H, 9CH_2 alkyl chain), 0.90 ppm (t, 3H, 3CH_3 alkyl chain); ^{13}C NMR (50 MHz, CD_3OD): δ=105.96 (C-1), 76.84 (C-5), 75.32 (C-3), 73.09 (OCH_2Alk), 72.96 (C-2), 70.95 (CH_2OAlk), 70.61 (C-4), 70.30 (CH_2OC-1), 62.72 (C-6), 46.78 (*C*(CH$_2$O)$_4$), 33.35, 31.09, 30.76, 27.67, 24.01 (CH_2 alkyl chains), 14.15 ppm (CH_3 alkyl chains); elemental analysis calcd (%) for $C_{35}H_{66}O_{19}\times1.5H_2O$ (817.90): C 51.39, H 8.50; found: C 51.34, H 8.41.

Tri-*O*-β-D-galactopyranosyl *O*-hexadecyl pentaerythritol (21h): Prepared from **18h** in 95% yield as described in Method A. White solid; $[\alpha]_D=-9.4°$ (c = 1.0, MeOH); ^{1}NMR and ^{13}C NMR spectra were similar to those reported for **21f** except for ^{1}H NMR (200 MHz, CD_3OD): δ=1.30 ppm (m, 26H, 13CH_2 alkyl chain); elemental analysis calcd (%) for $C_{39}H_{74}O_{19}\times2H_2O$ (883.01): C 53.04, H 8.90; found: C 53.00, H 8.86.

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