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Minireview

Recent progress in the synthesis of carbohydrate-based amphiphilic materials: the examples of sucrose and isomaltulose

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Abstract—In the context of the use of carbohydrates obtained from agricultural crops, the search for amphiphilic derivatives is one of the most developed aspects. Indeed, due to the high polarity and the functional richness of sugars, many different structures can be targeted, with a wide range of physicochemical properties, either for large scale products of industrial interest, or for fine applications at the chemistry–biology interface. Among carbohydrates arising from agricultural resources, sucrose is especially interesting because of its very large production scale in the world (ca. 160 Mt/year, ca. 20 Mt/year of which in the European Community). Here, we describe the research accomplished in our group dealing with the synthesis and the study of the properties of amphiphilic derivatives prepared from sucrose as well as from another very available disaccharide, isomaltulose.

Keywords: Sucrose; Isomaltulose; Surfactant; Amphiphiles; Liquid crystals

Contents

1. Introduction

Among diverse applications of carbohydrates as organic raw materials, the field of surfactants is an important one.[1–12] Different kinds of carbohydrate-based surfactants are depicted in Chart 1. Some of them are produced on a large scale, such as the glucose-based alkyl polyglucosides (APG),[13–15] which are the most

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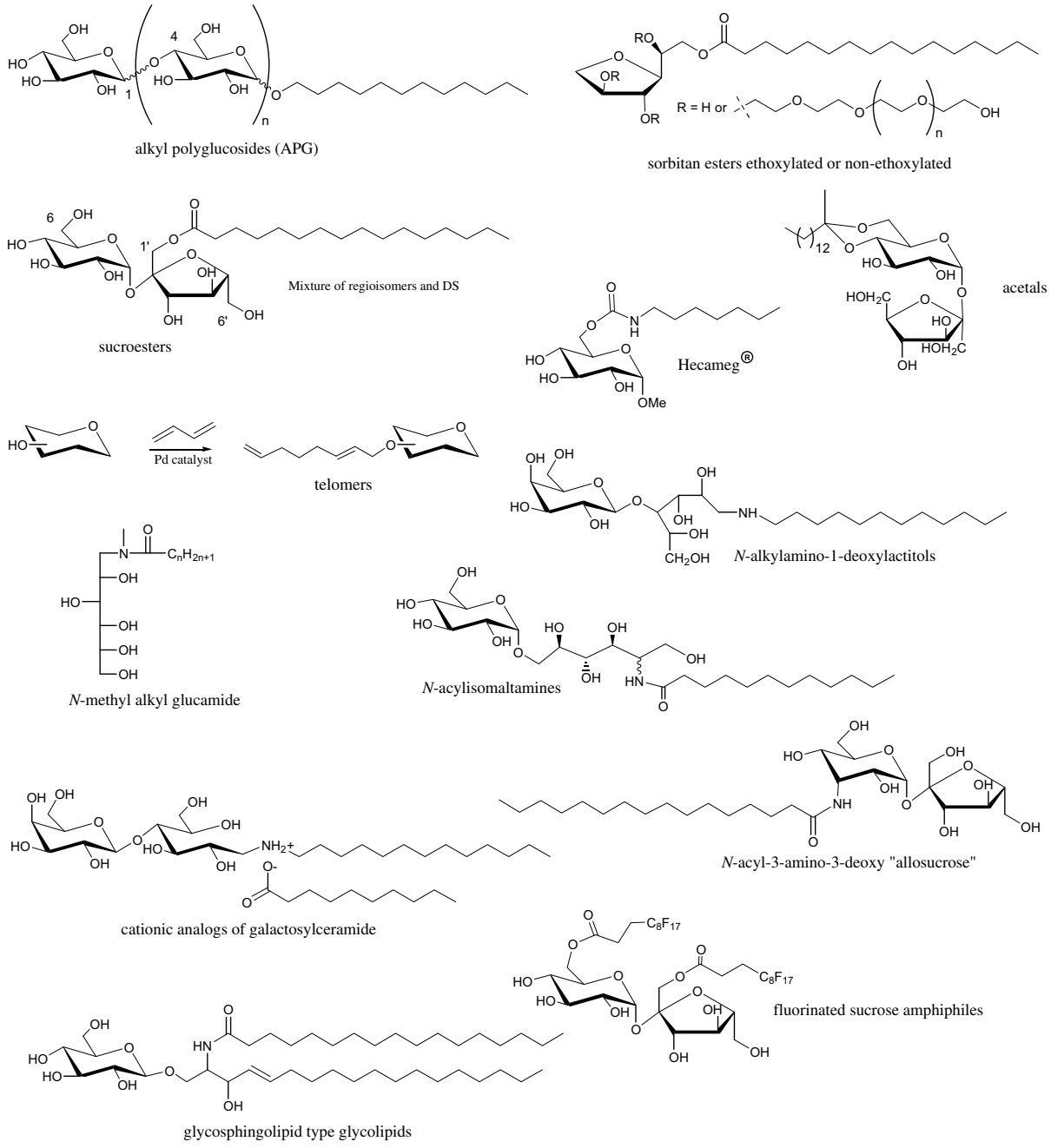


