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# Carbohydrate-based amphiphiles : a resource for bio-based surfactants

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**Keywords** : carbohydrates, amphiphiles, surfactants, bio-based chemicals

## GLOSSARY

**Carbohydrates** are a family of biomolecules, ubiquitous in Nature, based on a common polyhydoxylated backbone though varying in size (from small molecules to macromolecules), in fine structure (configuration and functionalization), and possessing a wide range of biological properties and roles making them indispensable to life.

**Amphiphiles** are molecular architectures with parts exhibiting different types of polarity, generally including hydrophilic and hydrophobic groups.

**Surfactants** are molecules possessing the ability to modulate interfacial tension, notably water surface tension.

**Bio-based chemicals** are chemical products which are obtained by transformation of a starting material arising from biomass, such as carbohydrates, fats, proteins, terpenes.

## DEFINITION OF THE SUBJECT

Surfactants are commodity chemicals used in an incredibly wide range of situations of the everyday life, and must therefore be improved constantly in terms of environmental impact, sustainability and performance. One way towards more sustainable surfactants is the use of renewable resources as raw materials for their manufacture, in place of fossil ones. Since the structure of surfactant combines a polar part to a hydrophobic one, carbohydrates, which are very polar molecules, appear as ideal candidates for serving as renewable building blocks in the synthesis of bio-based surfactants. Developed first with the aim of providing added-value to some agricultural crops and by products, this strategy shows nowadays a rebirth in the context of green and sustainable chemistry. The chapter illustrates, from the chemical point of view, the diversity of molecular structures which belong to the family of carbohydrate-based surfactants.

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## INTRODUCTION

Surfactants are amphiphilic organic molecules combining polar and non-polar moieties, and which exhibit specific physico-chemical properties connected to their ability to locate at the interface between phases of different polarity, either at the air/water, oil/water and solid/water, or to self-associate in micelles or liquid crystalline aggregates [1]. Their main property is to modulate the physicochemical characteristics of aqueous solutions such as interfacial tension or viscosity. This is the basis for their utilization in many applications, such as household and cleaning detergents, home and personal care products, cosmetics, foods, paints, inks, pesticides, polymers, textiles, lubricants, pharmaceutics, mining, oil and gas recovery [2]. In terms of fundamental science, these properties and applications relate to many topics, notably the physical chemistry of colloids and complex media, the physics of multiphasic chemical systems, and, in connection with biology, liquid crystalline architectures, membrane engineering, vaccine adjuvant technology, transfection methodologies, among others.

Surfactants are commodity and specialty chemicals characterized by i) their use by all human beings in their everyday life, ii) very large tonnages, and iii) a product end-of-life in the waste water or environment. Therefore they require a careful design for preventing undesired pollution or toxic effects. The large quantities which are produced also suggest that renewable resources, better than fossil ones, should be preferred for their design and manufacture. Nowadays, with the change of paradigm of the chemical industry towards more sustainable chemicals and processes, there is a renewal of interest for the development of novel kinds of bio-based surfactants, and novel cleaner and safer processes towards them. The goal is to meet the expectations of end-user consumers asking for safer products, and of authorities implementing regulations aiming at limiting the risk and hazards of industrial chemical production sites. In particular, “bio-based surfactants” dedicated to the personal care and detergents sectors are expected to account for significant growth in the surfactant market [3] even though petroleum-based surfactants still dominate due to their lower cost and already redeemed investments. Nevertheless, the surfactant market being a very competitive one, manufacturers are making constant efforts for broadening their products with improved performance and sustainability. Because of the concerns about the sustainability of existing products and the long-term availability of petrochemical feedstocks, bio-based surfactants will certainly gain market share.

Actually, the use of bioresources for the preparation of surfactants has already a long history, for two main reasons. Firstly, the natural hydrophilicity and hydrophobicity of some biomolecules, such as carbohydrates and lipids, provides the necessary duality for designing surfactants. Secondly, it has been an opportunity to provide added value to some low value agricultural crops. This is why several families of bio-based surfactants can be considered as "historical" ones, such as alkyl polyglycosides (APG) or carbohydrates fatty acid esters (Figure 1), with world markets in the 100 000 and 10 000 t/y range, respectively. The bio-based surfactants represent about 3.5 million tons (≈ 25%) of the surfactants and detergents market. With respect to the hydrophilic moiety, still almost half of the industrial nonionic and ionic surfactants are based on a polar moiety made from polyethoxylated units (polyethoxylated fatty alcohols, ethoxylated sorbitan esters, sodium laurylethersulfate), despite the safety and toxicity concerns and the fossil origin. Finding alternatives for the hydrophilic moiety is therefore an important issue, and carbohydrates, arising from renewable crops, and owing to their polyhydroxylated structure, appear as ideal candidates. Since fats (for the hydrophobic moiety) are also abundantly available from renewable resources, the combination of fats with carbohydrates is a straightforward way to synthesize 100% bio-based surfactants [4-12].

Besides synthetic carbohydrate based surfactants (CBS), naturally occurring ones also exist, referred to as glycolipids in biochemistry, mostly found in cell membranes form various types of living organisms, such as, among many others, the rhamnolipid depicted in Figure 1 [4-6,13,14]. Their amphiphilic character is not always taken into account; however, it certainly plays an important role in their biological properties, at it defines their location in organized architectures such as cell membranes where key biological processes take place. Being biomolecules of natural origin means that biotechnological processes can also be envisaged for the production of CBS.

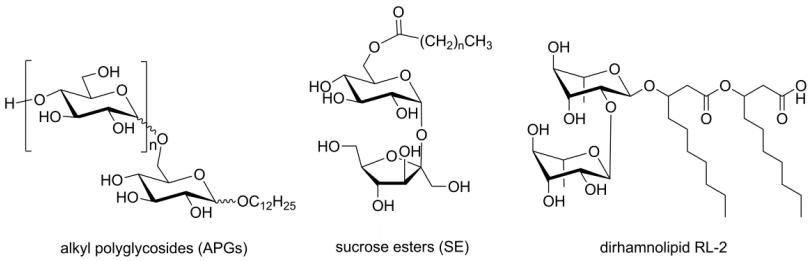



**Figure 1.** Typical examples of synthetic (APG, SE) and natural carbohydrate-based amphiphiles (dirhamolipid RL2).

The use of carbohydrates for designing bio-based chemicals is a wide topic which covers not only surfactants but also polymers, solvents, etc, and has become a complete topic as such in the scientific community, gathering all fields of chemistry (organic synthetic, catalytic, theoretical, physical, materials, analytical, biotechnological…) [15-23]. Carbohydrates are complex, multifunctional molecules with high oxygen content. Their chemistry is characterized by : i) moderate thermal stability requiring specific mild reaction conditions; ii) a limited choice of solvents able to match their high polarity; iii) selectivity issues of two kinds, regioselectivity and degree of substitution (DS); iv) complexity of products containing mixture of isomers with consequences on separation and isolation issues. Furthermore, structural differences arising from these selectivity issues lead to significant differences in the physicochemical properties and therefore to the possible applications. For example, mono- or disubstituted fatty esters of sucrose lead to inverse types of micelles (Figure 2), and two different monosubstituted ones, for which the chain is located to one or another position of the sugar backbone, will also exhibit aggregate morphology variation [24-26].

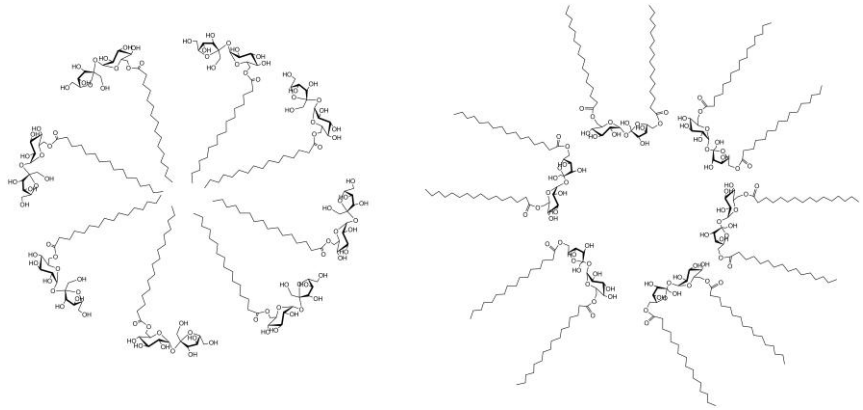


**Figure 2.** Influence of DS on solution properties: oil-in-water monostearoylsucrose stearate aggregates (left), water-in-oil disteraroyl sucrose aggregates (right).

One important challenge, typical for all reactions targeting amphiphilic compounds, is the difficulty to accommodate the reactants in one solvent, in spite of their opposite polarities. They tend to separate, at least partially, forming interfaces or concentration gradients preventing a precise monitoring of the stoichiometry. If catalysts are present, one question is to know where they will locate within this complex medium. In an heterogeneous medium, the first products obtained (monosubstituted) tend to stand at the interface and can be readily substituted again into a di- or polysusbtituted derivative, faster than the conversion of the naked starting sugar. Strong dependence of the solvent and medium heterogeneity of the

resulting DS is thus observed, and maintaining sufficient homogeneity, either by the use of additives of mixtures of solvents is necessary when low-substituted compounds are targeted. The amphiphilic products themselves help, thanks to their amphiphilic character, improving the homogeneity of the mixture (autocatalysis) [27-31].

The purpose of this chapter is to share the vision of carbohydrate chemists on synthetic carbohydrate-based surfactant (CBS) and to illustrate the diversity of molecular structures which can be found in this family; as a complement to important reviews, books and chapters published throughout the past decades [4-10,32,33]. The focus is made on the structural aspects and synthetic aspects, and giving basic information or referring to the relevant literature with respect to their physicochemical properties and applications. "Small molecule" surfactants (functionalized mono-, di-, oligosaccharides) are discussed below, whereas amphiphilic polysaccharides, being related to polymers and materials, differing from small molecules in synthetic, characterization and manufactures issues are not covered. Natural CBS, such as sophorolipids, viscosin, trehalolipids, cellobiolipids, will not be discussed either, however several reviews cover this topic [4-7]. The spine of the chapter (Figure 3) is the connective chemical function (acetal, ester, ether, nitrogen-related linkages, *C*-glycosidic, furanic) between the polar and the non-polar moieties. This connection is of prime importance because it relates firstly to the required reaction and manufacture processes, and secondly to the chemical sensitivity of the final products with respect to acid or basic conditions, and consequently to the range of possible applications. For example, esters, which are unstable under basic conditions, can generally not be used in detergency which often performs in basic conditions, whereas acetals (acid-sensitive) cannot be used in applications running in strongly acidic conditions.

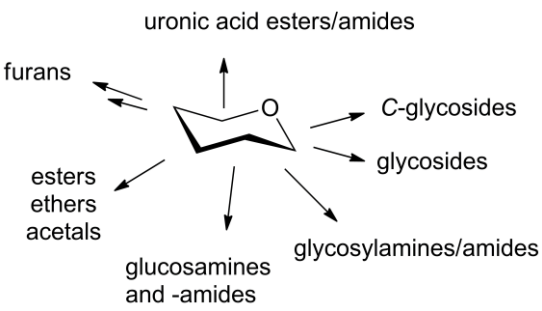



**Figure 3.** Main chemical connections found in carbohydrate-based amphiphiles.

## Glycosides and other acetals

In carbohydrate chemistry, two kinds of acetals can be distinguished, those involving the anomeric carbon, referred to as glycosides, and those involving simple hydroxyl groups on the backbone (Figure 4). They generally show excellent stability under basic conditions, a requirement for applications in detergency.

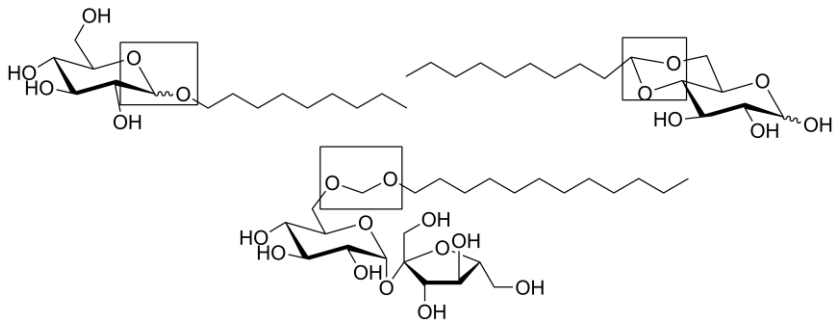



**Figure 4.** Various types of acetal linkages found in carbohydrate derivatives.

### *Glycosides*

The glycosylation reaction is central in carbohydrate chemistry. The most direct one, referred to as the Fischer reaction, is the acid catalyzed reaction of a carbohydrate (having its carbonyl group available or engaged in its hemicetal form) and an alcohol (Figure 5) [34]. The first step is the protonation of the hemiacetalic hydroxyl group and loss of a water molecule forming the glycosyl cation, a highly electrophilic species, stabilized by the pyranosic oxygen lone pairs. Then, any reactive nucleophilic molecule can add on this cation, forming the glycoside. The alcohol is often used in excess quantities, thus serving also as solvent to the process. Though simple at a first glance, the reaction shows some level of complexity because several products can be actually formed: furanosides or pyranosides ( 5 or 6 membered rings respectively), α or β anomers ( depending on the orientation of the glycosidic bond), as well as bicyclic anhydro products arising from intramolecular glycosidation or random oligomers produced by glycosylation of any carbohydrate hydroxy groups (instead of the external alkyl alcohol), with either pyranose or furanose rings and α or β configurations. This process is the theoretical basis for the manufacture of alkylpolygycosides (APGs).

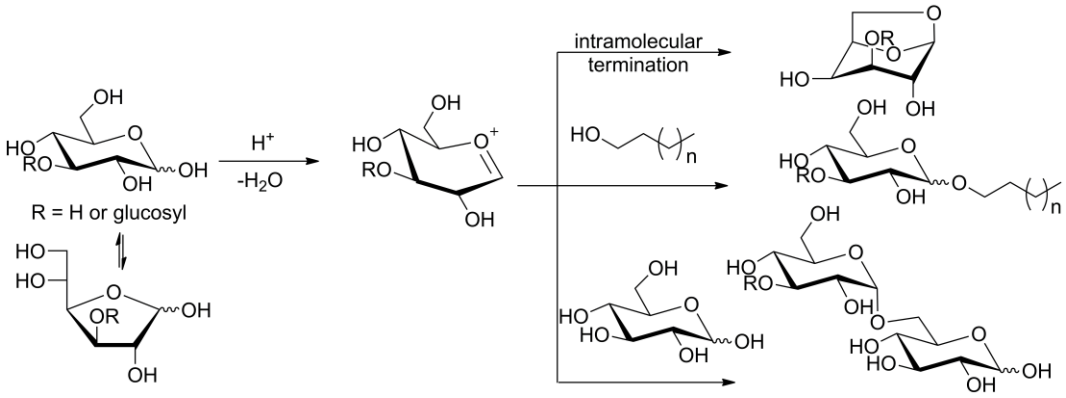



**Figure 5.** The Fischer reaction and its various possible products.

A base catalyzed alternative referred to as “anomeric alkylation” (Figure 6) which involves the reaction of the free anomeric hemiacetalate with electrophiles such as alkyl halides or alkyl sulfates is also a one-step access to alkyl glycosides [35,36]. Another process in which the anomeric OH serves as nucleophile is the telomerization of butadiene in presence of carbohydrates, which is more detailed in the “ether” section [37-43]. For targets of biological relevance for which a high level of selectivity is required, multistep sequences, using protecting-deprotecting selective strategies and subtle anomeric activations [44-46] are more appropriate than the less selective direct Fisher reaction. Fortunately, with respect to surfactants, the formation of mixtures of products and isomers is not an obstacle to their uses and applications, despite significant variations in their properties depending on their intimate structure.

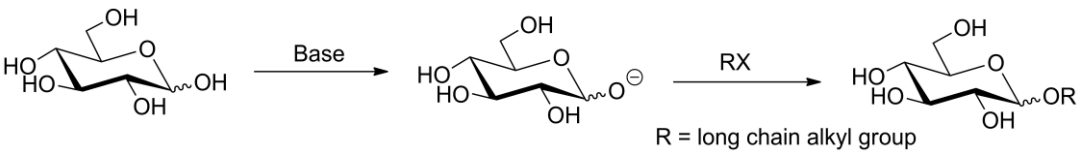



**Figure 6.** The alternative anomeric alkylation towards glycosides.

APGs exhibit very satisfactory safety for end users and excellent biodegradability, thus exhibiting no handicap with respect any environmental concern [47-51]. This is why APGs, alkyl polyglycoside could be developed with a real success, with first patents referring back to the 1930’s, [52] and the unusual physicochemical behavior of long chain glucosides was even already mentioned back in 1911 by Fischer and Helferich [53]. Real industrial production

started in the 1970s (Rohm & Hass) and have reached now a market close to 100 000 tons per year [47-51]. Main applications are uses in cosmetic and personal care formulations, in hard surface and laundry detergents, as adjuvants (notably for agrochemicals), with variations in properties depend essentially on the aglycone chain length. Their excellent compatibility with the skin make them ideal non-ionic surfactants used in hand dishwashing formations and other situations where contact with skin is frequent. Alternative uses of some specific glycosides, notably those incorporating a phenyl ring in the aglycone moiety, have been reported in the field of gelators [54-57]. When the phenyl ring is a galloyl residue, the compounds exhibit both surfactant and antioxidant properties [58]. Several important companies are involved in this sector, among other, Cognis, Henkel, Akzo Nobel, BASF, SEPPIC, KAO…. The field has been reviewed, with respect to process, manufacture, properties and applications in several reviews and chapters, covering the contributions of many academic and industrial research groups, notably by von Rybinski and Hill who have been more than any others involved in the development of APGs [47-51].