Chart 1. Examples of amphiphilic carbohydrate derivatives.

distinctive example. Sorbitol is also widely used for preparing amphiphilic derivatives, notably as esters of fatty acids, available from plant triglycerides. Sorbitan and sorbide esters are thus obtained, depending on the level of concomitant dehydration.[16] Among compounds which are already commercially available, sucrose fatty acid esters, also referred to as 'sucroesters', are efficient emulsifiers used in the food and cosmetic industries. Some of their chemistry and properties will be detailed in the following section. Esters of perfluorinated chains, among other fluorinated glycoamphiphiles for biomedical uses (notably blood substitutes), were prepared.[17–19] Anomeric esters have also been reported.[20] Besides glycosylation and esterification, other reactions have been used for connecting the fatty chain to the carbohydrate moiety such as acetal formation,[21] telomerisation[22–24] as well as etherification[25–28] and carbamation.[29–31] Reductive amination followed by substitution at the nitrogen atom can lead to the well-known glucamides.[10,32,33] Being efficient and having been achieved in very satisfactory conditions (only two-steps, water as solvent),

this strategy was applied to many sugars. For example, amphiphilic isomaltamides and isomaltamines were prepared in high yield from isomaltulose.[34] From isomaltamine, etherification with epoxides was also reported.[35] Reductive amination of 3-oxo glucose, obtained by microbial oxidation with *Agrobacterium tumefaciens*, followed by transesterification with fatty acid esters led to amphiphilic *N*-acyl-3-deoxy-3-amino sucrose derivatives.[36] From lactose, neutral or cationic aminodeoxy lactitols were designed for investigating some biological behaviour in relation with their physico-chemical properties.[37,38] Aldonamides are obtained from aldonic acids.[39] This also includes all the work on glycolipids, some of them behaving as liquid crystals.[40–44]

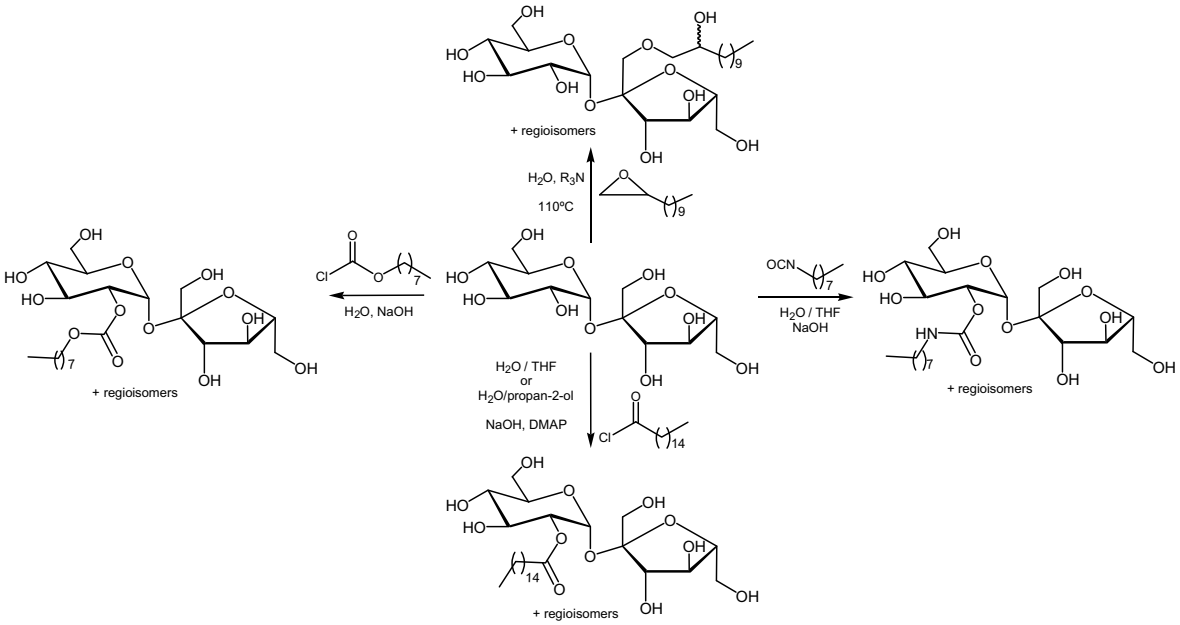
To cover all the reported structures of amphiphilic systems based on carbohydrates would be an immense task, and only selected references are given here about other structures such as gemini surfactants,[45] bolaamphiphiles,[46–48] macrocyclic,[49] dendrimeric,[50–53] and polymeric systems,[54–57] all kinds of which would deserve specific reviews. Also, the occurrence of glycolipids in living organisms has led to consider biosurfactants as very interesting compounds and to design tailor-made surfactants with specialized functions at the chemistry–biology interface.[58–61]