Besides selectivity, another important issue is the medium heterogeneity due to the use of hydrophobic alcohols (necessary to build the amphiphilic character of the target). Unlike for the reaction of glucose with methanol leading easily to methyl glycosides, when a long chain hydrophobic alcohol is used, the low solubility of the carbohydrate slows down the reaction, and side formation of anhydro products and oligomers, as well as formation of dialkylethers arising from the self reaction of the fatty alcohol, strongly limit the overall efficiency of the reaction. This can be circumvented by the implementation of a two-step protocol (Figure 7), involving a first stage using butanol, in which the starting carbohydrate is soluble enough, forming intermediate butyl glycosides, followed in a second stage by an acetal exchange with a long chain alcohol in an equilibrated process driven by the evaporation of the lighter butanol. Not only glucose can be used as substrate, but also short dextrans which depolymerize in situ. Sulfonic acids are the acid catalysts typically used in this reaction. Additives such as 2,5-furandicarboxylic acid (FDCA) [59], was found to improve the glucosylation of decanol, with less by-products formed therefore giving a lowered colored of the final product, an important parameter for applications such as cosmetic formulations [60-62].

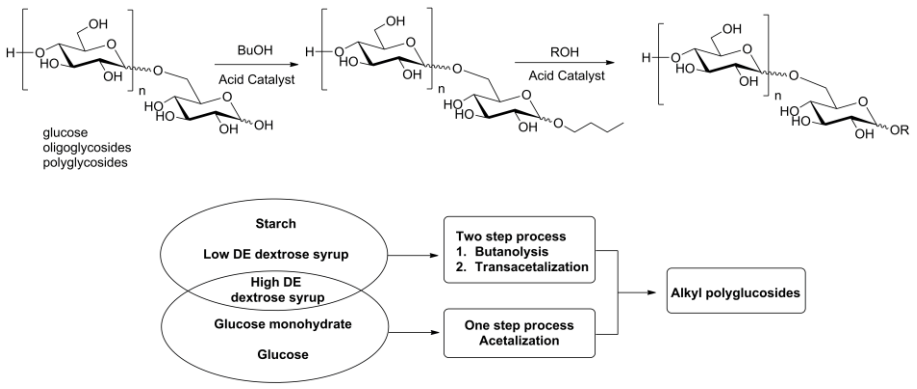



**Figure 7.** The two-step process towards alkylpolyglycosides via the butyl glycoside route.

First applied to the very available glucose, the one –step or two step processes have since be applied to a variety of starting carbohydrates, therefore all kinds of glycosides arising from other hexoses (galactose, mannose…). Uronic acid such as galacturonic acid, found in significant amount in sugar beet pulp, can be also used, leading to an ionic APG (Figure 8). The carboxylic acid present at position 6 can also be esterified in the course of the reaction, leading to bis-substituted amphiphilic compounds. Pentoses (xylose, arabinose) are also interesting substrates as they are widely present in some non-food hemicellulosic feedstocks. Similar strategies applied to mannuronic acid (obtained from alginate) lead to alkylmannopyranosiduronate surfactants [63-66]. More complex systems, such as gemini-type surfactants in which two APGs are connected covalently by their polar head, have been built either with ether or ester links between the two sugar moieties.

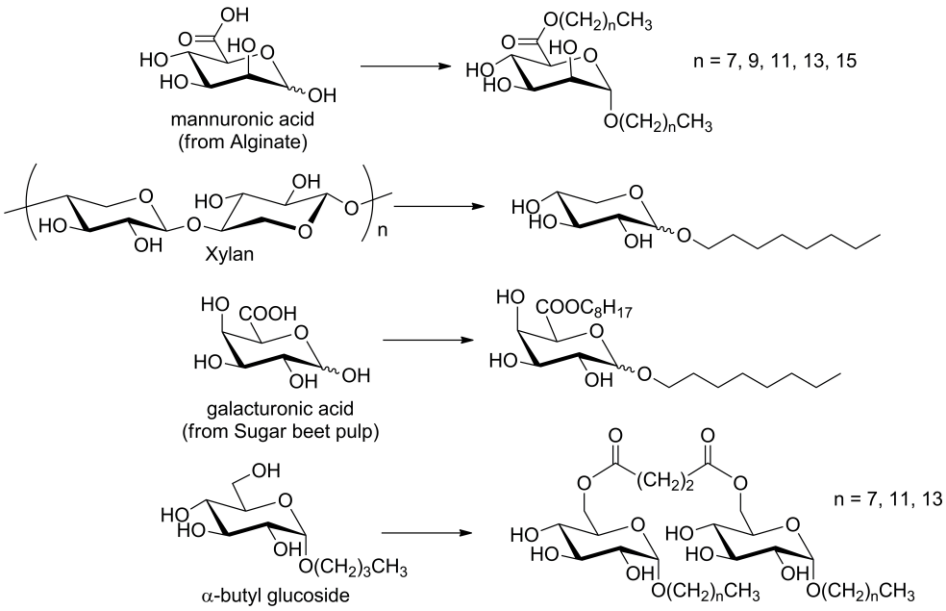



**Figure 8**. The wide range of structures possibly found in the APG family.

Presently, in order to get more cost effective processes towards APGs and enabling a wider range of applications, research is now focusing on using directly cheap and available non-food resources, such as cellulose or hemicelluloses. The processes must combine the depolymerisation (acid catalyzed hydrolysis) of the polysaccharides to monosaccharidic units and their reglycosylation with the external fatty alcohol. In this respect, several groups have recently proposed efficient catalytic systems (Figure 9). For example, Villandier and Corma used Amberlyst-15Dry for the reaction of cellulose to APGs with chain length up to $C_{12}$ [67-69]. For longer alcohols, for which yields tend to decrease in the direct glycosylation reaction, an alternative strategy is to run first the depolymerisation-glycosylation in methanol to get the methyl glycosides under the conditions of Zhang and Wang using, as acid catalyst, an heteropolyacid such as $H_3PW_{12}O_{40}$, and subsequently a transglycosylation with a longer alcohol, using Amberlyst-15Dry which was found to be the most efficient catalyst [70]. Perfluorosulfonic acid (PFSA) Aquivion PW98, an amphiphilic solid superacid, was recently reported to provide good yields of decylglycosides from cellulose and decanol, with a mecanocatalytic depolymerisation step. The catalyst was found to be easily recyclable [71]. Under sub-critical conditions, the acidity of alcohols can reach the level which is required for promoting the depolymerization-glycosylation reaction, thus enabling a direct conversion without any additional catalyst [72]. Direct transformation of agricultural by-products such as wheat straw, which contain hemicellulose as major component, can be performed. Carefully optimized pretreatment allows satisfactory valorization of the all components of the resource including lignin derivatives and hydroxymethylfurfural (HMF) besides the formation of alkylpentosides [73]. Other efficient media for the direct transformation of polysaccharides include the use of ionic liquids, as in the case of the transformation of xylan into alkyl xylosides [74].

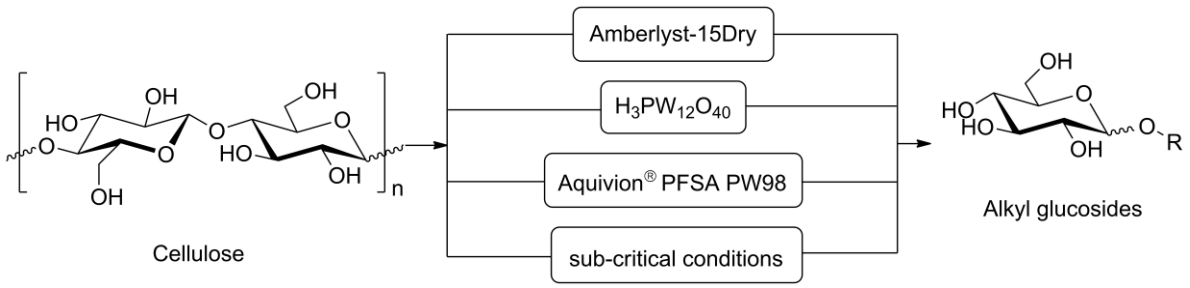
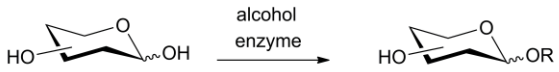



**Figure 9.** Catalysts used in the direct transformation of polysaccharides towards APGs.

Biotechnological processes leading to APGs have been proposed. Glycosidases (enzymes which cleave glycosidic bonds) and glycosyl-transferases (enzymes which make glycosidic bonds) are widely distributed in living organisms, and are able to work either in their natural pathway or in the reverse one. Glycosidase, when used in presence of high quantities of alcohol and low water content can reverse their activity towards the synthesis of glycosides (Figure 10) [75-86]. APGs with hydrophobic chains have been prepared using many types of purified enzymes and, sometimes, crude plant extracts containing enzymes. Though the processes appear efficient, the yields tend however to decrease upon increasing the alcohol chain length. Intense research is conducted to overcome these yield issues and will likely propose soon efficient alternatives to the chemical route, either by glycosylation or transglycosylations. Difficulties to be overcome are the availability of the enzymes and the possibility to use simple carbohydrates donors, instead of activated ones which are less available for large scale processes. Nowadays novel strategies also involve enzyme engineering and directed mutagenesis, offering taylored enzymes exhibiting improved efficiency, better adaptability to a wider range of media, able to accommodate to a larger substrate diversity and showing increased product selectivity. It is foreseen that biorefineries will include more and more biological steps in the future due to the rapid progress of the availability of novel biocatalysts.




| substrate | enzyme | alcohol | product |
|---|---|---|---|
| glucose | Almond β-glucosidase | 6-hydroxyhexanol | 6-hydroxyhexyl β-D-glucopyranoside |
| glucose | Almond β-glucosidase | octanol | octyl β-D-glucopyranoside |
| cellobiose | *Candida molischiana* 35M5N β-glucosidase | decanol | decyl β-D-glucopyranoside |
| lactose | CloneZyme Gly-001-02 from *Diversa* | heptanol | heptyl β-D-glucopyranoside |
| methyl glucoside | Cell bound β-glucosidase of *Pichia etchellsii* | dodecanol | dodecyl β-D-glucopyranoside |
| birchwood xylan | Xylanase from *Thermobacillus xylanilyticus* | octanol | octyl β-D-xylotrioside |

**Figure 10**. Examples of glycosidases used for biotechnological accesses towards APGs.

Finally, APGs can be functionalized further (Figure 11), for example by carboxymethylation or succinylation, thus proposing a bio-based solution to applications requiring anionic surfactants [47,50,13,76]. Polycarboxylates obtained by esterification with citric anhydride [87], polyphosphates [88], cationic systems obtained by transtesterification with glycine betaine butyl ester [89], as well as systems including pH and photocontrollable functional group [90] have also been reported. Let us also mention that thio analogues of APGs, in which the O-glycosidic atom is replaced by a sulfur one have been prepared by reaction of

carbohydrate peracetates and long chain thiols using catalytic amounts indium bromide as catalyst [91]. Long chain alkyl glycosides, being amphiphilic, are soluble in a wider range of solvents and can therefore be preferred to unprotected carbohydrates for some transformations, such as their addition to epoxidized fatty esters, leading to novel bolaphilic systems [92] or in some enzymatic esterifications [93].

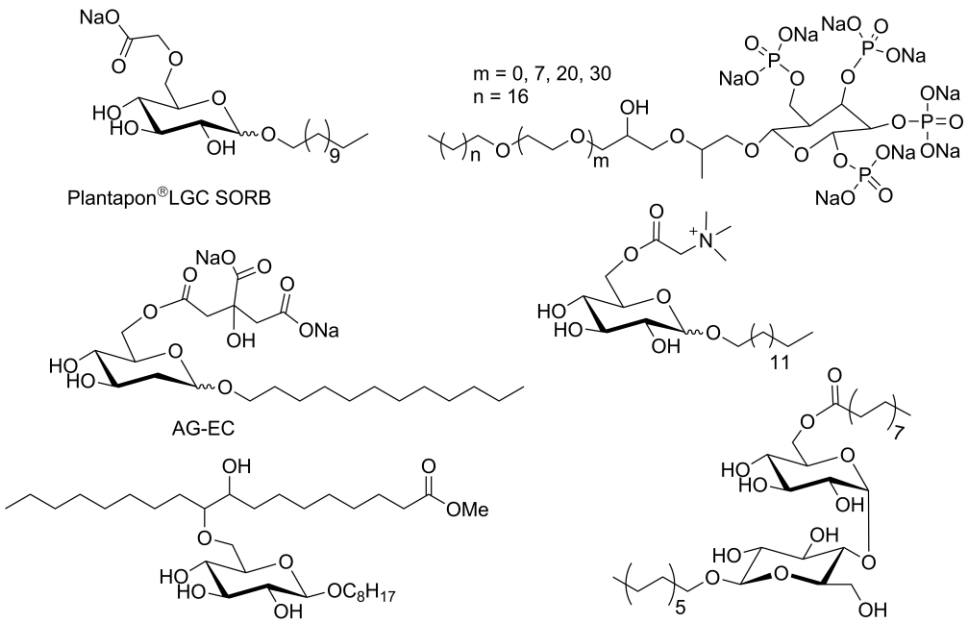



**Figure 11.** Examples of modified APGs.

***Acetals***

The reaction of a pair of carbohydrate hydroxyl groups with an external carbonylated compound is frequently used in strategies requiring a temporary protection. For example, the acid catalyzed reactions of carbohydrate diols with acetone or benzaldehyde are classical accesses to selectively protected carbohydrates, with preferred formation of 5- or 6-membered ring acetals, respectively. If the carbonyl compound exhibits some hydrophobic character, amphiphilic acetals are obtained. First examples were reported by Mietchen in 1988 [94] who prepared 4,6-O-alkylidene D-glucose derivatives from aliphatic $C_7$ to $C_{12}$ aldehydes (Figure 12) [26]. Bethel, the same year, studied the effect of chain length on the mutarotation (the equilibrium between the equatorial and axial forms of the anomeric hemacetal) in various solvents, demonstrating the subtlety of the self-association properties as a function of structures. Later on, Thiem and Mietchen [95] studied the liquid crystalline properties of these acetals. Okahara and colleagues [96] reported an interesting example of novel amphiphilic acetals prepared in two steps, first the acetalization of glucono-1,5-lactone, followed by

alkaline hydrolysis of the lactone linkage. The obtained amphiphiles, with three hydroxy groups, a sodium carboxylate group and a long chain acetal are possibly cleavable under acid conditions [97].

An important work has been done on the use of sucrose (the very available sugar used in food, produced from sugar beet or sugar cane) as a raw material towards diverse kinds of chemicals [18], including various types of amphiphilic derivatives as it will be seen in several sections of this chapter. Amphiphilic acetals of sucrose have been described by Gelas [98], then by Queneau [99,100]. Sucrose is a disaccharide in which glucose and fructose are connected through a very acid-sensitive glycosidic bond, an issue in the acetalization reaction which requires acid catalysis. Starting from a dimethylacetal of the aldehyde, there is no need to eliminate water from the medium, and lower reaction temperatures and milder acidic conditions can be used, preventing the undesired acid-catalyzed hydrolysis of the disaccharidic backbone. Even milder conditions can be used if the starting dimethylacetal is formed from an α,β-unsaturated aldehyde, making possible to use very mild acidic resins prepared from lanthanide triflates. Amphiphilic acetals of methyl glycoside [101] can be further reduced to amphiphilic ethers [102,103] (vide infra). Reaction of sugars with alkylhalogenomethylethers in basic conditions lead to mixed acetals and are alternative carbohydrate-based acid labile amphiphilic acetals [104,105]. Other systems with a more equilibrated hydrophilic-lipophilic balance can exhibit gelating properties, such as 4,6-benzylidene acetals of methylglucoside variously substituted on the phenyl ring [106-108].

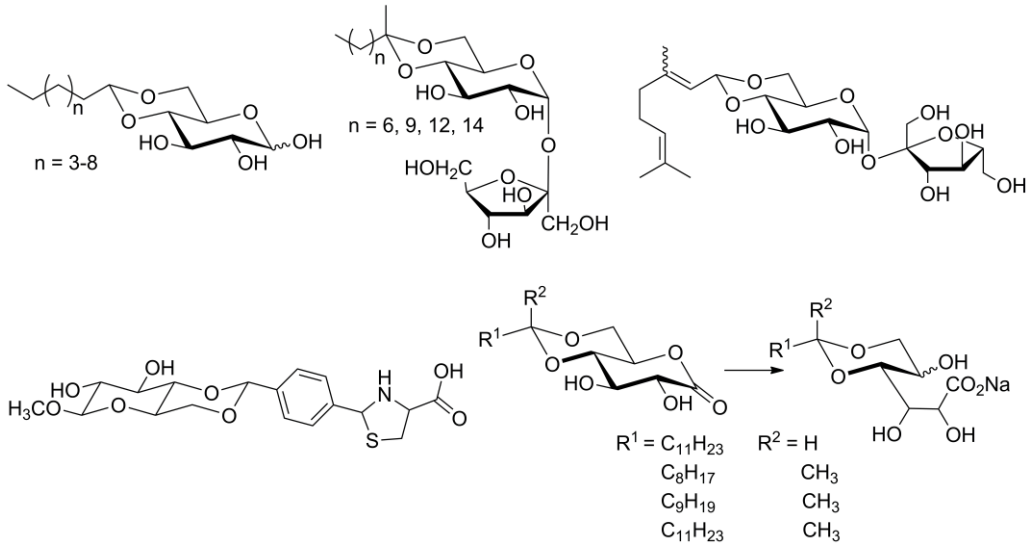



**Figure 12.** Examples of amphiphilic carbohydrate acetals (other than APGs).

## Esters

Carbohydrate based amphiphilic esters can be obtained by esterification of carbohydrates hydroxyl groups with fatty acids, or transtesterifications with fatty acid methyl esters. Most processes use polyols, such as sucrose or sorbitol, as starting materials, though some examples with reducing carbohydrates, having their anomeric hydroxyl group unprotected, have also been reported. The alternative sense of esterification by reaction of sugar acids or lactone with a fatty alcohol is also well documented (Figure 13) [109-115].

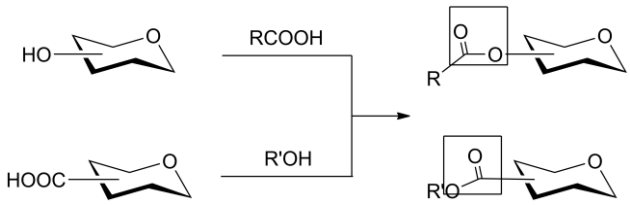



**Figure 13.** The two types of ester linkages arising from carbohydrate OH and fatty acids (up) or carbohydrate acids (onic, uronic) and fatty alcohols (down).

Direct esterification or transesterification of totally unprotected carbohydrates (including a free anomeric hemiacetal) have been reported. The reaction using glucose and α-hydroxyacids, in absence of any other catalyst, produces esters with good 6-*O*-selectivity [116] however this is less appropriate for the industrial scale due to the lower availability of hydroxyacids compared to aliphatic ones. Another original protocol is the acylation of mannose as a mercaptopropanoyl ester at O-6, followed by thiol-ene ractions with alkynes of various chain lengths, leading to a range of amphiphiphilic products via a unique intermediate (Figure 14) [117,118]. In a two step procedure from malic acid, fatty acids and glucose, interesting glucose esters have been reported [119]. It is important to note that glucose esters can be also obtained in a very short procedure using directly some lignocellulosic biomass hydrolysate [120].

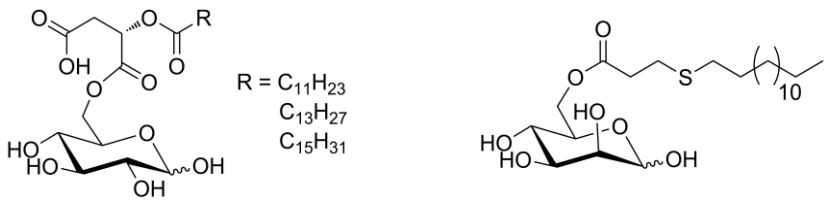



**Figure 14.** Esters prepared from carbohydrates having a free anomeric OH.

However, due to its “carbonyl character”, the anomeric (hemiacetalic) hydroxy group complexifies the situation, with possible side reactions resulting in more difficult separation of the desired products and possible coloration. Moreover, anomeric esters are also known to be even less stable than at other positions. This is why polyols, such as sucrose or sorbitol, which do not have any free anomeric OH, have been preferred in for developing the industrial manufacture of amphiphilic esters.

Sucrose esters (SE) are a historical example of carbohydrate based surfactants and are still produced and marketed. The processes which are very close to those still in use were patented in the 1950s [121-123]. Their manufacture thus relies more on the know-how than on PI. Esters being moderately stable in basic conditions, thus are less applicable to the field of detergency, but are appropriate for serving as food or cosmetic emulsifiers, with a market in the range of 10 000 tons per year. Triglycerides can be used instead of fatty acid methyl esters, leading to mixtures of sucroesters and mono- and diglycerides and glycerol, a complex mixture exhibiting however useful emulsifying properties. The chemistry of sucrose, reviewed in several accounts, is characterized by: i) a very acid sensitive interglycosidic bond, limiting the possibility to used strong acids; ii) intramolecular hydrogen bonds which reinforce the peculiar reactivity of the hydroxy groups at position 2, 1’ and 3’; iii) for steric hindrance sensitive reactions, a preference for reactions at positions 6 and 6’; like other disaccharides, with 8 hydroxy groups, a large number of possible products depending on degree of substitution and regiochemistry [18].

Choosing the length of the fatty ester and degree of substitution provides a palette of compounds which cover the whole range of emulsification properties, from water-in-oil to oil-in-water (cf introduction and Figure 2). Extensive structure-properties relationships studies have been conducted [111-113,124,125]. Several manufacturers produce sucrose fatty acid esters, among which Dai-Ichi Kogyo, Mitsubishi Kagaku Food, Croda, Sisterna, Evonik, Stearinerie Dubois. Depending on the DS and on the hydrophilic-hydrophobic balance (HLB), SE find a wide range of applications in food, cosmetic, pharmaceutical, personal care sectors, as emulsifiers, solubilizers, control relase agents, adsorption and penetration enhancers, lubricants or disintegrants. The most classical process is a transesterification reaction between sucrose and fatty acid methyl esters using a dipolar solvent such as DMSO and a basic catalyst such as potassium carbonate, under vacuum for displacing the equilibrium by removing methanol (Figure 15). Technical issues are the thermal stability of the solvent and

sucrose, the monitoring of the reaction progress, notably with respect to the degree of substitution, and the separation and isolation of the products from the reaction mixture. The homogeneity of the medium is important for preventing undesired over-substitution. Variations in the process include the use of no solvent conditions and the presence of fatty acid soaps as emulsifiers [28,29,126-129]. Subtle liquid-liquid extraction protocols allow efficient separation of sucrose esters of different DS, mono-, di- and triesters being the most interesting with respect to amphiphilic properties. Though the regioselectivity is also known to influence some physicochemical properties, the products are obtained and used as mixtures of regioisomers, with the ester groups located essentially at the primary positions. Indeed, whatever the outcome of the transesterification, intramolecular transesterifications take place and ester groups move from secondary towards primary positions [130-131].

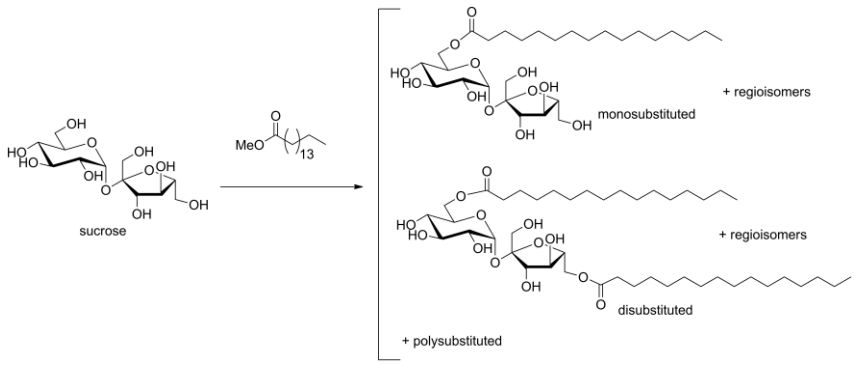



**Figure 15.** The base-catalyzed process towards amphiphilic sucrose esters.

Thermotropic properties of sucrose esters were investigated using a series of mono- and di-substituted esters, prepared using a sequence of chemical and enzymatic steps leading to all possible mono and homo- or hetero-diesters on the primary positions, with various chain length and level of unsaturation. This study demonstrates how much the chain length, the level flexibility (linked to the unsaturation level) and the regiochemistry influences the stability of the liquid crystalline phases, in connection with the molecular shape (Figure 16) [132-135].

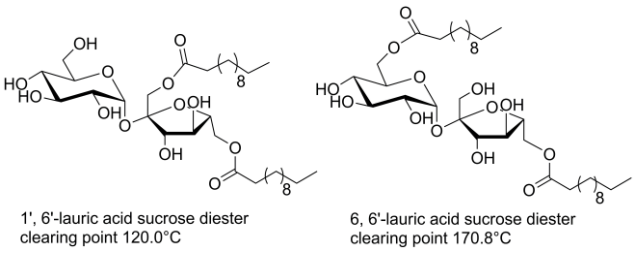



**Figure 16.** Influence of chain position on the sucrose backbone on the transition (liquid crystal to isotropic liquid) in two regiosiomers of sucrose dilaurates.

The hydrophilic-hydrophobic balance (HLB) is a common parapeter used for indicating the polarity of surfactants, however, in the case of SE it can be misleading because their supramolecular behavior depends significantly on their molecular shape (which varies as a function of degree of substitution and regiochemistry whereas the calculated HLB keeps constant). Moreover, in commercial sucroesters, traces of remaining methyl ester or soap can still be present, leading to even more delicate comparisons between samples. It has been shown the Winsor diagrams provide richer information than the simple HLB calculation [136]. Another analytical limitation is due to the high polarity of the sugar esters and their resulting hygroscopicity, which can be a problem for physicochemical characterizations requiring a precise measurement of the concentration. This can be solved by using in situ concentration measurements using the ERETIC NMR spectroscopy method [137].

The reaction of sucrose in water with hydrophobic acid chloride and chloroformates was studied by Queneau and coworkers, showing i) that sucrose, being more acidic than water, reacts with the acid chloride faster than water, ii) the reaction takes place first on the more reactive secondary positions, then acyl or alkyloxycarbonyl group migrations occur iii) medium heterogeneity (increasing when using longer fatty chains) is responsible for oversubstitution except when using huge excess of sucrose [27,138], whereas the reaction performs easily for short acids chlorides. Similar observations were made when studying the aqueous reaction of sucrose with isocyanates leading to carbamates (*vide infra*). Direct reaction with fatty acids is not compatible with sucrose due to ist low stability in acidic conditions. Epoxidized unsaturated fatty acid esters, can be used in place of simple aliphatic ones, like in the recent work in which the reaction of several carbohydrates with methyl epoxyoleate. The obtained esters were subsequently hydrated to diols exhibiting interesting self-organization ability benefiting to selective formation of polyurethanes [139,140].

Esterification of carbohydrates using enzymes have been extensively studied [111, 141-143]. Hydrolases, such as lipases or proteases, have a hydrolytic function of esters or amides, in the presence of water. When these enzymes are used in other solvents and in absence of water, if an acyl group donor and an alcohol (here the carbohydrate) are present, they can work in the synthetic sense, reverse to their natural function. The high specificity towards substrates and high selectivity towards products of enzymatic reactions is a very interesting advantage for reactions which normally lead to complex mixtures. The main issues in enzymatic synthesis of carbohydrate esters are: the availability of the enzymes, the type of acyl donor (activated or

native carboxylic acids), the choice of the solvent. This latter must solubilize the unprotected carbohydrate (not so difficult for monosaccharides but often a limitation for disaccharides or larger carbohydrates) while keeping the enzyme in an active three-dimensional conformation. Though water must be excluded for preventing the enzyme to work in the hydrolysis sense, some small amounts of water must be however present for preserving the H-bond network responsible for the 3D structure of the protein, and keeping its catalytic activity. A subtle balance in the water content must be thus defined for each case, since several parapeters influence the hydration equilibrium (nature of solvent, hydration of the carbohydrate substrate, quantity of enzyme, temperature…). Whereas some enzymatic procedures require the use of activated acyl donors, such as a vinyl ester, cyanoethyl, or trifluoroethyl esters, some can proceed directly with the carboxylic acid, and are therefore more appropriate in strategies of industrial relevance. Two consecutive enzymatic reactions or combination of chemical and enzymatic steps can lead to tailored disubstituted esters with mixed chain length and functions, for example one fatty chain and one polymerizable group [93]. Other complex systems design for organogelation have been prepared through enzymatic procedures [144].

Sorbitol (other name of glucitol, the hydrogenation product of glucose) is another very available polyol, produced on the industrial scale and applied as ingredient or additive in foods, cosmetics or pharmaceutical formulations. When heated with fatty acids, the esterification takes place, leading to mixtures of esters at primary and secondary positions, with, like in other polyols and carbohydrates, possible migrations form one OH to the neighbouring one. The final products are therefore the thermodynamic mixture of various esters at all positions. Like other carbohydrates and polyols, the esterification of sorbitol can lead to mono- di- or polyesters, which will exhibit significant differences in their properties. The acidity of the medium, heating, and removal of water promote the concomitent cyclodehydration of sorbitol to sorbitan, and further to isosorbide (Figure 17). These products posses only four and two hydroxyl groups, respectively, which undergo esterification. Alternative enzymatic esterifications of sorbitan are also reported [145,146]. A wide range of products showing hydrotropic properties can therefore be obtained [147].

Glucuronic acids or their lactone derivatives are useful resources for the preparation of carbohydrate esters, by reaction with fatty alcohols. Both chemical and enzymatic procedures towards amphiphilic glucuronates have been reported (Figure 18) [148-156]. Though very

close in structure compared to acylated sugars, this change in the OCOR vs COOR linkage has some influence on the properties [157].

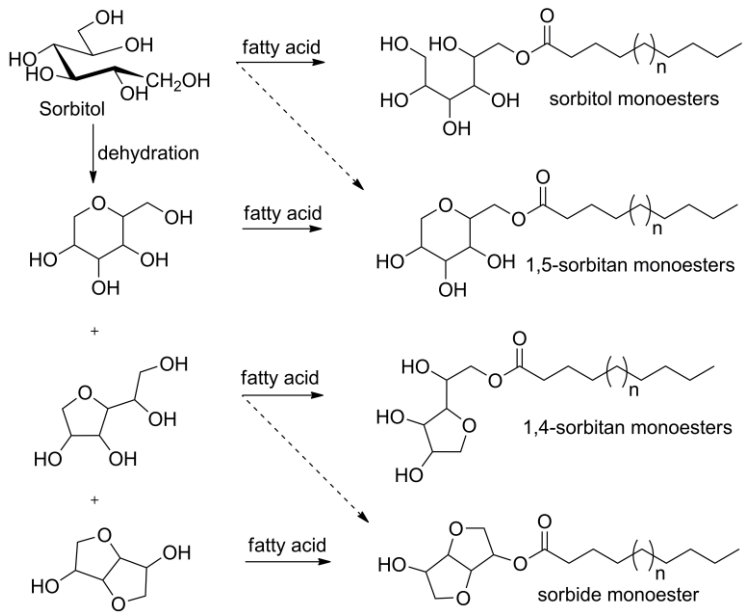



**Figure 17.** The competition between esterification and dehydration during the reaction of sorbitol with fatty acids.

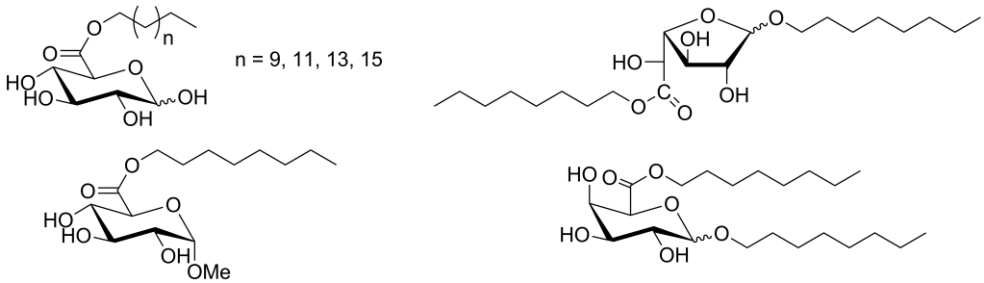



**Figure 18.** Amphiphilic uronates obtained using fatty alcohols.

## Ethers

This section concerns amphiphilic ethers obtained by alkylation of carbohydrates hydroxyl groups (other than the anomeric one) using hydrophobic electrophilic reagents. Such products are characterized by their high chemical stability under acid and under basic conditions. They differ from the alkylation products of the anomeric hydroxyl group of carbohydrates, which

are acid sensitive glycosides (those are discussed in the APG-acetal section, vide supra). Several direct methods leading to ethers are discussed below (Figure 19).

The most classical method is the Williamson reaction, namely the base catalyzed reaction of carbohydrate hydroxyl groups with fatty alkyl halides (chlorides, bromides…). The reaction produces one equivalent of salt as side product [158]. Like other base-catalyzed processes, easier is to use polyols (sucrose, sorbitol and other alditols) than substrates which still possess their free anomeric hemiacetal. Monitoring the reaction with respect to regioselectivity and the degree of substitution remains, like in previous types of derivatives, a key issue. Alternative multistep procedures have also been reported [10, 134,159,160] and interesting studies on the structure-properties relationships of liquid crystalline hexitol ethers could be established.

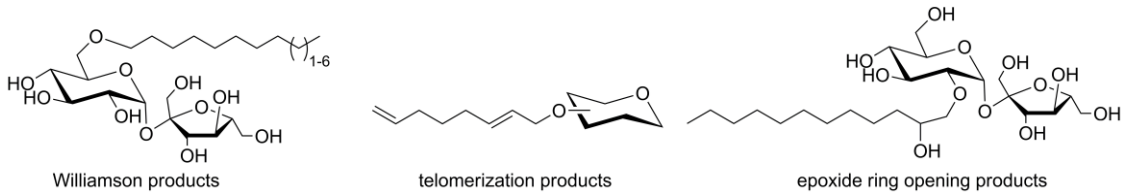



**Figure 19.** Examples of amphiphilic carbohydrate ethers.

Some level of selectivity resulting from the relative kinetic reactivity of the various hydroxyl groups can be observed. All carbohydrates differ from each other in the configuration of their hydroxyl groups, resulting in stereoelectronic effects and possible hydrogen bonding which influence, for each sugar, a specific order of reactivity. The anomeric carbon (acetal) also influences the reactivity of OH groups located on its neighboring positions. In vicinal diols with a cis relationship equatorial-axial, the equatorial OH group is more reactive, like OH-2 of an α-glucoside; or OH-3 of a mannose derivative. This is why the simple order of reactivity for primary vs secondary alcohols cannot explain the reactivity of polyols and specifically carbohydrates. In sucrose, position 2, 1’ and 3’ are more reactive when steric hindrance is not involved. In some conditions, good selectivity for etherification at position 2 can be observed [161-164,18,23], whereas bulky electrophiles lead to substitution at the primary positions (6 and 6’ first, then 1’ which suffers from a neighboring quaternary carbon atom).