The potential of using unprotected carbohydrates as chemical starting materials on a large scale is connected with the possibility to achieve simple and direct transformations. However, in the case of sucrose, its structural complexity makes its chemistry rather difficult to control, since any chemical function present in sucrose is multiple (3 primary alcohols, 5 secondary alcohols, 2 anomeric carbons). Comprehensive reviews on the reactivity of sucrose are available,[62–65] and we herein limit this point to reminding the basic aspects of its nucleophilic behaviour. A realistic view, even simplified, of the competition between primary and secondary hydroxyl groups must reflect its dependence on the nature of the electrophilic reagent. Substitution of primary hydroxyls is obtained with sterically hindered reagents with the C-6,C-6′ positions being more reactive than the neopentylic C-1′. In contrast, for smaller electrophilic reagents, secondary positions are more reactive, because of electronic and conformational factors. In this respect, OH-2 is the most reactive position, and OH-1′ and OH-3′ have also peculiar behaviour. The consequences on the distribution of the products are easy to relate to the order of reactivity in the case of very stable formed bonds, such as ethers, contrary to unstable systems, such as esters, for which intramolecular migrations easily occur leading to a thermodynamic product distribution. These elements on the relative reactivity of all eight positions only concern the kinetics of the first substitution, second and further substitutions being often more difficult to explain.

2. Sucrose transformations in aqueous medium. Esters, ethers, carbamates

Widely used as emulsifiers in food and cosmetic formulations,[66,67] sucrose esters of fatty acids are prepared on the multi-ton scale by base-catalyzed transesterification from fatty acid methyl esters, generally in DMSO.[68,69] Increasingly severe regulations concerning allowed content of remaining solvent, and the related costs for the removal of traces of solvent, have motivated research towards no-solvent processes using emulsions or microemulsion systems.[70,71] For example, the TAL process leads to sucrose esters by solvent-free direct transesterification of triglycerides.[72] Also, a process in which emulsification of the crude sugar–fatty acid methyl ester mixture was achieved using sodium stearate was reported.[73] Another example, using multivalent cation salts, was described.[74] A kinetic model of the solvent-free transesterification of fatty acid methyl esters by sucrose in the presence of solid bases was developed, in which the overcrossing of the interfacial barrier and the contact between the two solids was considered as the main contribution to the activation constant.[75]

Our first approach towards amphiphilic sucrose esters was the study of their synthesis in aqueous medium (Scheme 1).[76] The acidity of OH-2 makes sucrose significantly more acidic than water, therefore water-sensitive acylating agents, such as acyl chlorides, can be used. Yet competitive hydrolysis of both the acyl donor and the ester products cannot be totally prevented. Use of highly concentrated sugar syrups allowed to limit the undesired hydrolyses but the increased lipophobic character of the medium led to increased heterogeneity, and consequently to an amplified tendency towards polysubstitution. Already observed for octanoyl chloride, this behaviour appeared to be a real limitation when longer chain fatty-acid chlorides were used. A possibility was thus to change the solvent by lowering its cohesive energy density. Indeed, the specific nature of water is importantly related to its exceptionally high cohesive energy density, responsible for what is referred to as 'hydrophobic effects'.[77,78] When fatty reagents are part of the mixture, water (and in an even more intense manner, water–sucrose mixtures), the repulsive effects towards lipophilic molecules makes the rate of the second and further substitutions much faster compared to the first one. Adding THF or 2-propanol as co-solvent limits the polysubstitution by breaking the water structure. DMAP also helped, by bringing the acyl chain closer to the interface as an ionic intermediate. Similarly, carbonates were obtained by reaction with alkyl chloroformates,[79] and carbamates from isocyanates.[80] Amphiphilic and bolaform sucrose carbamates had been previously reported.[31,81] On the side of the regiochemistry, a detailed structural and analytical study (NMR and HPLC) allowed us to demonstrate how significant the



Scheme 1. Accesses towards sucrose ethers, esters, carbonates and carbamates.