The use of epoxides as electrophile is interesting because no salt is formed during the reaction. From terminal epoxides, either acid or base catalyzed processes are possible,

whereas disubstituted epoxides require acid catalyzed processes only, because the base catalyzed opening of epoxide is very sensitive to steric hindrance. The synthesis of amphiphilic sucrose hydroxyalkylethers has been studied by several groups. A tertiary amine appears to be an efficient basic catalyst, likely because it produces a strongly basic quarternary ammonium-hydroxylate intermediate acting as a surfactant, thus contributing to a better homogeneity of the medium, even in dipolar aprotic solvents such as DMSO [30,31,165,166]. Based on these observations, heterogeneous catalysts such as strongly basic functionalized polystyrene resins (N-MeIm or N-OH) with appropriate interfacial characteristics were designed, and efficiently applied to the etherification of sucrose and other polyols such as trehalose and isomalt (Figure 20) [31]. In terms of regioselectivity, the typical preference for sucrose etherification at O-2 and 1' was confirmed in this reaction [166,167]. The investigation of the thermotropic properties of each regioisomer highlighted the importance of regioselectivity in the self-organizing behavior, with some isomers exhibiting to lamellar mesophases, whereas columnar mesophases were observed for others. This was rationalized by changes in the intramolecular hydrogen bond network due to the functionalization of the key O-2 position, thus modifying the molecular shape of the disaccharide backbone and therefore the overall shape of the molecules [168]. Using a monosaccharidic series made from methyl glucoside and epoxides of various lengths [169], the cross effects of chain length and regiochemistry on the thermotropic liquid crystalline behavior could be rationalized in terms of competition between intra- and intermolecular hydrogen bonding.

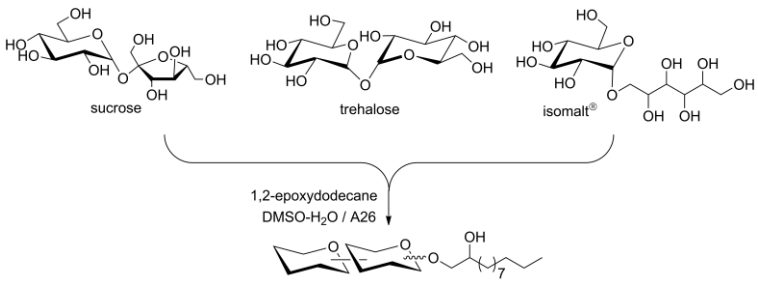



**Figure 20.** Amphiphilic hydroxyalkylethers obtained from disaccharides and 1,2-epoxydodecane.

Non-terminal epoxides have been used for designing amphiphilic bio-based ethers by opening with various alcohols or polyols. For example, lanthanide triflates are efficient Lewis-acid type catalysts for the opening in organic solvents of epoxides derived from unsaturated fatty acids esters such as methyl oleate [92,170,171].

The palladium catalyzed telomerization of butadiene in presence of carbohydrates is another etherification method which does not produce any salt as side product. In carbohydrate chemistry, it was first reported for the case of glucose and sucrose in the early 1990's by Hill and colleagues [172,173]. Shortly after, Mortreux and colleagues reported the use of aqueous conditions and of the water-soluble phosphine TPPTS [174,175]. The reaction was further investigated by the Pinel team with respect to the type of palladium precursor salt and the solvent [176]. Applied to pentoses such as xylose and arabinose, the Henin, Muzart, Bouquillon and Estrine teams investigated notably the influence of the presence of amines, and of the nature of the solvent on the efficiency and selectivity of the reaction (Figure 21) [37-42]. Gebbink and Wechuysen investigated the possibility to avoid base by using other phosphines such as TOMPP, and established the appropriate conditions for a wide range of substrates, defining the following order of reactivity : sucrose > hexoaldoses > pentoaldoses > ketoses [43]. The reaction has been also applied isomaltitol [174] or isosorbide [177] for which a strong solvent effect on the regioselectivity was observed, and to starch by Pinel and colleagues, showing how the issue of solvent and the presence of surfactants is important for such less soluble substrates [178-180]. It was also used with *N*-methyl glucamine and the renewable polyene β-myrcene [181] (see section on N-containing compounds). This reaction has attracted significant interest due to its wide scope, efficiency and ability to undergo in clean and safe conditions [182-186].

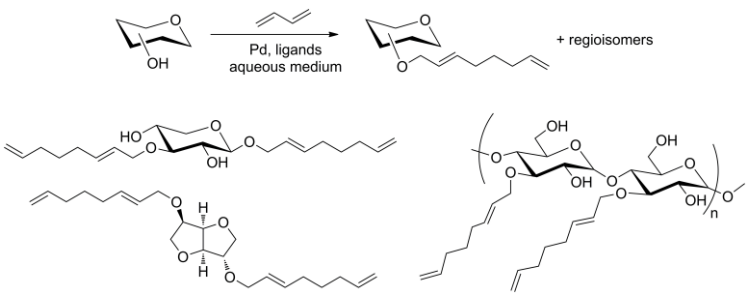



**Figure 21.** Examples of amphiphilic butadienylethers obtained by telomerization of butadiene in presence of various carbohydrates.

Carbohydrate ethers can also be prepared by reductive cleavage of acetals (Figure 22). Like in the case of glycerol ethers [187-190] the acetalation using a hydrophobic aldehyde followed by palladium catalyzed reduction in presence of hydrogen provides corresponding ethers in a rather straigtforward two-step procedure using simple and clean reagents. This strategy was applied to methyl glucoside and sorbitan ethers [101-103, 191].

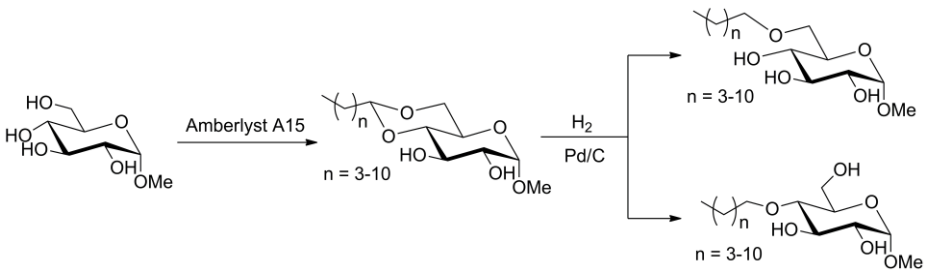



**Figure 22.** Reductive acetal opening towards amphiphilic carbohydrate ethers.

## Nitrogen-containing derivatives

Nitrogen atoms are sources of high polarity, either in amines, which are strong nucleophiles and can be protonated, or in amides, which can produce strong hydrogen bonding. Compared to sugar esters, sugar amides are particularly resistant towards the hydrolysis in alkaline media, which is of high interest for many applications [192-195,25]. There are several types of nitrogen containing carbohydrate based surfactants: i) with nitrogen already present in the starting carbohydrate (like in glucosamine); ii) from transformed hemiacetals into glycosylamines or reductive amination; iii) by amidification of carboxylic acids or lactones derived from carbohydrates; iv) or carbamatation of carbohydrate hydroxyl groups (Figure 23).

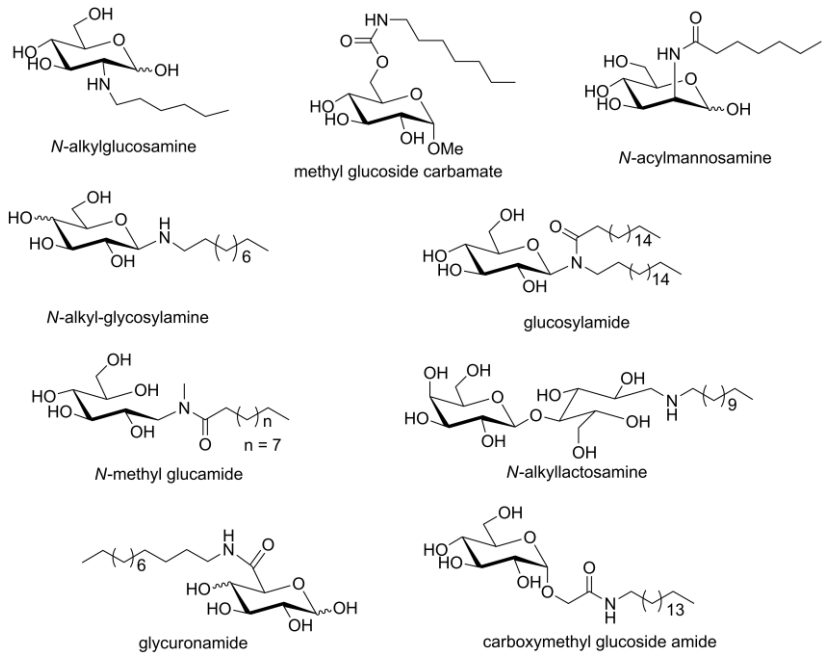



**Figure 23.** The wide range of nitrogen-containing glyco-amphiphiles.

*From glucosamine*

Glucosamine can be commercially produced by hydrolysis of chitin (found in the shells of shellfish). There are two ways to get surfactants from glucosamine, either involving glucosamine in the reductive amination of a fatty aldehyde, or by acylating the amino group with a fatty anhydride or an acyl chloride. The *N*-alkylglucosamines may be prepared from acetylated glucosamine with aldehydes under excess amount of $NaBH_3CN$, leading in most cases to mono- and dialkylated products [196,197]. Acylation of glucosamines leads to *N*-acylglucosamine surfactants [198,199] by treatment with the appropriate acid anhydrides in anhydrous methanol or with an acyl chloride in water (Figure 24).

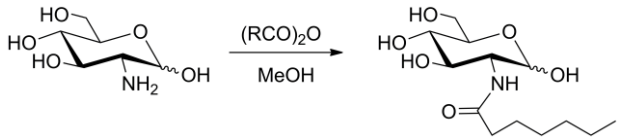



**Figure 24.** *N*-heptanoyl glucosamine.

*From glycosylamines*

*N*-Alkylglycosylamines can be easily prepared by reacting glucose with a long-chain amine. The reaction is very slow and proceeds in a mixture of ethanol and water at room temperature for one to several days [200-202]. Similarly, treatment of carbohydrates with primary amines or aqueous ammonia yields glycosylamines or *N*-methyl glycosylamines [203], which are often isolated by simple filtration. They can also be made from sugars like glucose, galactose and maltose in a multi-step process involving peracetylation, selective bromination, substitution and hydrolysis [204]. The *N*-alkyl glycosylamines are aminals which are not stable in acidic or aqueous solution, however, their acyl derivatives are quite stable. The acylation is conducted using water and ethanol as solvent, a fatty acyl chloride or anhydride, leading to the amphiphilic *N*-acyl glycosylamines (glycosylamides) (Figure 25) [205,206]. This can also be performed in solventless conditions in a ball mill under microwave irradiation [207].

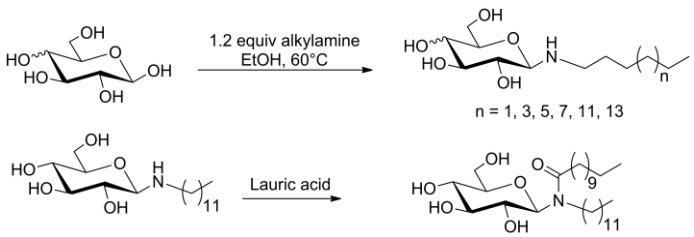



**Figure 25** *N*-alkyl glycosylamines and amides.

*Reductive amination*

Reductive amination of carbohydrates starts by forming an imine from the (masked) aldehyde with an amine, which then undergoes a reduction step. It is a more selective way to get mono-aminated products than direct alkylation of glycosylamines which often produces over-alkylation. Amphiphilic *N*-alkylglucamines can be obtained from glucose by reaction with fatty amines in refluxing methanol, followed by reduction over Raney nickel under hydrogen pressure or using sodium borohydride. Glucamide surfactants can be subsequently obtained by acylation using various conditions (Figure 26) [208-211]. The formation of by-products and co-products can be avoided when using an enzymatic route [212,213]. Telomerization of the renewable1,3-diene β-myrcene in presence of *N*-methylglucamine using Pd as the catalyst has been recently shown to lead to a new type of mono-*N*-alkylated $C_{20}$-*N*-methylglucamine derivative [181]. Isomaltulose, a reducing keto-disaccharide, can undergo directive reductive amination with alkylamine resulting the formation of alkyl aminopolyols. The isomaltamines [214-216] can be selectively acylated in aqueous solution when acting with acid halides and acid anhydrides. From a keto sugar such as 3-ketosucrose obtained by microbial oxidation of sucrose, "allosucrose" surfactants could be obtained by transformation to the oxime and futher hydrogenation into 3-amino-allo-sucrose, then *N*-acylation [217,218].

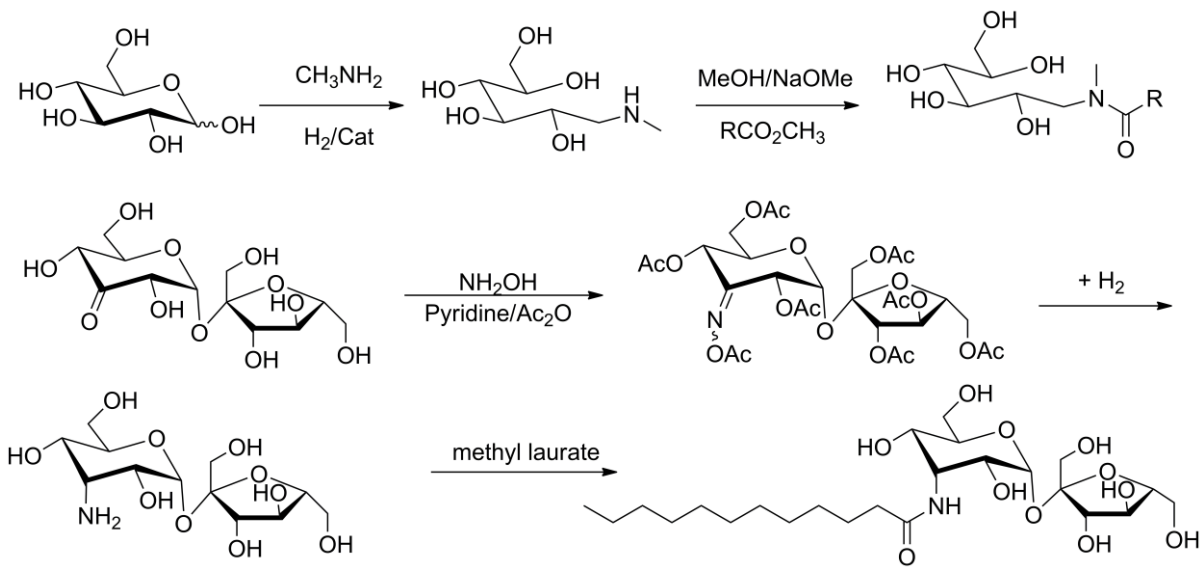



**Figure 26.** Amphiphilic *N*-acyl-carbohydrate derivatives obtained after reductive amination of the anomeric carbon (up) or of 3-keto sucrose (down).

*From carbohydrate acids and lactones*

Aldonic acids (or their lactones) are common compounds and some of them are even commercially available and can easily lead to nitrogen containing systems [219-221,153]. Carbohydrate lactones are also very available, either by selective oxidation of aldoses, or dehydrogenation of alditols and aldoses using transition metal catalysts such as palladium, chromium, gold, etc. Carbohydrate lactones undergo ring opening conversion into gluconamides by reaction with alkylamines (Figure 27) [222-224]. Uronic acid lactones are thus often used as precursors of amphiphilic carbohydrate-based amides [225,226] and recently a polyguluranate was used for the preparation of novel surafactant compositions [66]. Bicyclic systems like carboxymethylglycoside lactones (CMGLs) prepared from isomaltulose [227-228] or from the oxidation of corresponding allyl glycosides [229] provide amphiphilic amides by treatment with fatty amines in anhydrous $CH_2Cl_2$. Let us note that further functionalization of glucamides can be performed, such as in the case of sulfated urnoamides [230,231]. Analogous sugar thioamides have been obtained using Lawesson's reagent and the peracteylated glucamide [232].

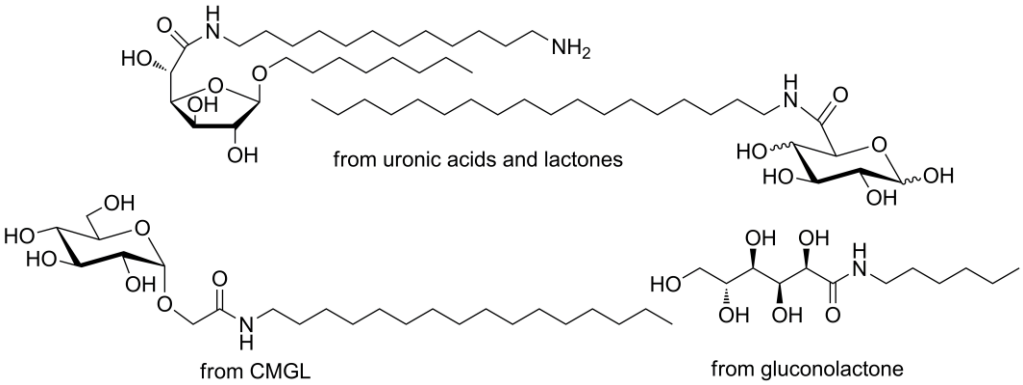



**Figure 27.** Amphiphilic amides prepared from carbohydrate lactones.

*Carbamates*

Other *N*-linked surfactants like sucrose carbamates, cationic analogs of galactosylceramide have been reported (Figure 28). Plusquellec, Queneau, Pucci and others reported the preparation of carbohydrate carbamates by reaction with isocyanates [233-237]. The carbamatation of sucrose, which is more reactive than water, can be performed in aqueous media such as water/isopropanol mixtures.