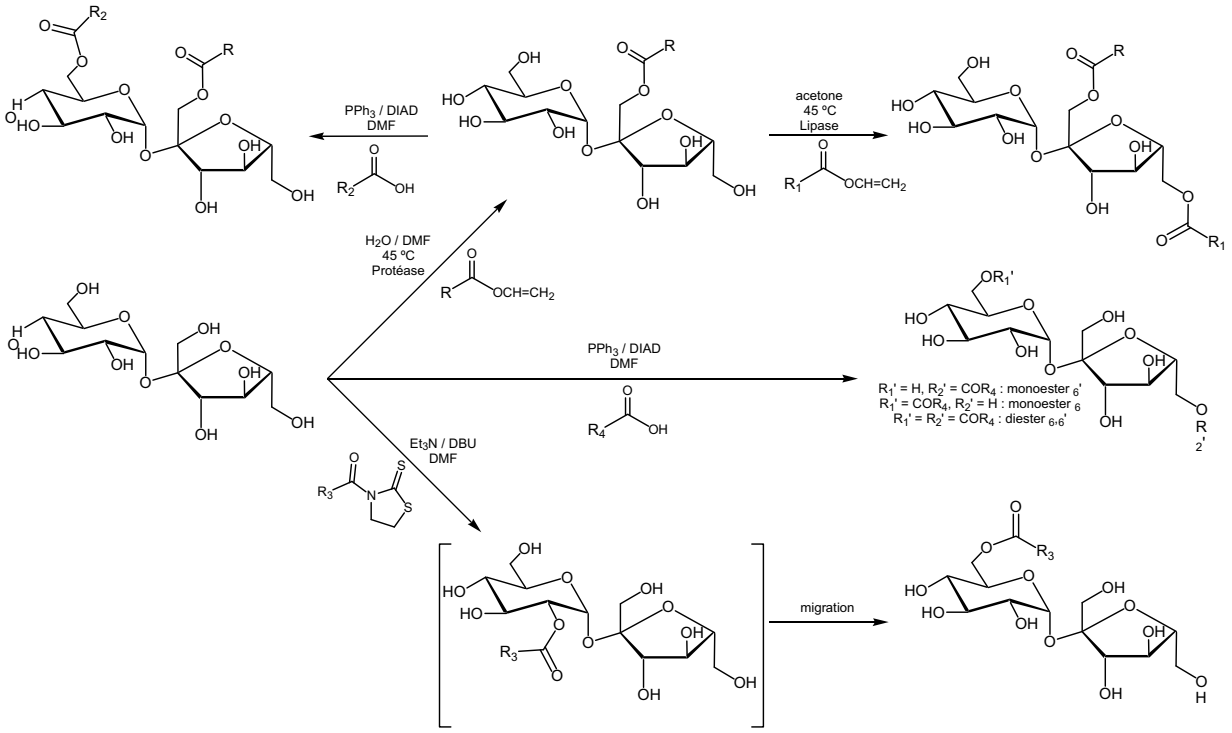
substitution at secondary positions was, and how migrations led to the final mixtures of products, mainly those substituted on their primary positions.[82] In the case of carbamates, hydrolysis and migrations were significantly slower, confirming their higher stability towards basic conditions by comparison with esters and carbonates.

Hydroxyalkylethers of sucrose were obtained by reaction with epoxydodecane.[83,84] Again in this case, water can be used as the solvent, with the same typical trends as for esters. The main products were the ethers substituted at positions 2 and 1′. Tertiary amines proved to be the best catalysts for this reaction, and heterogeneous systems were specifically designed with well-adapted hydrophilic–lipophilic balance, as this parameter proved to be an important one.[85] The reaction could be applied to other disaccharides such as trehalose and isomaltulose.

3. Synthesis of a series of sucrose esters substituted at primary positions

In most base-catalyzed processes, sucroesters are obtained as mixtures of regioisomers (principally at the primary positions due to rapid acyl group migrations). Important variations of their physicochemical properties are observed depending on the distribution of the compounds in the mixture (related to stoichiometry and reaction time), and eventually on the presence of the remaining fatty acid and soaps (related to concomitant hydrolysis and to the efficiency of the purification procedures).[86] Whereas the structure–properties relationship dependence on the chain length and the number of chains is well documented,[87–90] the influence of the position of the chains on the sucrose backbone has been less studied,[91–95] because of the limited availability of the compounds. For the purpose of investigating this issue, we needed a series of sucrose mono- and di-esters of different chain length and level of unsaturation at defined positions, and, taking into account the ability of acyl chains located at secondary positions to migrate towards primary ones, we selected only esters substituted on the primary positions. Thus, the samples would have no tendency to undergo a change of structure during the physico-chemical studies. Esters at primary positions were obtained by chemical or enzyme-catalyzed reactions, with combinations of both for the preparation of diesters (Scheme 2). These methods that are clearly not satisfactory for large scale synthesis were chosen for their reported high regioselectivity, as the first purpose was to obtain ultra pure compounds.