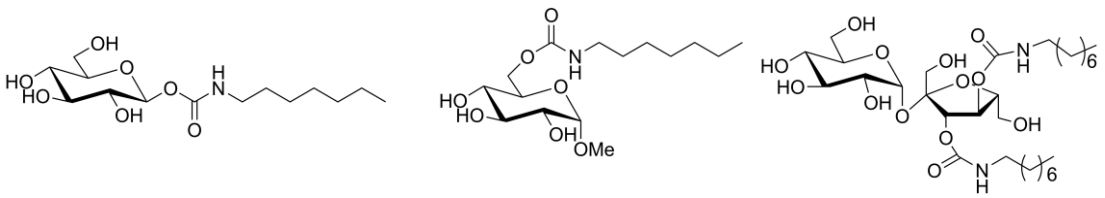


**Figure 28.** Examples of amphiphilic carbohydrate carbamates.

Catanionic compounds can be obtained by mixing two oppositely charged surfactants. For example, adding an amino sugar to the same amount of monocarboxylic acid led quantitatively to two-chain catanionic analogs, whereas adding the half amount of dicarboxylic acid, led to the gemini catanionic analogs of galactosylceramide [238,239]. Condensation of carbohydrates with alkoxyamines provide oxime-ether type carbohydrate based surfactants which are much more stable than traditional acetal-, ester-, and even than amide-linked surfactants, in acidic and basic solutions. Using this strategy, Palandoken synthesized many oxime ether surfactants from glyceraldehyde, glucose and maltose in aqueous media [240]. One of the advantages of their method is precluding the protection-deprotection sequence of hydroxy group in sugars, which can improve the overall yields and shorten the process.

## *Triazoles*

Triazoles are new kinds of linkages used in the design of carbohydrate based surfactants, benefiting from the recent development of the 1,3-dipolar cycloadditions of azides and alkynes (Huisgen reaction) notably using Cu(I)-catalyzed conditions leading to high yields and excellent 1,4-regioselectivity [241,242]. Using this strategy, several examples of carbohydrate based surfactants or hydrogels with triazoles linkage have been reported (Figure 29). Glycosyl azides are easily synthesized at room temperature by displacement of the corresponding sugar-chlorides with $NaN_3$ or by direct conversion of sugars using ADMP in aqueous solution [243]. Different kinds of azidoalkyl derivatives may be furnished as a precursor for Huisgen cycloaddition [244], and find wide applications as pseudo-glycoconjugates thanks to their stability under a wide range of chemical conditions. The azide-products then undergo the Huisgen reaction with long-chain propargyl ethers [245] or thioethers leading to many different kinds of surfactants and gelators [246-248]. The alkyne triple bond can be induced into sugar skeleton firstly by glycosylation of carbohydrates with

excess amount of propargyl alcohol or etherification with propargyl halides. The formed propargyl derivatives then undergo Huisgen reaction with alkyl azides [249].

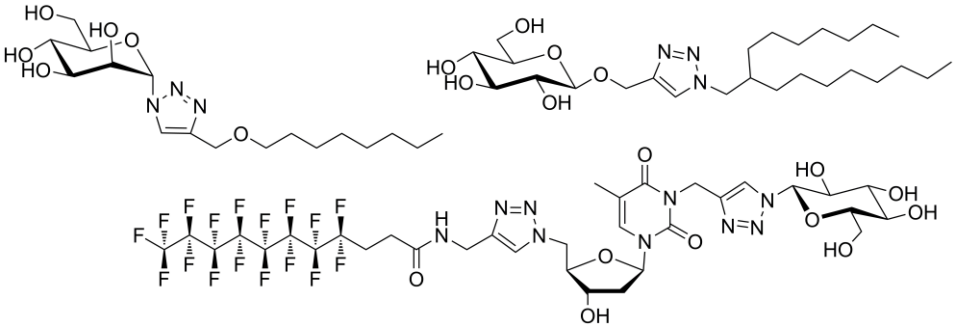


**Figure 29.** Examples of amphiphilic triazoles obtained from carbohydrate azides or alkynes.

### *C*-glycosides

*C*-glycosyl derivatives are because substituting the oxygen atom of the glycosidic bond by a carbon atom transforms the acetal into a regular carbon-carbon bond which cannot undergo acid or enzymatic hydrolysis anymore. They are therefore interesting biologically relevant targets, but have become also attractive for designing novel bio-based chemicals. Direct and clean methods towards C-glycosyl compounds have been reported, such as the metal catalyzed addition of allyl bromide on unprotected carbohydrates [250], and the indium catalyzed addition of bromomethylacrylate on unprotected carbohydrates in aqueous conditions [251]. These two methods have essentially been applied to biologically relevant targets and would be useful to revisit in the context of green low-added value chemicals. Below we focus on two short and direct strategies which have been applied to the preparation of amphiphilic *C*-glycosyl derivatives, both being conducted is aqueous media [252].

The Knoevenagel condensation of unprotected carbohydrates towards C-glycosides has been first reported for the synthesis of *C*-glycosyl barbiturates by Galbis Perez [253,254] and Wulff [255]. Kozikowski [256] used acetylacetone and zinc chloride as catalyst and found that the reaction led to mixtures of tetrahydrofuranic products. Lubineau and Canac reported in 2000 [257] that the reaction of glucose and several other mono and disaccharides with acetylacetone in water and in the presence of $NaHCO_3$ was a clean and efficient way to obtain selectively β-*C*-glycosides in quantitative yields. As for targets of industrial relevance, this very interesting and direct method was first applied to the synthesis of the cosmetic active Proxylane ® (by reaction of xylose with acetylacetone, then reduction of the ketone) [258],

and was later developed by Scherrmann [259], towards *C*-glycosidic amphiphiles using betadiketones with longer alkyl chains (Figure 30). The atom economy of the reaction was later improved by Foley and Anastas [260] who reported a two-step sequence keeping the very available acetylacetone as starting diketone and using the intermediate 2-oxopropyl *C*-glycoside as substrate for aldolisations and crotonisations using long chain aldehydes.

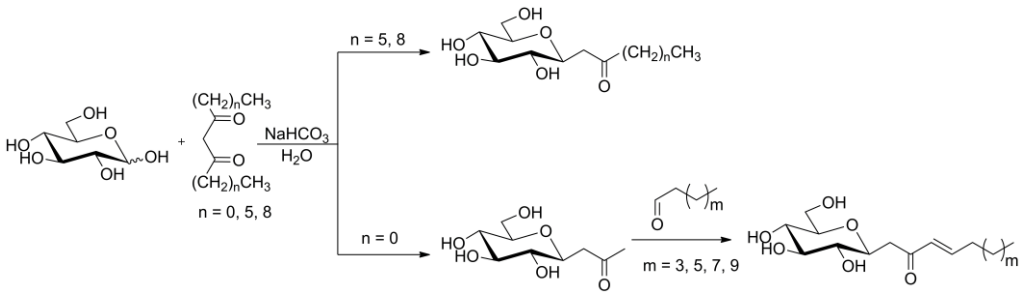



**Figure 30.** Aqueous Knoevenagel reaction of unprotected carbohydrates to *C*-glycosides by condensation with β-diketones.

The other straightforward method towards amphiphilic *C*-glycosides has been reported by the Benvegnu group, using the Horner-Wadsworth-Emmons (HWE) reaction from commercially or easily available 2-oxoalkylphosphonates and unprotected carbohydrates (Figure 31). The reaction involves the aldehyde function present in the open chain form of the starting carbohydrate on the aldehydic form and can be conducted in a very clean and simple basic aqueous medium. Four products can be obtained (α or β of the *C*-pyranosides and *C*-furanosides), with in most cases a strong or total selectivity in the β-*C*-pyranosides. The reaction can be extended to disaccharides and a wide range of chain lengths, and has also been conducted under solvent free conditions [32,261,262].

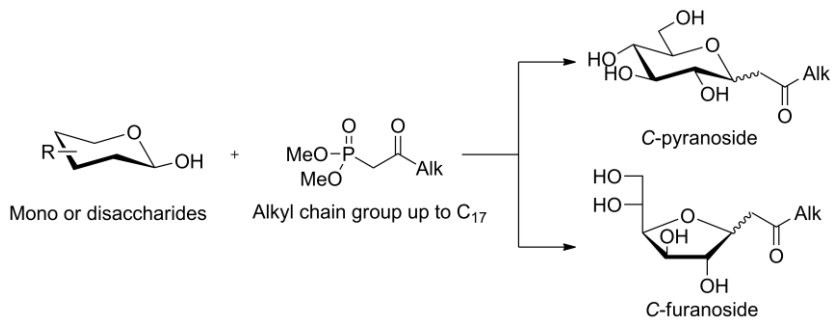



**Figure 31.** Aqueous Horner-Wadsworth-Emmons access to amphipilic *C*-glycosides.

## Furanic derivatives

Fuans, notably furfural and hydroxymethylfurfural (HMF) obtained by acid-catalyzed dehydration of carbohydrates are now considered as major bio-based resources for the design of novel bio-based chemicals [263-265]. Though essentially dedicated to targets other than surfactants (monomers, solvents…), there are however a few interesting pieces of work related to surfactants in which the furan part serves essentially as a connecting section between the polar and non-polar appendages. For example, a series of Diels-Alder (DA) adducts were obtained from long chain 2-alkyl furans with *N*-substituted maleimides (Figure 32) [266]. Interestingly, such DA adducts can undergo retro-Diels Alder reaction and thus be thermally cleaved by simple exposure to high temperature. From HMF, Stensrud and Wicklund reported in a 2016 patent [267]. several amphiphilic structures. Notably, from furandimethanol, one OH can be enzymatically esterified with a fatty acid, leading to very non-polar surfactants (as only one OH group remains). Alternatively, after esterification of HMF with fatty acids, the aldehyde can be transformed into the imine using various amines, including polar ones such as aminoethyl hydroxyethylamine or bis (aminoethyl)amine. Then the imines are reduced to the corresponding amines. More recently, Dauenhauer and coworkers reported the 2-acylation of furan with activated fatty acid derivatives and the subsequent sulfonation at C-5 providing a novel family of ionic surfactants. A second chain can be introduced by aldolisation prior the sulfonation step [268].

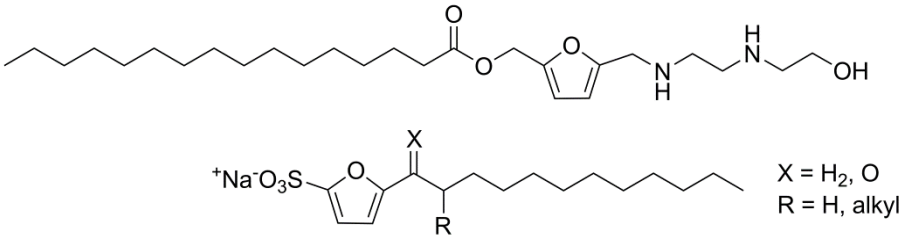



**Figure 32.** Examples of amphiphilic derivatives arising from furanic platform molecules arising from carbohydrates.

A furan moiety is also present in glucosyloxymethylfurfural, the glycosylated equivalent of HMF obtained by dehydration of the commercially available disaccharide isomaltulose. Its oxidation to the carboxylic acid followed by esterification with fatty alcohols, or its reductive amination with fatty amines, or its use as substrate in Baylis Hillmann reactions with alkylacrylates are all rather short sequences towards surfactants constructed on a furanic central backbone (Figure 33) [269-274].

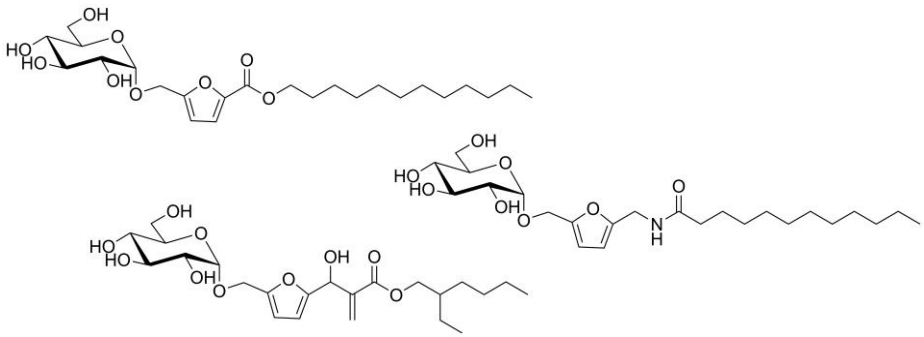


**Figure 33**. Amphiphilic derivatives obtained by the chemistry of glycosyloxymethyl furfural (GMF).

## CONCLUSION / FUTURE DIRECTIONS

Carbohydrate-based surfactants are ideal examples of bio-based chemicals, because both moieties arise from renewable resources. The diversity of carbohydrate structures available in Nature provides a huge choice for designing bio-based surfactants, and several examples have successfully reached the market. Whereas first motivations were to give extra added-value to unused agricultural crops, the evolution of chemistry towards greener, safer, cleaner products and processes has provided a renewal of interest for bio-based surfactants. Although conjectural parameters, primarily those affecting the relative price of fossil resources versus agricultural crops, will inevitably modulate the economic impetus for developing novel bio-based chemicals, and among those, bio-based surfactants, it is interesting to see that the structural innovation illustrated by novel examples is also the way to renew and widen the scope of properties and uses, and offer opportunities for new IP in a very competitive sector. With respect to the specific field of surfactants, why and how a bio-sourced surfactant can be considered as a promising substitute to a fossil-based surfactant? The renewability of the starting materials is not, as such, a sufficient reason. Sustainability must be accompanied by economic viability and maintaining (at least) the technical performance, both in terms of applicative, physical (stability) and environmental properties [7]. Regulations aiming at improving the biocompatibility of chemicals used in the everyday life, and at decreasing the dependence on fossil resources will also play increasing roles in strategies. Thus, both the societal and economic aims join in strategies dedicated to the use of biomass towards chemicals, offering a wide playground to chemists, academic and industrial, for future research and innovation.

## References


[1] Rosen MJ, Kunjappu JT (2012) Surfactants and Interfacial Phenomena. Wiley & Sons, New Jersey
[2] Zoller U (2008) Handbook of detergents, part E: applications. Taylor & Francis, California
[3] Surfactants Market by Type (Anionic, Non-Ionic, Cationic, and Amphoteric), Substrate (Synthetic, and Bio-based), Application (Detergents, Personal Care, Textile, Elastomers & Plastics, Crop Protection, Food & Beverage) - Global Forecast to 2021 MarketsandMarkets.com ; oct 2016, 170 pages
[4] Kjellin M, Johansson I (eds) (2010) Surfactants from Renewable Resources. John Wiley & Sons, Stockholm
[5] Holmberg K (2001) Natural surfactants. Current Opinion in Colloid & Interface Science 6:148–159
[6] Hubbard A (2004) Novel Surfactants: Preparation, Applications, and Biodegradability. Marcel Dekker, New York
[7] Jessop PG, Ahmadpour F, Buczynski MA, Burns TJ, Green II NB, Korwin R, Long D, Massad SK, Manley JB, Omidbakhsh N, Pearl R, Pereira S, Predale RA, Sliva PG, Van der Bilt H, Weller S, Wolf MH (2015) Opportunities for greener alternatives in chemical formulations. Green Chem 17:2664–2678
[8] Foley P, Kermanshahi-pour A, Beach ES, Zimmerman JB (2012) Derivation and synthesis of renewable surfactants. Chem Soc Rev 41:1499–1518
[9] Razafindralambo H, Blecker C, Paquot M (2012) Carbohydrate-Based Surfactants: Structure-Activity Relationships. In: Advances in Chemical Engineering. InTech, Rijeka
[10] Almeida MVD, Hyaric ML (2005) Carbohydrate-Derived Surfactants. Mini-Reviews in Organic Chemistry 2:283–297
[11] Nakamura S (1999) Application of Sucrose Fatty Acid Esters as Food Emulsifiers. in: Karsa DR (ed) Industrial Applications of Surfactants IV, 1st edn. The Royal Society of Chemistry, Manchester, pp 73-87
[12] Hayes DG, Kitamoto D, Solaiman D, Ashby R (eds) Biobased Surfactants and Detergents: Synthesis, Properties, and Applications. AOCS press, Urbana.
[13] Pöhnlein M, Hausmann R, Lang S, Syldatk C (2015) Enzymatic synthesis and modification of surface-active glycolipids. Eur J Lipid Sci Technol 117:145–155
[14] Bogaert INAV, Saerens K, Muynck CD, Develter D, Soetaert W, Vandamme EJ (2007) Microbial production and application of sophorolipids. Appl Microbiol Biotechnol 76:23–34
[15] Besson M, Gallezot P, Pinel C (2014) Conversion of Biomass into Chemicals over Metal Catalysts. Chem Rev 114:1827–1870
[16] Bödiger M, Demharter S, Mülhaupt R (2007) Carbohydrates as Organic Raw Materials III, Wiley-VCH, New York
[17] Corma A, Iborra S, Velty A (2007) Chemical Routes for the Transformation of Biomass into Chemicals. Chemical Reviews 107:2411–2502
[18] Queneau Y, Jarosz S, Lewandowski B, Fitremann J (2007) Sucrose Chemistry and Applications of Sucrochemicals. In: Horton D (ed) Advances in Carbohydrate Chemistry and Biochemistry. Elsevier, London, pp 217–292
[19] Rauter AP, Vogel P, Queneau Y (eds) (2010) Carbohydrates in Sustainable Development I. Springer, Heidelberg
[20] Rauter AP, Vogel P, Queneau Y (eds) (2010) Carbohydrates in Sustainable Development II. Springer, Heidelberg
[21] Sheldon RA (2014) Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chem 16:950–963
[22] Chatterjee C, Pong F, Sen A (2014) Chemical conversion pathways for carbohydrates. Green Chem 17:40–71
[23] Queneau Y, Fitremann J, Trombotto S (2004) The chemistry of unprotected sucrose: the selectivity issue. Comptes Rendus Chimie 7:177–188
[24] Molinier V, Fenet B, Fitremann J, Bouchu A, Queneau Y (2005) PFGSE–NMR study of the self-diffusion of sucrose fatty acid monoesters in water. J Colloid Interface Sci 286:360–368
[25] Queneau Y, Chambert S, Besset C, Cheaib R (2008) Recent progress in the synthesis of carbohydrate-based amphiphilic materials: the examples of sucrose and isomaltulose. Carbohydr Res 343:1999–2009