Protease-catalyzed transesterification of activated acyl donors led to the esters substituted at OH-1′ with very good regioselectivity.[96,97] Crude proteases in DMF, or better, in a slurry of DMSO, much less toxic compared to DMF, could also be used. Monoesters at position 6 can be obtained by controlled migration from position 2, after selective reaction with the very reactive acyl-thiazolidine thione[98–101] though small amounts of other esters limited the efficiency of the preparative HPLC purification step. The Mitsunobu conditions, which provides 6,6′-diesters, can also provide 6 and 6′ monoesters as side products, and in this case, the mixture of monoesters is composed only of 6 and 6′ esters. All three types of monoesters were thus prepared with variations in the chain length and the saturation level.[102] The



Scheme 2. Accesses towards sucrose esters substituted at primary positions.

samples of 6,6′-diesters were carefully purified to remove small amounts of anhydro compounds (6-*O*-acyl-3′,4′- or 3′,6′-anhydrosucrose), side products obtained by intramolecular etherification which competes with desired intermolecular esterification. Extension of this study to sucrose-based trisaccharides has been achieved recently.[103] Diesters (6,6′- and 6,1′-) having two different chains were obtained by two successive Mitsunobu reactions or starting from a monoester substituted at OH-1′ (obtained from protease catalyzed transesterification). 1′,6′-Diesters were prepared by lipase-catalyzed transesterification starting from 1′-monoesters.[104]

4. Properties of sucroamphiphiles in solution and in the pure state

4.1. Properties in solution

Our approach towards the solution behaviour of sucrose esters was the measurement of their self-diffusion coefficients, which are related to the size and shape of micelles or aggregates, via the pulse gradient field spin-echo (PGFSE) two-dimensional NMR method, which had never been used for such compounds.[105] This method provides a dimensional information, by giving a value of the hydrodynamic radius of the aggregates based on the hypothesis that the micelles are spherical, in addition to the rough evaluation of the CMCs. A limitation is that for very long fatty chains, the very low CMC or lower solubility of sucrose esters in water prevents the study of the longer chain esters, and of the diesters, because of insufficient signal-on-noise ratio. The CMCs observed for pure or regioisomeric mixtures of monoesters are consistent with those measured by other techniques. Typical decrease of the CMCs was observed for longer chains, and the effect of an unsaturation was also clearly seen. Micellar growth could even be observed upon increasing the concentration of the sucrose esters. In the case of palmitic esters, a significant change in the size of the aggregates was observed depending on the position (6, 1′, 6′), whereas no effect was observed for shorter chains (Table 1). By changing the calculation model from spherical to rod-like, a consistent value of 40 Å diameter was measured for the 6-, and 6′-monopalmitate *spherical* micelles, or for 1′-monopalmitate *cylindrical* micelles. It is assumed that substitution at OH-1′ changes the conformation of the disaccharidic backbone due to disruption of the hydrogen bond network, which normally involves OH-1′ and connects the glucose and the fructose moieties of the molecule. To access the self-diffusion coefficients by this 2D NMR spectroscopy technique, the precise concentration of sucrose and sucrose ester solutions should be known. However, this concentration is not always accurately given by simple weighing, because of the high hygroscopic character of the sucrose derivatives. This difficulty was circumvented by determining the actual concentrations by the ERETIC (electronic reference to access in vivo concentrations) NMR method.[106]

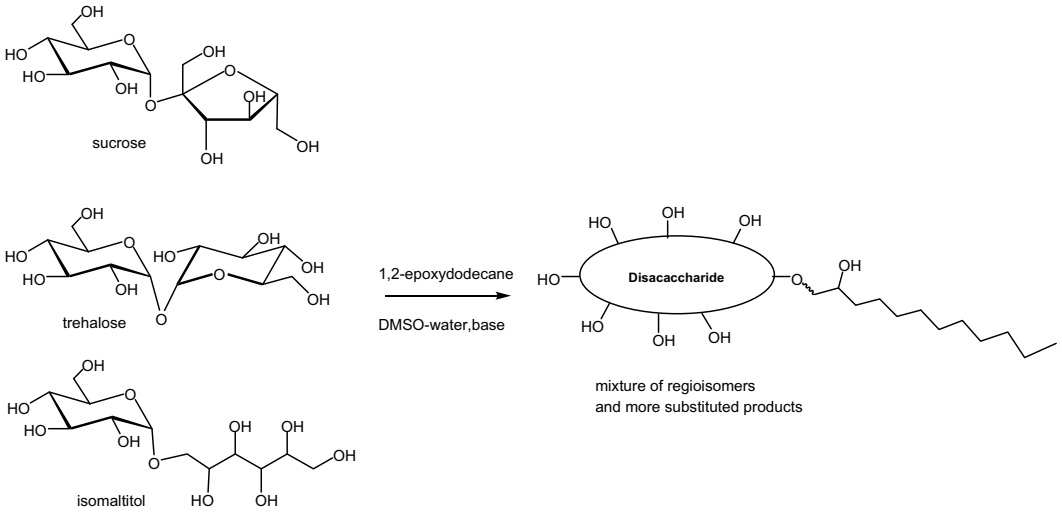
Table 1. Critical micellar concentration (CMC at 25 °C), self-diffusion coefficients and hydrodynamic radius (R_h) for micelles of sucrose esters from PFGSE-NMR data, with comparison to selected other compounds

	CMC (mmol L^{-1})	$D_{rmic} \times 10^{-11}$ m^2 s^{-1}	R_h (Å)
Sucrose monoesters			
C8	33.2	15.1	13[e]
C10	4.18	8.2	24
C12	0.28	6.75	29
C12:1	1.21	6.9	28
C14	0.022	5.3	36
C16–6	—	7.23	40
C16–6′	—	6.69	36
C16–1′	—	71.47	206 (Sphere) ~40 × 1200 (Cylinder)
C_{12}–C_{14}-APG	0.17	Ref. 15	
N-*n*-Dodecyl isomaltamine	6.3	Ref. 116	
Sucrose hydroxydodecyl ether	1.0	Ref. 85	

A mixture of sucrose mono-*O*-hydroxydodecylethers, prepared by reaction with 1,2-epoxydodecane, was also studied by this method. They appeared to have an intermediate self-diffusion coefficient as compared to esters in C_{10} and C_{12}, due to the presence of a supplementary hydroxyl group which increases the hydrophilicity of the polar moiety and decreases in the same time the hydrophobic character of the fatty chain of one CH_2 group. They also exhibit a higher CMC value than C_{12} esters. Purified monoethers obtained by this method applied to isomaltitol and trehalose (Scheme 3),[85] were evaluated for their foaming properties, showing that this series of compounds behave similarly, in this respect, to APGs.

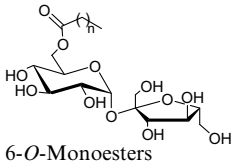
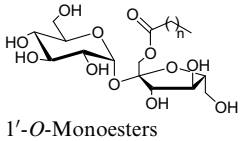
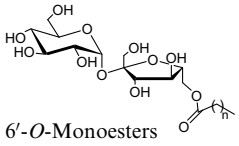
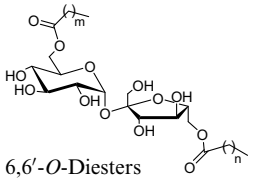
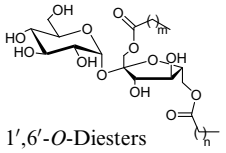
4.2. Thermotropic properties

Glycolipids often exhibit liquid crystalline phases.[41–44] For the series of sucrose esters which we had in hands, we could observe significant differences in the thermotropic properties, with respect to chain length, the presence of unsaturations, and to the attachment position of the fatty residue on the sugar backbone. This study included polarized-light microscopy, differential scanning calorimetry, and small-angle X-ray diffraction experiments (Table 2).[107–109] For the monoesters, it was found that short chain esters exhibit columnar liquid crystal phases, whereas lamellar phases are observed for longer chains. The columnar phases are constructed with the fatty hydrocarbon chains towards the inside of the column and the carbohydrate moieties outside. Some X-ray observations also suggested that the liquid state is still significantly organized through strong polar–polar interactions. For the diesters, our work established new evidences for significant variations in the stability of the mesophases exhibited by these compounds. Notably, 1′,6′-diesters were found to be much less stable as compared to the 6,6′-diesters, as seen by differences in the temperature range and the clearing points. For example, clearing points for 1′,6′-diesters are about 50° lower compared to the corresponding 6,6′-diesters. Also, significant differences in the transition enthalpies and entropies for the transition from the liquid crystal phase to the isotropic phase were observed.



Scheme 3. Etherification of disaccharides under basic catalysis.

Table 2. Compared thermotropic behaviour of mono and disubstituted sucrose esters

Type of esters	*n*, *m*	Type of phase	Clearing point (°C)	Δ*H* (J/g)	Δ*S* (mJ/g/K)
 6-*O*-Monoesters	$n = 6$	Col	95.6		
	$n = 8$	Col	107		
	$n = 10$	Sma	179.5		
	$n = 14$	Sma	212		
	$n = 16$	Sma	212		
 1′-*O*-Monoesters	$n = 6$	Col	90		
	$n = 8$	Sma	145		
	$n = 10$	Sma	186.8		
	$n = 14$	Sma	209.5		
	$n = 16$	Sma	210		
 6′-*O*-Monoesters	$n = 6$	Col	105		
	$n = 10$	Sma	204.5		
	$n = 14$	Sma	225.5		
	$n = 16$	Sma	211		
 6,6′-*O*-Diesters	$n = m = 6$	Sma	146.3	5.731	13.7
	$n = m = 8$	Sma	163	4.373	10.0
	$n = m = 10$	Sma	170.8	3.070	6.9
	$n = m = 14$	Sma	167.8	1.633	3.7
	$n = m = 16$	Sma	164.3	1.147	2.6
	$n, m = 14, 10$	Sma	167.8	1.972	4.5
 1′,6′-*O*-Diesters	$n = m = 10$ n, $m = 14, 10$	Sma	120	n.d.	n.d.
		Sma	115.9	0.537	1.4