[26] Bethell D, Galsworthy PJ, Jones K (1988) Mutarotation of glucose derivatives in solutions of surfactants in organic solvents: co-operativity and bimodal catalytic behaviour. J Chem Soc, Perkin Trans 2:2035–2043
[27] Thévenet S, Descotes G, Bouchu A, Queneau Y (1997) Hydrophobic Effect Driven Esterification of Sucrose in Aqueous Medium . J Carbohydr Chem 16:691–696
[28] Fitremann J, Queneau Y, Maître J-P, Bouchu A (2007) Co-melting of solid sucrose and multivalent cation soaps for solvent-free synthesis of sucrose esters. Tetrahedron Letters 48:4111–4114
[29] Le Coënt A-L, Tayakout-Fayolle M, Couenne F, Briançon S, Lieto J, Fitremann-Gagnaire J, Queneau Y, Bouchu A (2003) Kinetic parameter estimation and modelling of sucrose esters synthesis without solvent. Chemical Engineering Science 58:367–376
[30] Pierre R, Adam I, Fitremann J, Jérôme F, Bouchu A, Courtois G, Barrault J, Queneau Y (2004) Catalytic etherification of sucrose with 1,2-epoxydodecane: investigation of homogeneous and heterogeneous catalysts. Comptes Rendus Chimie 7:151–160
[31] Villandier N, Adam I, Jérôme F, Barrault J, Pierre R, Bouchu A, Fitremann J, Queneau Y (2006) Selective synthesis of amphiphilic hydroxyalkylethers of disaccharides over solid basic catalysts: Influence of the superficial hydrophilic–lipophilic balance of the catalyst. Journal of Molecular Catalysis A: Chemical 259:67–77
[32] Peyrot C, Lafite P, Lemiègre L, Daniellou R (2017) Low molecular weight carbohydrate-based hydrogelators. In: Rauter AP, Lindhorst TK, Queneau Y (eds) Carbohydrate Chemistry- Chemical and Biological Approaches, Volume 43, The Royal Society of Chemistry, Cambridge, pp 245–265
[33] Renault L, Pessel F, Benvegnu T (2017) Surfactants based on green/blue sugars: towards new functionalities in formulations. In: Rauter AP, Lindhorst TK, Queneau Y (eds) Carbohydrate Chemistry- Chemical and Biological Approaches, Volume 43, The Royal Society of Chemistry, Cambridge, pp 196–244
[34] Fischer E (1893) Ueber die Glucoside der Alkohole. Ber Dtsch Chem Ges 26:2400–2412
[35] Klotz W, Schmidt RR (1993) Anomeric O-alkylation, 11. Anomeric O-Alkylation of O-Unprotected Hexoses and Pentoses – Convenient Synthesis of Decyl, Benzyl, and Allyl Glycosides. Liebigs Ann Chem 1993:683–690
[36] El-Nokaly MA, El-Taraboulsy MA (1980) Preparation of O-Dodecyl Sucrose Surfactant. Journal of Dispersion Science and Technology 1:373–392
[37] Bessmertnykh A, Hénin F, Muzart J (2005) Palladium-catalysed telomerization of butadiene with aldoses: A convenient route to non-ionic surfactants based on controlled reactions. Journal of Molecular Catalysis A: Chemical 238:199–206
[38] Damez C, Estrine B, Bessmertnykh A, Bouquillon S, Hénin F, Muzart J (2006) Effects of the reactants concentration in the butadiene telomerization with D-xylose and parallel influence of triethylamine as additive. Journal of Molecular Catalysis A: Chemical 244:93–98
[39] Hadad C, Damez C, Bouquillon S, Estrine B, Hénin F, Muzart J, Pezron I, Komunjer L (2006) Neutral pentosides surfactants issued from the butadiene telomerization with pentoses: preparation and amphiphilic properties. Carbohydrate Research 341:1938–1944
[40] Estrine B, Bouquillon S, Hénin F, Muzart J (2004) Telomerization of Butadiene with L-Arabinose and D-Xylose in DMF: Selective Formation of their Monooctadienyl Glycosides. Eur J Org Chem 2004:2914–2922
[41] Estrine B, Bouquillon S, Henin F, Muzart J (2005) Telomerization of butadiene with pentoses in water: selective etherifications. Green Chem 7:219–223
[42] Bouquillon S (2011) D-Xylose and L-Arabinose-based surfactants: Synthesis, reactivity and physico-chemical properties. Comptes Rendus Chimie 14:716–725
[43] Hausoul PJC, Bruijnincx PCA, Klein Gebbink RJM, Weckhuysen BM (2009) Base-free Pd/TOMPP-Catalyzed Telomerization of 1,3-Butadiene with Carbohydrates and Sugar Alcohols. ChemSusChem 2:855–858
[44] Toshima K, Tatsuta K (1993) Recent progress in O-glycosylation methods and its application to natural products synthesis. Chem Rev 93:1503–1531
[45] Schmidt RR, Michel J (1980) Facile Synthesis of α- and β-O-Glycosyl Imidates; Preparation of Glycosides and Disaccharides. Angew Chem Int Ed Engl 19:731–732
[46] Pougny J-R, Sinaÿ P (1976) Reaction d'imidates de glucopyranosyle avec l'acetonitrile. Applications synthetiques. Tetrahedron Letters 17:4073–4076
[47] von Rybinski W, Hill K (1998) Alkyl Polyglycosides—Properties and Applications of a new Class of Surfactants. Angewandte Chemie International Edition 37:1328–1345

[48] Nickel D, Förster T, Rybinski W (2008) Alkyl Polyglycosides: Technology, Properties and Applications. Wiley-VCH, Weinheim
[49] Guilbot J, Kerverdo S, Milius A, Escola R, Pomrehn F (2013) Life cycle assessment of surfactants: the case of an alkyl polyglucoside used as a self emulsifier in cosmetics. Green Chem 15:3337–3354
[50] Hill K (2005) Industrial Development and Application of Biobased Oleochemicals. In: Kamm B, Gruber PR, Kamm M (eds.) Biorefineries-Industrial Processes and Products. Wiley-VCH Verlag GmbH, Potsdam, pp 291–314
[51] Geetha D, Tyagi R (2012) Alkyl Poly Glucosides (APGs) Surfactants and Their Properties: A Review. TSD 49:417–427
[52] Bertsch H, Rauchalles G, Akiengesellschaft B (1936) Verwendung von hochmolekularen synthetischen Glucosiden als Saponinersatz, als Emulgierungs-, Reinigungs- und Netzmittel. German Patent DE593422C
[53] Fischer E, Helferich B (1911) Über neue synthetische Glucoside. Justus Liebigs Ann Chem 383:68–91
[54] Cui J, Zheng J, Qiao W, Wan X (2008) Solvent-tuned multiple self-assembly of a new sugar-appended gelator. Journal of Colloid and Interface Science 326:267–274
[55] Bao C, Lu R, Jin M, Xue P, Tan C, Zhao Y, Liu G (2004) Synthesis, self-assembly and characterization of a new glucoside-type hydrogel having a Schiff base on the aglycon. Carbohydrate Research 339:1311–1316
[56] Jung JH, John G, Masuda M, Yoshida K, Shinkai S, Shimizu T (2001) Self-Assembly of a Sugar-Based Gelator in Water: Its Remarkable Diversity in Gelation Ability and Aggregate Structure. Langmuir 17:7229–7232
[57] Jung JH, Rim JA, Han WS, Lee SJ, Lee YJ, Cho EJ, Kim JS, Ji Q, Shimizu T (2006) Hydrogel behavior of a sugar-based gelator by introduction of an unsaturated moiety as a hydrophobic group. Org Biomol Chem 4:2033–2038
[58] Maldonado OS, Lucas R, Comelles F, Jesús González M, Parra JL, Medina I, Morales JC (2011) Synthesis and characterization of phenolic antioxidants with surfactant properties: glucosyl- and glucuronosyl alkyl gallates. Tetrahedron 67:7268–7279
[59] Es DSV, Marinkovic S, Oduber X, Estrine B (2013) Use of Furandicarboxylic Acid and Its Decyl Ester as Additives in the Fischer's Glycosylation of Decanol by D-Glucose: Physicochemical Properties of the Surfactant Compositions Obtained. J Surfact Deterg 16:147–154
[60] Bergfeld DMJ, Seifert DJ (1994) Method for the continuous production of alkylglycosides. European Patent EP0617045A2
[61] Oberholz DA, Kahsnitz DJ, Schmidt DS (1995) Process for manufacturing alkyl glycosides and alkyl oligoglycosides. European Patent EP0482325B1
[62] Eskuchen R, Nitsche M (2008) Technology and Production of Alkyl Polyglycosides in: Alkyl Polyglycosides: Technology, Properties and Applications. Wiley-VCH, Weinheim
[63] Roussel M, Benvegnu T, Lognoné V, Le Deit H, Soutrel I, Laurent I, Plusquellec D (2005) Synthesis and Physico-Chemical Properties of Novel Biocompatible AlkylD-Mannopyranosiduronate Surfactants Derived from Alginate. Eur J Org Chem 3085–3094
[64] Castro MJL, Kovensky J, Fernández Cirelli A (2002) New Family of Nonionic Gemini Surfactants. Determination and Analysis of Interfacial Properties. Langmuir 18:2477–2482
[65] Liu S, Sang R, Hong S, Cai Y, Wang H (2013) A Novel Type of Highly Effective Nonionic Gemini Alkyl O-Glucoside Surfactants: A Versatile Strategy of Design. Langmuir 29:8511–8516
[66] Sari-Chmayssem N, Pessel F, Guégan JP, Taha S, Mawlawi H, Benvegnu T (2016) Direct and one-pot conversion of polyguluronates and alginates into alkyl-L-guluronamide-based surfactant compositions. Green Chem 18:6573–6585
[67] Villandier N, Corma A (2011) Transformation of Cellulose into Biodegradable Alkyl Glycosides by Following Two Different Chemical Routes. ChemSusChem 4:508–513
[68] Villandier N, Corma A (2010) One pot catalytic conversion of cellulose into biodegradable surfactants. Chem Commun 46:4408–4410
[69] Climent MJ, Corma A, Iborra S, Martínez-Silvestre S (2016) Transformation of Cellulose into Nonionic Surfactants Using a One-Pot Catalytic Process. ChemSusChem 9:3492–3502
[70] Deng W, Liu M, Zhang Q, Tan X, Wang Y (2010) Acid-catalysed direct transformation of cellulose into methyl glucosides in methanol at moderate temperatures. Chem Commun 46:2668–2670

[71] Karam A, De Oliveira Vigier K, Marinkovic S, Estrine B, Oldani C, Jérôme F (2017) Conversion of Cellulose into Amphiphilic Alkyl Glycosides Catalyzed by Aquivion, a Perfluorosulfonic Acid Polymer. ChemSusChem 10:3604–3610
[72] Zou M, Chen J, Wang Y, Li M, Zhang C, Yang X (2016) Alcoholysis of Starch to Produce Alkyl Polyglycosides with Sub-Critical Isooctyl Alcohol. J Surfact Deterg 19:879–884
[73] Marinkovic S, Bras JL, Nardello-Rataj V, Agach M, Estrine B (2011) Acidic Pretreatment of Wheat Straw in Decanol for the Production of Surfactant, Lignin and Glucose. International Journal of Molecular Sciences 13:348–357
[74] Sekine M, Kimura T, Katayama Y, Takahashi D, Toshima K (2013) The direct and one-pot transformation of xylan into the biodegradable surfactants, alkyl xylosides, is aided by an ionic liquid. RSC Adv 3:19756–19759
[75] Turner P, Svensson D, Adlercreutz P, Karlsson EN (2007) A novel variant of Thermotoga neapolitana β-glucosidase B is an efficient catalyst for the synthesis of alkyl glucosides by transglycosylation. Journal of Biotechnology 130:67–74
[76] Agach M, Moity L, Renault B, Marinkovic S, Estrine B, Nardello-Rataj V (2014) Succinylation of Non-ionic Surfactants: Physicochemical Characterization, Functional Properties, Biodegradability and Mathematical Modeling of the Polarity Tuning. J Surfact Deterg 17:591-602
[77] Drouet P, Zhang M, Legoy MD (1994) Enzymatic synthesis of alkyl β-D-xylosides by transxylosylation and reverse hydrolysis. Biotechnol Bioeng 43:1075–1080
[78] Vic G, Thomas D, Crout DHG (1997) Solvent effect on enzyme-catalyzed synthesis of β-D-glucosides using the reverse hydrolysis method: Application to the preparative-scale synthesis of 2-hydroxybenzyl and octyl β-D-glucopyranosides. Enzyme and Microbial Technology 20:597–603
[79] Ochs M, Muzard M, Plantier-Royon R, Estrine B, Remond C (2011) Enzymatic synthesis of alkyl β-D-xylosides and oligoxylosides from xylans and from hydrothermally pretreated wheat bran. Green Chem 13:2380–2388
[80] Rather MY, Mishra S (2013) β-Glycosidases: An alternative enzyme based method for synthesis of alkyl-glycosides. sustain chem process 1:7
[81] Papanikolaou S (2001) Enzyme-catalyzed synthesis of alkyl-β-glucosides in a water–alcohol two-phase system. Bioresource Technology 77:157–161
[82] Montiel C, Bustos-Jaimes I, Bárzana E (2013) Enzyme-catalyzed synthesis of heptyl-β-glycosides: Effect of water coalescence at high temperature. Bioresource Technology 144:135–140
[83] Younis Rather M, Mishra S, Verma V, Chand S (2012) Biotransformation of methyl-β-D-glucopyranoside to higher chain alkyl glucosides by cell bound β-glucosidase of Pichia etchellsii. Bioresource Technology 107:287–294
[84] Bousquet M-P, Willemot R-M, Monsan P, Boures E (1998) Production, purification, and characterization of thermostable α-transglucosidase from Talaromyces duponti–application to α–alkylglucoside synthesis. Enzyme and Microbial Technology 23:83–90
[85] Dahiya S, Ojha S, Mishra S (2015) Biotransformation of sucrose into hexyl-α-D-glucopyranoside and -polyglucosides by whole cells of Microbacterium paraoxydans. Biotechnol Lett 37:1431–1437
[86] Richard G, Morel S, Willemot R-M, Monsan P, Remaud-Simeon M (2003) Glucosylation of α-butyl- and α-octyl-D-glucopyranosides by dextransucrase and alternansucrase from Leuconostoc mesenteroides. Carbohydrate Research 338:855–864
[87] Jin Z, Zhang J, Yang X, Zhou Y (2016) Synthesis of Alkyl Monoglucoside Citric Monoester and Properties of Its Sodium Salt. J Surfact Deterg 19:885–891
[88] Lin L-H, Lai Y-C, Chen K-M, Chang H-M (2015) Oxyethylene chain length affects the physicochemical properties of sugar-based anionic surfactants with phosphates groups. Colloids and Surfaces A: Physicochemical and Engineering Aspects 485:118–124
[89] Perusse D, Guegan JP, Rolland H, Guilbot J, Benvegnu T (2016) Efficient solvent-free cationization of alkylpolyglycoside based surfactant compositions using natural glycine betaine. Green Chem 18:1664–1673
[90] Tabor RF, Tan DD, Han SS, Young SA, Seeger ZLE, Pottage MJ, Garvey CJ, Wilkinson BL (2014) Reversible pH- and Photocontrollable Carbohydrate-Based Surfactants. Chem Eur J 20:13881–13884