With respect to the sensitivity of the mesophases to temperature, variable temperature X-ray diffraction measurements showed that diesters exhibit very large changes in the layer spacing as a function of temperature, with, in the case of the 6,6′-C_{18}-diester, unusual and novel phase behaviour in the lamellar phases.[107,109]

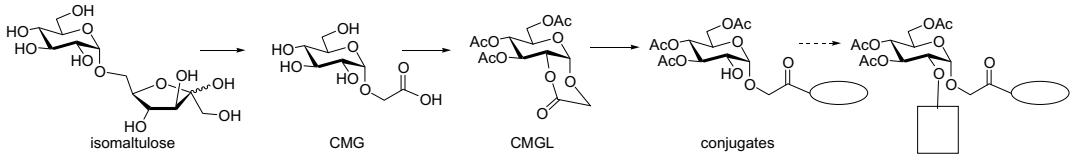
In the case of sucrose hydroxyalkylethers, the comparison of the various regioisomers could be extended to all possible isomers, which are all formed and stable. Most of them could be separated, generally as mixtures of two epimers at the hydroxyalkyl position.[110] This allowed to highlight the influence of chain position on thermotropic properties, likely related to the perturbations of the hydrogen-bonding network which contribute to the conformation of the disaccharide. Notably, derivatives substituted at OH-2 and OH-3′ were shown to exhibit a columnar arrangement as compared to all others, which were smectic A* phases.

5. Chemistry of isomaltulose: access to amphiphilic carboxymethyl glycosides

Recently, we have also studied the use of another disaccharide, namely isomaltulose (6-α-D-glucopyranosyl-D-fructofuranose) obtained in one step from sucrose by bioconversion.[111,112] Being available on the ton scale, the chemistry of this disaccharide has been studied with regard to its potent use as a raw material for various applications.[113–115] In this context, the groups of Kunz and Lichtenthaler have reported many efficient and interesting reactions,[116–118] some of them being in the field of surfactants, such as the formation of isomaltamides and glycosyloxymethylfurfural derivatives.[34,54,119–122]

We started our contribution to this chemistry when we found that carboxymethyl α-D-glucopyranoside (CMG) could be obtained by simple hydrogen peroxide oxidation, and that this later provides a bicyclic lactone (CMGL) upon acetylation (Scheme 4).[123] Isomalt, the hydrogenated analog of isomaltulose, could also be used in the reaction.[124]

An interesting use of carboxymethylglycoside lactone (CMGL) originates from its ability to readily combine with nucleophilic species, thus forming glucoconjugates, for example, glycolipids (Scheme 4). Though only simple conjugates have been prepared yet, our ultimate goal is to prepare bis-functionalized systems taking advantage of the hydroxyl at position 2, which is produced after the coupling. Also, it must be stressed that the very mild



Scheme 4. Conjugates from carboxymethyl glycoside lactone (CMGL).

condition and the absence of any catalyst for the coupling step might bring opportunities in the case of sensitive substrates.

The ability of CMGL to react with nucleophilic species was first observed when the corresponding ethyl ester was identified as an impurity of CMGL recrystallised in ethanol, and confirmed to be very general with many different alcohols and amines. The most efficient use of CMGL as a carbohydrate delivery system for making conjugates proved to be the reaction with amines, leading to amides, which are very stable under a wide range of chemical conditions, unlike the esters obtained by reaction with alcohols. Notably, deprotection of the three remaining acetyl groups is problematic in this later case. Different targets were prepared using this method, such as sugar-aminoacid hybrids, pseudodisaccharides, analogs of nucleotide–sugars, sugar-containing porphyrins designed for photochemotherapy, and other CMG amides with very diverse additional functions (Chart 2).[125–127] Similar lactones constructed on other carbohydrate backbones, or bearing other protecting groups, were prepared from allyl glycosides and subsequent oxidation by $RuCl_3$–$NaIO_4$ or ozonolysis.[128]

Among the amines used for evaluating the reactivity of CMG lactones, aliphatic (C_6, C_8, C_{10}, C_{12}, C_{14}, C_{16}) amines and the amines derived from cholesterol and

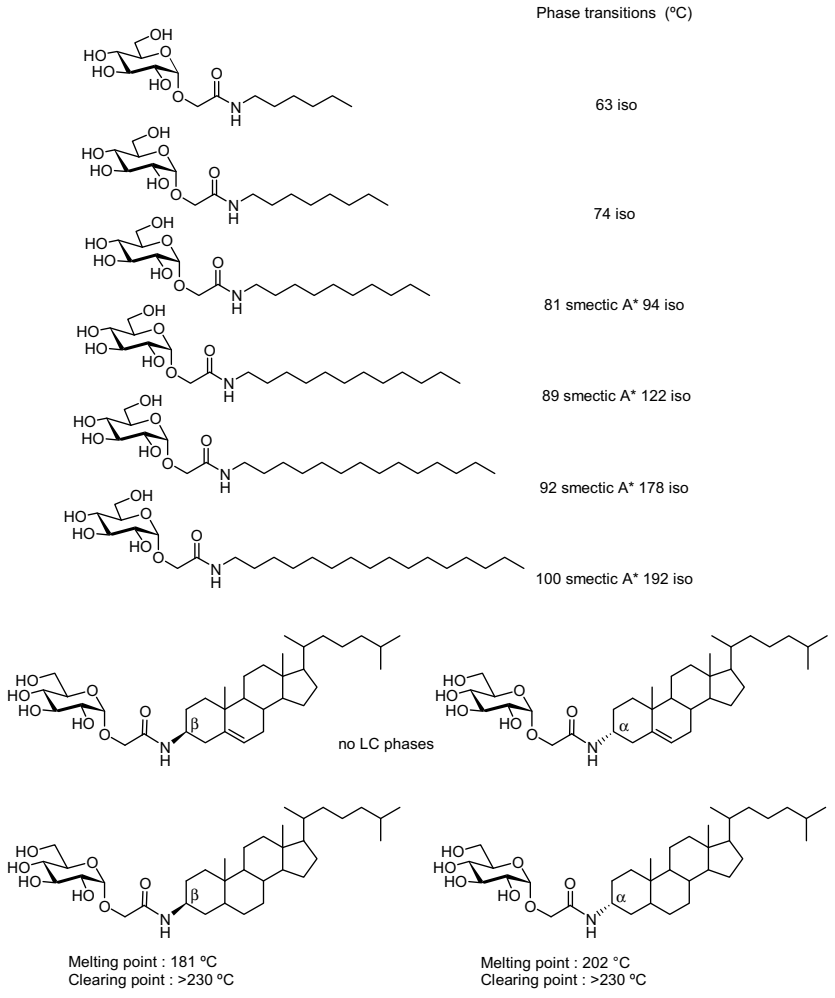


Chart 2. Amphiphilic amides obtained from carboxymethyl glycoside.

cholestanol were used, thus leading to new types of glycolipids (Chart 2) the properties of which as liquid crystalline species were evaluated by microscopy under cross polarisation, as well as by differential scanning calorimetry.[129] Shorter chains (C_6 and C_8) did not exhibit any liquid crystalline phase whereas longer systems were all found to form smectic A^* phases. An important difference with sucrose esters is that these amides are much more stable, meaning that the DSC investigations could be performed several times with cooling and heating cycles on the same sample without concomitant degradation. Among the four glycosteroids prepared, only the saturated compounds exhibited a liquid crystalline behaviour (lamellar) on a rather limited range of temperature, whereas the unsaturated ones did not melt before degradation at temperatures around 230 °C. Obviously these compounds are too rigid, and a new series of products will be prepared, either being substituted at OH-2, using the CMGL approach, or having a spacer between the carbohydrate and the steroid, which eventually will bring increased flexibility to the molecules and allow them to better adapt and interdigitate when heated.

6. Conclusions

The high polar density of the carbohydrates is well adapted for serving as the polar head of amphiphilic systems. Sucrose and isomaltulose are interesting sugars for serving as starting materials towards synthetic glycolipids. In addition to variations in chain length and degree of substitution, the disaccharidic complexity brings new possibilities for tuning the surfactants, due to their conformational dependence on perturbations of their intramolecular hydrogen bond network. Clear evidences for the importance of the position of the chain on the sugar backbone have been presented here, for the properties in solution and as pure materials. Isomaltulose, which was already known to be another useful sugar for accessing many new structures, following the work of different teams notably those of Kunz and Lichtenthaler, was used in a complementary strategy based on the carboxymethyl glycoside intermediate. In applications as a synthon for fine chemistry, its corresponding bicyclic lactone was shown to spontaneously couple with nucleophilic species, leading to new analogs of glycoconjugates, among which new glycolipids with liquid crystal properties.

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