[91] Szabó LZ, Hanrahan DJ, Jones EM, Martin E, Pemberton JE, Polt R (2016) Preparation of S-glycoside surfactants and cysteine thioglycosides using minimally competent Lewis acid catalysis. Carbohydrate Research 422:1–4
[92] Epoune Lingome C, Gadenne B, Alfos C, Queneau Y, Moebs-Sanchez S (2017) Ring opening of epoxidized methyl or ethyl oleate by alkyl glycosides. Eur J Lipid Sci Technol 119:1600413-1600421
[93] Potier P, Bouchu A, Descotes G, Queneau Y (2001) Lipase-Catalysed Selective Synthesis of Sucrose Mixed Diesters. Synthesis 3:458–462
[94] Miethchen R, Peters D (1988) Ultraschallforcierte Reaktionen; Synthese und Charakterisierung amphiphiler 4, 6-O (n-Alkyliden)-D-glucopyranosen. Z Chem 28:298–299
[95] Thiem J, Vill V, Miethchen R, Peters D (1991) Flüssigkristalline 4,6-O-(n-Alkyliden)-D-glucopyranosen. J Prakt Chem 333:173–175
[96] Ono D, Masuyama A, Okahara M (1990) Preparation of new acetal type cleavable surfactants from epichlorohydrin. J Org Chem 55:4461–4464
[97] Kida T, Masuyama A, Okahara M (1990) Preparation of trihydroxycarboxylates bearing a long-chain alkyl acetal group from glucono-1,5-lactone. Tetrahedron Letters 31:5939–5942
[98] Fanton E, Fayet C, Gelas J (1997) Long-chain acetals derived from sucrose as a new class of surfactants. Carbohydrate Research 298:85–92
[99] Porwanski S, Salanski P, Panaud N, Descotes G, Bouchu A, Queneau Y (2000) Regioselectivity in acid- or base-catalysed acetalation of sucrose: selection of [OH-2, OH-3] or [OH-4, OH-6] diols. Topics in Catalysis 13:335–338
[100] Porwanski S, Salanski P, Descotes G, Bouchu A, Queneau Y (2000) Selective Synthesis of 4,6-O-Alkenylidene and -Benzylidene Acetals from Unprotected Sucrose by Lanthanide(III) Resin-Catalyzed Transacetalization. Synthesis 2000:525–528
[101] Gozlan C, Duguet N, Lemaire M, Queneau Y, Redl A (2016) Method for preparing long-chain alkyl cyclic acetals made from sugars. WIPO Patent WO2014199345A1
[102] Belmessieri D, Gozlan C, Duclos M-C, Molinier V, Aubry J-M, Dumitrescu O, Lina G, Redl A, Duguet N, Lemaire M (2017) Synthesis, surfactant properties and antimicrobial activities of methyl glycopyranoside ethers. European Journal of Medicinal Chemistry 128:98–106
[103] Gozlan C, Lafon R, Duguet N, Redl A, Lemaire M (2014) Catalytic reductive cleavage of methyl α-D-glucoside acetals to ethers using hydrogen as a clean reductant. RSC Adv 4:50653–50661
[104] Ames GR, Blackmore HM, King TA (1964) The reaction of sugars with alkyl halogenomethyl ethers. J Appl Chem 14:503–506
[105] Ames GR, Blackmore HM, King TA (1964) Alkyloxymethyl ethers of sucrose and glucose as surfactants. J Appl Chem 14:245–249
[106] Gronwald O, Shinkai S (2001) “Bifunctional” sugar-integrated gelators for organic solvents and water-on the role of nitro-substituents in 1-O-methyl-4,6-O-(nitrobenzylidene)-monosaccharides for the improvement of gelation ability. J Chem Soc, Perkin Trans 2 1933–1937
[107] Kowalczuk J, Jarosz S, Tritt-Goc J (2009) Characterization of low molecular-weight gelator methyl-4,6-O-(p-nitrobenzylidene)-α-D-glucopyranoside hydrogels and water diffusion in their networks. Tetrahedron 65:9801–9806
[108] Chen Q, Lv Y, Zhang D, Zhang G, Liu C, Zhu D (2010) Cysteine and pH-Responsive Hydrogel Based on a Saccharide Derivative with an Aldehyde Group. Langmuir 26:3165–3168
[109] Allen DK, Tao BY (1999) Carbohydrate-alkyl ester derivatives as biosurfactants. J Surfact Deterg 2:383–390
[110] Gumel AM, Annuar MSM, Heidelberg T, Chisti Y (2011) Lipase mediated synthesis of sugar fatty acid esters. Process Biochemistry 46:2079–2090
[111] Neta NS, Teixeira JA, Rodrigues LR (2015) Sugar Ester Surfactants: Enzymatic Synthesis and Applications in Food Industry. Critical Reviews in Food Science and Nutrition 55:595–610
[112] Szűts A, Szabó-Révész P (2012) Sucrose esters as natural surfactants in drug delivery systems—A mini-review. International Journal of Pharmaceutics 433:1–9
[113] Plat T, Linhardt RJ (2001) Syntheses and applications of sucrose-based esters. J Surfact Deterg 4:415–421
[114] Baker IJA, Matthews B, Suares H, Krodkiewska I, Furlong DN, Grieser F, Drummond CI (2000) Sugar

fatty acid ester surfactants: Structure and ultimate aerobic biodegradability. J Surfact Deterg 3:1–11
[115] Drummond CJ, Fong C, Krodkiewska I, Boyd BJ, Baker IJA (2004) Sugar Fatty Acid Esters. In: Hubbard A (ed) Novel Surfactants: Preparation, Applications, and Biodegradability. Marcel Dekker, New York, pp 95-128
[116] Bromann R, König B, Fischer L (1999) Regioselective Synthesis of Sugar Esters without Catalyst Using α-Hydroxycarboxylic Acids. Synthetic Communications 29:951–957
[117] Boyère C, Broze G, Blecker C, Jérôme C, Debuigne A (2013) Monocatenary, branched, double-headed, and bolaform surface active carbohydrate esters via photochemical thiol-ene/-yne reactions. Carbohydrate Research 380:29–36
[118] Boyère C, Favrelle A, Broze G, Laurent P, Nott K, Paquot M, Blecker C, Jérôme C, Debuigne A (2011) Lipase catalysis and thiol-Michael addition: a relevant association for the synthesis of new surface-active carbohydrate esters. Carbohydrate Research 346:2121–2125
[119] Nandi S, Altenbach H-J, Jakob B, Lange K, Ihizane R, Schneider MP, Gün Ü, Mayer A (2012) Amphiphiles Based on D-Glucose: Efficient Low Molecular Weight Gelators. Org Lett 14:3826–3829
[120] Wang K, Jiang J, Liang X (2016) Design, synthesis and evaluation of novel glycosyl surfactant—lignocellulosic hydrolysate esters from shrub willow. Industrial Crops and Products 92:127–135
[121] Zief M (1950) Unsaturated Esters of Sucrose. J Am Chem Soc 72:1137–1140
[122] Hass HB, Snell FD, York WC, Osipow LI (1959) Process for producing sugar esters. US Patent 2893990
[123] Osipow L, Snell FD, York WC, Finchler A (1956) Methods of Preparation Fatty Acid Esters of Sucrose. Ind Eng Chem 48:1459–1462
[124] Nelen BAP, Bax L, Cooper JM (2015) Sucrose Esters. in: Norn V (ed) Emulsifiers in Food Technology, 2nd Edition. Wiley & Sons, Juelsminde, pp 147-180
[125] Marti-Mestres G (2000) Main surfactants used in the pharmaceutical field. In: Nielloud F (ed) Pharmaceutical Emulsions and Suspensions, 2nd Edition, Marcel Dekker, New York, pp 1–18
[126] Nakamura S, Nagahara H, Kawaguchi J (1999) Process for production of high-monoester sucrose higher fatty acid esters. European Patent EP0560081B1
[127] Wilson DC (1999) Continuous process for the synthesis of sucrose fatty acid esters. US Patent 5872245
[128] Parker KJ, James K, Hurford J (1977) Sucrose Ester Surfactants—A Solventless Process and the Products Thereof In: Sucrochemistry. American Chemical Society, pp 97–114
[129] Liu X, Gong L, Xin M, Liu J (1999) The synthesis of sucrose ester and selection of its catalyst. Journal of Molecular Catalysis A: Chemical 147:37–40
[130] Thévenet S, Wernicke A, Belniak S, Descotes G, Bouchu A, Queneau Y (1999) Esterification of unprotected sucrose with acid chlorides in aqueous medium: kinetic reactivity versus acyl- or alkyloxycarbonyl-group migrations. Carbohydrate Research 318:52–66
[131] Molinier V, Wisniewski K, Bouchu A, Fitremann J, Queneau DY (2003) Transesterification of Sucrose in Organic Medium: Study of Acyl Group Migrations. Journal of Carbohydrate Chemistry 22:657–669
[132] Molinier V, Kouwer PJJ, Fitremann J, Bouchu A, Mackenzie G, Queneau Y, Goodby JW (2006) Self-Organizing Properties of Monosubstituted Sucrose Fatty Acid Esters: The Effects of Chain Length and Unsaturation. Chem Eur J 12:3547–3557
[133] Molinier V, Kouwer PJJ, Fitremann J, Bouchu A, Mackenzie G, Queneau Y, Goodby JW (2007) Shape Dependence in the Formation of Condensed Phases Exhibited by Disubstituted Sucrose Esters. Chemistry - A European Journal 13:1763–1775
[134] Goodby JW, Gortz V, Cowling SJ, Mackenzie G, Martin P, Plusquellec D, Benvegnu T, Boullanger P, Lafont D, Queneau Y, Chambert S, Fitremann J (2007) Thermotropic liquid crystalline glycolipids. Chem Soc Rev 36:1971–2032
[135] Molinier V, Kouwer PHJ, Queneau Y, Fitremann J, Mackenzie G, Goodby JW (2003) A bilayer to monolayer phase transition in liquid crystal glycolipids. Chem Commun 2860–2861
[136] Muller A-S, Gagnaire J, Queneau Y, Karaoglanian M, Maitre J-P, Bouchu A (2002) Winsor behaviour of sucrose fatty acid esters: choice of the cosurfactant and effect of the surfactant composition. Colloids and Surfaces A: Physicochemical and Engineering Aspects 203:55–66
[137] Molinier V, Fenet B, Fitremann J, Bouchu A, Queneau Y (2006) Concentration measurements of sucrose and sugar surfactants solutions by using the 1H NMR ERETIC method. Carbohydrate Research 341:1890–1895

[138] Wernicke A, Belniak S, Thevenet S, Descotes G, Bouchu A, Queneau Y (1998) Synthesis of sucrose carbonates in aqueous medium. J Chem Soc, Perkin Trans 1 1179–1182
[139] Boyer A, Lingome CE, Condassamy O, Schappacher M, Moebs-Sanchez S, Queneau Y, Gadenne B, Alfos C, Cramail H (2013) Glycolipids as a source of polyols for the design of original linear and cross-linked polyurethanes. Polym Chem 4:296–306
[140] Cramail H, Boyer A, Lingome CE, Alfos C, Gadenne B, Cloutet E, Queneau Y, Moebs S (2014) Preparation of polyurethanes and polyesters from glycolipid type compounds US Patent 20140235814A1
[141] Ferrer M, Cruces MA, Plou FJ, Pastor E, Fuentes G, Bernabé M, Parra JL, Ballesteros A (2000) Chemical versus enzymatic catalysis for the regioselective synthesis of sucrose esters of fatty acids. In: Corma A, Melo FV, Mendioroz S, Fierro JLG (eds) Studies in Surface Science and Catalysis. Elsevier, Amsterdam, pp 509–514
[142] Potier P, Bouchu A, Descotes G, Queneau Y (2000) Proteinase N-catalysed transesterifications in DMSO–water and DMF–water: preparation of sucrose monomethacrylate. Tetrahedron Letters 41:3597–3600
[143] Potier P, Bouchu A, Gagnaire J, Queneau Y (2001) Proteinase N-catalysed regioselective esterification of sucrose and other mono- and disaccharides. Tetrahedron: Asymmetry 12:2409–2419
[144] Vemula PK, Li J, John G (2006) Enzyme Catalysis: Tool to Make and Break Amygdalin Hydrogelators from Renewable Resources: A Delivery Model for Hydrophobic Drugs. J Am Chem Soc 128:8932–8938
[145] Xu Y, Wang D, Mu XQ, Ni YQ (2003) Efficient esterification of sorbitan oleate by lipase in a solvent-free system. J Amer Oil Chem Soc 80:647–651
[146] Sarney DB, Barnard MJ, Virto M, Vulfson EN (1997) Enzymatic synthesis of sorbitan esters using a low-boiling-point azeotrope as a reaction solvent. Biotechnol Bioeng 54:351–356
[147] Lavergne A, Moity L, Molinier V, Aubry J-M (2013) Volatile short-chain amphiphiles derived from isosorbide: Hydrotropic properties of esters vs. ethers. RSC Adv 3:5997–6007
[148] Moreau B, Lognay GC, Blecker C, Brohée J-C, Chéry F, Rollin P, Paquot M, Marlier M (2004) Synthesis of novel D-glucuronic acid fatty esters using Candida antarctica lipase in tert-butanol. Biotechnology Letters 26:419–424
[149] Moreau B, Lognay G, Blecker C, Destain J, Gerbaux P, Chéry F, Rollin P, Paquot M, Marlier M (2007) Chromatographic, Spectrometric and NMR Characterization of a New Set of Glucuronic Acid Esters Synthesized by Lipase. Biotechnol Agron Soc Environ 11:9–17
[150] Blecker C, Piccicuto S, Lognay G, Deroanne C, Marlier M, Paquot M (2002) Enzymatically Prepared n-Alkyl Esters of Glucuronic Acid: The Effect of Hydrophobic Chain Length on Surface Properties. Journal of Colloid and Interface Science 247:424–428
[151] Lu H, Drelich A, Omri M, Pezron I, Wadouachi A, Pourceau G (2016) Catalytic Synthesis of a New Series of Alkyl Uronates and Evaluation of Their Physicochemical Properties. Molecules 21:1301
[152] Richel A, Nicks F, Laurent P, Wathelet B, Wathelet J-P, Paquot M (2012) Efficient microwave-promoted synthesis of glucuronic and galacturonic acid derivatives using sulfuric acid impregnated on silica. Green Chemistry Letters and Reviews 5:179–186
[153] Xavier NM, Rauter AP, Queneau Y (2010) Carbohydrate-Based Lactones: Synthesis and Applications. In: Rauter AP, Vogel P, Queneau Y (eds) Carbohydrates in Sustainable Development II. Springer Berlin Heidelberg, Heidelberg, pp 19–62
[154] Allam A, Behr J-B, Dupont L, Nardello-Rataj V, Plantier-Royon R (2010) Synthesis, physico-chemical properties and complexing abilities of new amphiphilic ligands from D-galacturonic acid. Carbohydrate Research 345:731–739
[155] Auvray X, Labulle B, Petipas C, Bertho J-N, Benvegnu T, Plusquellec D (1997) Thermotropic liquid-crystalline properties of some novel hexuronicacid derivatives bearing a single or two alkyl chains. J Mater Chem 7:1373–1376
[156] Bertho J-N, Ferrières V, Plusquellec D (1995) A new synthesis of D-glycosiduronates from unprotected D-uronic acids. J Chem Soc, Chem Commun 0:1391–1393
[157] Razafindralambo H, Blecker C, Mezdour S, Deroanne C, Crowet J-M, Brasseur R, Lins L, Paquot M (2009) Impacts of the Carbonyl Group Location of Ester Bond on Interfacial Properties of Sugar-Based Surfactants: Experimental and Computational Evidences. J Phys Chem B 113:8872–8877
[158] Gaertner VR (1961) Sucrose ether- and ester-linked surfactants. J Am Oil Chem Soc 38:410–418
[159] Raaijmakers HWC, Arnouts EG, Zwanenburg B, Chittenden GJF, van Doren HA (1995) The synthesis and

properties of some mesogenic 3–O-alkyl derivatives of D-glucitol and D-mannitol. Recl Trav Chim Pays-Bas 114:301–310
[160] Goodby JW, Watson MJ, Mackenzie G, Kelly SM, Bachir S, Bault P, Gode P, Goethals G, Martin P, Ronco G, Villa P (1998) The dependence of mesomorphic behaviour on the extent of hydrogen-bonding in sugar derived polyols. Liquid Crystals 25:139–147
[161] Houdier S, Pérez S (1995) Assessing Sucrose Hydroxyl Acidities Through Semiempirical Calculations. Journal of Carbohydrate Chemistry 14:1117–1132
[162] Lichtenthaler FW, Immel S, Pokinskyj P (1995) Molecular modeling of saccharides, 8. Selective 2-O-benzylation of sucrose: A facile entry to its 2-deoxy- and 2-keto-derivatives and to sucrosamine. European Journal of Organic Chemistry 1995:1939–1947
[163] Hamann CH, Fischer S, Polligkeit H, Wolf P (1993) The Alkylation of Mono- and Disaccharides Via an Initialising Electrochemical Step. Journal of Carbohydrate Chemistry 12:173–190
[164] Chauvin C, Baczko K, Plusquellec D (1993) New highly regioselective reactions of unprotected sucrose. Synthesis of 2-O-acylsucroses and 2-O-(N-alkylcarbamoyl)sucroses. J Org Chem 58:2291–2295
[165] Gérard E, Götz H, Pellegrini S, Castanet Y, Mortreux A (1998) Epoxide–tertiary amine combinations as efficient catalysts for methanol carbonylation into methyl formate in the presence of carbon dioxide. Applied Catalysis A: General 170:297–306
[166] Gagnaire J, Toraman G, Descotes G, Bouchu A, Queneau Y (1999) Synthesis in water of amphiphilic sucrose hydroxyalkyl ethers. Tetrahedron Letters 40:2757–2760
[167] Gagnaire J, Cornet A, Bouchu A, Descotes G, Queneau Y (2000) Study of the competition between homogeneous and interfacial reactions during the synthesis of surfactant sucrose hydroxyalkyl ethers in water. Colloids and Surfaces A: Physicochemical and Engineering Aspects 172:125–138
[168] Queneau Y, Gagnaire J, West JJ, Mackenzie G, Goodby JW (2001) The effect of molecular shape on the liquid crystal properties of the mono-O-(2-hydroxydodecyl)sucroses. J Mater Chem 11:2839–2844
[169] Singh MK, Xu R, Moebs S, Kumar A, Queneau Y, Cowling SJ, Goodby JW (2013) Hydrophobic and Hydrophilic Balance and Its Effect on Mesophase Behaviour in Hydroxyalkyl Ethers of Methyl Glucopyranoside. Chem Eur J 19:5041–5049
[170] Dalpozzo R, Nardi M, Oliverio M, Paonessa R, Procopio A (2009) Erbium(III) Triflate is a Highly Efficient Catalyst for the Synthesis of β-Alkoxy Alcohols, 1,2-Diols and β-Hydroxy Sulfides by Ring Opening of Epoxides. Synthesis 2009:3433–3438
[171] Likhar PR, Kumar MP, Bandyopadhyay AK (2001) Ytterbium Trifluoromethanesulfonate $Yb(OTf)_3$: An Efficient, Reusable Catalyst for Highly Selective Formation of β-Alkoxy Alcohols via Ring-Opening of 1,2-Epoxides with Alcohols. Synlett 2001:0836–0838
[172] Gruber B, Weese KJ, Mueller H, Hill K, Behr A, Tucker JR (1993) Octyl ethers and octadienyl ethers. US Patent 5236909
[173] Hill K, Gruber B, Weese KJ (1994) Palladium catalyzed telomerization of butadiene with sucrose: A highly efficient approach to novel sucrose ethers. Tetrahedron Letters 35:4541–4542
[174] Pennequin I, Mortreux A, Petit F, Mentech J, Thiriet B (1994) telomerization of conjugated dienes with polyols such as nonreducing sugars. French Patent FR 2693188 A1
[175] Pennequin I, Meyer J, Suisse I, Mortreux A (1997) A further application of TPPTS in catalysis: Efficient sucrose-butadiene telomerization using palladium catalysts in water. Journal of Molecular Catalysis A: Chemical 120:139–142
[176] Desvergnes-Breuil V, Pinel C, Gallezot P (2001) Green approach to substituted carbohydrates: telomerisation of butadiene with sucrose. Green Chem 3:175–177
[177] Lai J, Bigot S, Sauthier M, Molinier V, Suisse I, Castanet Y, Aubry J-M, Mortreux A (2011) Telomerisation of 1,3-Butadiene with 1,4:3,6-Dianhydrohexitols: An Atom-Economic and Selective Synthesis of Amphiphilic Monoethers from Agro-Based Diols. ChemSusChem 4:1104–1111
[178] Donzé C, Pinel C, Gallezot P, Taylor PL (2002) Palladium-Catalyzed Telomerization of Butadiene with Starch. Adv Synth Catal 344:906–910
[179] Mesnager J, Quettier C, Lambin A, Rataboul F, Pinel C (2009) Telomerization of Butadiene with Starch under Mild Conditions. ChemSusChem 2:1125–1129
[180] Mesnager J, Quettier C, Lambin A, Rataboul F, Perrard A, Pinel C (2010) Telomerization of butadiene with

starch in water: role of the surfactants. Green Chem 12:475–482
[181] Faßbach TA, Sommer FO, Behr A, Romanski S, Leinweber D, Vorholt AJ (2017) Non-ionic surfactants from renewables - amphiphilic ligands in biphasic reactions. Catal Sci Technol 7:1650–1653
[182] Mesnager J, Lambin A, Quettier C, Rataboul F, Pinel C (2010) Efficient Telomerization of Butadiene with Starch in Water: The Role of the Surfactant. Top Catal 53:1282–1284
[183] Bouquillon S, Muzart J, Pinel C, Rataboul F (2010) Palladium-Catalyzed Telomerization of Butadiene with Polyols: From Mono to Polysaccharides. In: Carbohydrates in Sustainable Development II. Springer, Berlin, Heidelberg, pp 93–119
[184] Queneau Y, Pinel C, Scherrmann M-C (2011) Some chemical transformations of carbohydrates in aqueous medium. Comptes Rendus Chimie 14:688–699
[185] Pito DS, Castanheiro JE (2013) Reactions of Sucrose in the Presence of Solid Catalysts. In: Magazù S (ed) Sucrose: Properties, Biosynthesis and Health Implications, Nova Science, New York
[186] Sauthier M, Mortreux A, Suisse I (2014) From conventional to greener catalytic approaches for carbohydrates etherification. In: Pilar Rauter A, Lindhorst T, Queneau Y (eds) Carbohydrate Chemistry: Volume 40. The Royal Society of Chemistry, Cambridge, pp 73–98
[187] Shi Y, Dayoub W, Favre-Réguillon A, Chen G-R, Lemaire M (2009) Straightforward selective synthesis of linear 1-O-alkyl glycerol and di-glycerol monoethers. Tetrahedron Letters 50:6891–6893
[188] Shi Y, Dayoub W, Chen G-R, Lemaire M (2010) Selective synthesis of 1-O-alkyl glycerol and diglycerol ethers by reductive alkylation of alcohols. Green Chem 12:2189–2195
[189] Moity L, Shi Y, Molinier V, Dayoub W, Lemaire M, Aubry J-M (2013) Hydrotropic Properties of Alkyl and Aryl Glycerol Monoethers. J Phys Chem B 117:9262–9272
[190] Sutter M, Silva ED, Duguet N, Raoul Y, Métay E, Lemaire M (2015) Glycerol Ether Synthesis: A Bench Test for Green Chemistry Concepts and Technologies. Chem Rev 115:8609–8651
[191] Gozlan C, Deruer E, Duclos M-C, Molinier V, Aubry J-M, Redl A, Duguet N, Lemaire M (2016) Preparation of amphiphilic sorbitan monoethers through hydrogenolysis of sorbitan acetals and evaluation as bio-based surfactants. Green Chem 18:1994–2004
[192] Eellis GP, Honeyman J (1955) Glycosylamines. In: Wolfrom ML (ed) Advances in Carbohydrate Chemistry. Elsevier, New York, pp 95–168
[193] Pestman JM (1998) Carbohydrate-derived surfactants containing an N-Acylated amine functionality: fundamental aspects and practical applications. University of Groningen, Groningen
[194] Zhu Y-P, Rosen MJ, Vinson PK, Morrall SW (1999) Surface properties of N-alkanoyl-N-methyl glucamines and related materials. J Surfact Deterg 2:357–362
[195] Hildreth JEK (1982) N-D-Gluco-N-methylalkanamide compounds, a new class of non-ionic detergents for membrane biochemistry. Biochemical Journal 207:363–366
[196] Liberek B, Melcer A, Osuch A, Wakieć R, Milewski S, Wiśniewski A (2005) N-Alkyl derivatives of 2-amino-2-deoxy-D-glucose. Carbohydrate research 340:1876–84
[197] Vega-Pérez JM, Espartero JL, Alcudia F (1993) Oxazolidines From Sugars. III. A New Method for N-Alkyl and N,N-Dialkyl-D-Glucosamine Derivatives. Journal of Carbohydrate Chemistry 12:477–486
[198] Humphrey AJ, Fremann C, Critchley P, Malykh Y, Schauer R, Bugg TDH (2002) Biological Properties of N-Acyl and N-Haloacetyl Neuraminic Acids: Processing by Enzymes of Sialic Acid Metabolism, and Interaction with Influenza Virus. Bioorganic & Medicinal Chemistry 10:3175–3185
[199] Inouye Y, Onodera K, Kitaoka S, Hirano S (1956) Some Fatty Acid Derivatives of D-Glucosamine. J Am Chem Soc 78:4722–4724
[200] El Ghoul M, Latge P, Rico I, Lattes A, Godefroy L (1996) N-alkyl, n-acetylglycosylamines. US Patent 5539091A
[201] Lockhoff O, Stadler P (1998) Syntheses of glycosylamides as glycolipid analogs. Carbohydrate Research 314:13–24
[202] Neto V, Voisin A, Héroguez V, Grelier S, Coma V (2012) Influence of the Variation of the Alkyl Chain Length of N-Alkyl-β-D-glycosylamine Derivatives on Antifungal Properties. J Agric Food Chem 60:10516–10522
[203] Lubineau A, Augé J, Drouillat B (1995) Improved synthesis of glycosylamines and a straightforward preparation of N-acylglycosylamines as carbohydrate-based detergents. Carbohydrate Research 266:211–219

[204] Bogaert PMP, Langezaal WPC, Van Haveren J, Slaghek TM, van der Meeren P (1999) Non-reductive coupling of branched amino fatty acid esters with mono and disaccharides: synthesis of a new class of alkyl glycosylamines. Fett/Lipid 101:64–70
[205] Au V, Harichian B, Hung A, Vermeer R (1999) Compositions comprising glycosylamide surfactants. US Patent 5872111A
[206] Bhattacharya S, Acharya SNG (1999) Pronounced Hydrogel Formation by the Self-Assembled Aggregates of N-Alkyl Disaccharide Amphiphiles. Chem Mater 11:3504–3511
[207] Epoune Lingome C, Pourceau G, Gobert-Deveaux V, Wadouachi A (2014) Efficient synthesis of glycosylamines in solventless conditions promoted by mechanical milling. RSC Advances 4:36350–36356
[208] Latge P, Rico I, Garelli R, Lattes A (1991) Synthesis of Long Chain N-Alkyllactylahines from Unprotected Lactose a New Series of Non-Ionic Surfactants. Journal of Dispersion Science and Technology 12:227–237
[209] Laughlin RG, Fu Y-C, Wireko FC, Scheibel JJ, Munyon RL (2004) N-Alkanoyl-N-Alkyl-1-Glycamines in: Novel Surfactants: Preparation, Applications, and Biodegradability. Marcel Dekker, New York, pp 1-34
[210] Maugard T, Remaud-Simeon M, Petre D, Monsan P (1998) Enzymatic amidification for the synthesis of biodegradable surfactants: Synthesis of N-acylated hydroxylated amines. Journal of Molecular Catalysis B: Enzymatic 5:13–17
[211] Wang ZD, Sheikh SO, Cox S, Zhang Y, Massey K (2007) Direct Preparation of N-Glycosidic Bond-Linked Nonionic Carbohydrate-Based Surfactant (NICBS) via Ritter Reaction. Eur J Org Chem 2007:2243–2247
[212] Maugard T, Remaud-Simeon M, Petre D, Monsan P (1997) Enzymatic synthesis of glycamide surfactants by amidification reaction. Tetrahedron 53:5185–5194
[213] Gaber Y, Tornvall U, Orellana-Coca C, Ali Amin M, Hatti-Kaul R (2010) Enzymatic synthesis of N-alkanoyl-N-methylglucamide surfactants: solvent-free production and environmental assessment. Green Chem 12:1817–1825
[214] Guderjahn L, Kunz M, Schuettenhelm M (1994) New carbohydrate surfactants derived from Palatinose. Tenside Surfactants Detergents 31:146–150
[215] Klein J, Behrens W, Kunz M (1989) Isomaltamines and their N-acyl derivatives, methods for their production, and their uses as surfactants and monomers. US Patent 4843154
[216] Kunz MD, Guderjahn L, Schüttenhelm M, Kowalczyk JD (1997) N-alkylisomaltamines, their preparation from isomaltulose and their application as surfactants. European Patent EP0618216B1
[217] Jäger M, Minnaard AJ (2015) Regioselective modification of unprotected glycosides. Chem Commun 52:656–664
[218] Pietsch M, Walter M, Buchholz K (1994) Regioselective synthesis of new sucrose derivatives via 3-ketosucrose. Carbohydrate Research 254:183–194
[219] Fieser M, Fieser LF, Toromanoff E, Hirata Y, Heymann H, Tefft M, Bhattacharya S (1956) Synthetic Emulsifying Agents. J Am Chem Soc 78:2825–2832
[220] Pilakowska-Pietras D, Lunkenheimer K, Piasecki A (2004) Synthesis of novel N,N-di-n-alkylaldonamides and properties of their surface chemically pure adsorption layers at the air/water interface. Journal of Colloid and Interface Science 271:192–200
[221] Laurent P, Razafindralambo H, Wathelet B, Blecker C, Wathelet J-P, Paquot M (2011) Synthesis and Surface-Active Properties of Uronic Amide Derivatives, Surfactants from Renewable Organic Raw Materials. J Surfact Deterg 14:51–63
[222] Berchel M, Lemiègre L, Jeftić J, Benvegnu T (2008) Synthesis of unsymmetrical spin-labelled bolaamphiphiles. Tetrahedron Letters 49:4690–4692
[223] Berchel M, Lemiègre L, Trépout S, Lambert O, Jeftić J, Benvegnu T (2008) Synthesis of unsymmetrical saturated or diacetylenic cationic bolaamphiphiles. Tetrahedron Letters 49:7419–7422
[224] Guilbot J, Benvegnu T, Legros N, Plusquellec D, Dedieu J-C, Gulik A (2001) Efficient Synthesis of Unsymmetrical Bolaamphiphiles for Spontaneous Formation of Vesicles and Disks with a Transmembrane Organization. Langmuir 17:613–618
[225] Bosco M, Rat S, Kovensky J, Wadouachi A (2010) Fast synthesis of uronamides by non-catalyzed opening of glucopyranurono-6,1-lactone with amines, amino acids, and aminosugars. Tetrahedron Letters 51:2553–2556
[226] Raaijmakers HWC, Zwanenburg B, Chittenden GJF (1994) The synthesis and properties of some long-chain alkyl-D-glucofuranosidurono-6,3-lactones, D-glucofuranosides and derivatives thereof. Recl Trav Chim

Pays-Bas 113:79–87
[227] Pierre R, Chambert S, Alirachedi F, Danel M, Trombotto S, Doutheau A, Queneau Y (2008) Carboxymethyl glucosides and carboxymethyl glucoside lactones: A detailed study of their preparation by oxidative degradation of disaccharides. Comptes Rendus Chimie 11:61–66
[228] Trombotto S, Bouchu A, Descotes G, Queneau Y (2000) Hydrogen peroxide oxidation of palatinose and trehalulose: direct preparation of carboxymethyl α-D-glucopyranoside. Tetrahedron Letters 41:8273–8277
[229] Listkowski A, Ing P, Cheaib R, Chambert S, Doutheau A, Queneau Y (2007) Carboxymethylglycoside lactones (CMGLs): structural variations on the carbohydrate moiety. Tetrahedron: Asymmetry 18:2201–2210
[230] Mehltretter CL, Mellies RL, Rankin JC (1954) Substituted gluconamides. US Patents 2670345A
[231] Au V, Vermeer R, Harichian B (1997) Sulfated polyhydroxy compounds as anionic surfactants and a process for their manufacture. US patent US5686603A
[232] Arévalo MJ, Avalos M, Babiano R, Cabanillas A, Cintas P, Jiménez JL, Palacios JC (2000) Optically active sugar thioamides from δ-gluconolactone. Tetrahedron: Asymmetry 11:1985–1995
[233] Plusquellec D, Lefeuvre M (1987) Sugar chemistry without protecting groups: A regioselective addition of the primary hydroxyl of monosaccharides to alkylisocyanates. Tetrahedron Letters 28:4165–4168
[234] Plusquellec D, Roulleau F, Brown E (1984) Chimie des sucres sans groupements protecteurs: synthèse de carbamates, d'urées et de thiourées en position 1 du lactose. Tetrahedron Letters 25:1901–1904
[235] Plusquellec D, Chevalier G, Talibart R, Wro´blewski H (1989) Synthesis and characterization of 6-O-(N-heptylcarbamoyl)-methyl-α-D-glucopyranoside, a new surfactant for membrane studies. Analytical Biochemistry 179:145–153
[236] Prata C, Mora N, Lacombe J-M, Maurizis JC, Pucci B (1997) Stereoselective synthesis of glycosyl carbamates as new surfactants and glycosyl donors. Tetrahedron Letters 38:8859–8862
[237] Christian D, Fitremann J, Bouchu A, Queneau Y (2004) Preparation of amphiphilic sucrose carbamates by reaction with alkyl isocyanates in water–alcohol mixtures. Tetrahedron Letters 45:583–586
[238] Rico-Lattes I, Blanzat M, Franceschi-Messant S, Perez É, Lattes A (2005) Catanionic sugar derived surfactants, polymers and dendrimers: from molecules to targeted self-organized systems. Comptes Rendus Chimie 8:807–814
[239] Rico-Lattes I, Lattes A (1997) Synthesis of new sugar-based surfactants having biological applications: key role of their self-association. Colloids and Surfaces A: Physicochemical and Engineering Aspects 123–124:37–48
[240] Ewan HS, Muli CS, Touba S, Bellinghiere AT, Veitschegger AM, Smith TB, Pistel WL, Jewell WT, Rowe RK, Hagen JP, Palandoken H (2014) Synthesis of sugar oxime ether surfactants. Tetrahedron Letters 55:4962–4965
[241] Padwa A (1984) 1,3-dipolar cycloaddition chemistry. Wiley, New York
[242] Meldal M, Tornøe CW (2008) Cu-Catalyzed Azide−Alkyne Cycloaddition. Chem Rev 108:2952–3015
[243] Lim D, Brimble MA, Kowalczyk R, Watson AJA, Fairbanks AJ (2014) Protecting-Group-Free One-Pot Synthesis of Glycoconjugates Directly from Reducing Sugars. Angew Chem Int Ed 53:11907–11911
[244] Aich U, Loganathan D (2005) Synthesis of N-(β-Glycopyrano-syl)azidoacetamides. Journal of Carbohydrate Chemistry 24:1–12
[245] Paul KJV, Loganathan D (2008) Synthesis of novel glycolipids derived from glycopyranosyl azides and N-(β-glycopyranosyl)azidoacetamides. Tetrahedron Letters 49:6356–6359
[246] Schuster T, Schellenberger S, Friedrich R, Klapper M, Müllen K (2013) Branched fluorinated amphiphiles based on carbohydrates. Journal of Fluorine Chemistry 154:30–36
[247] Latxague L, Ramin MA, Appavoo A, Berto P, Maisani M, Ehret C, Chassande O, Barthélémy P (2015) Control of Stem-Cell Behavior by Fine Tuning the Supramolecular Assemblies of Low-Molecular-Weight Gelators. Angew Chem Int Ed 54:4517–4521
[248] Mangunuru HPR, Yerabolu JR, Liu D, Wang G (2015) Synthesis of a series of glucosyl triazole derivatives and their self-assembling properties. Tetrahedron Letters 56:82–85
[249] Sani FA, Heidelberg T, Hashim R, Farhanullah (2012) Alkyl triazole glycosides (ATGs)—A new class of bio-related surfactants. Colloids and Surfaces B: Biointerfaces 97:196–200
[250] Schmid W, Whitesides GM (1991) Carbon-carbon bond formation in aqueous ethanol: diastereoselective transformation of unprotected carbohydrates to higher carbon sugars using allyl bromide and tin metal. J Am

Chem Soc 113:6674–6675
[251] Chan T-H, Li C-J (1992) A concise chemical synthesis of (+)-3-deoxy-D-glycero-D-galacto-nonulosonic acid (KDN). J Chem Soc, Chem Commun 0:747–748
[252] Lalitha K, Muthusamy K, Prasad YS, Vemula PK, Nagarajan S (2015) Recent developments in β-C-glycosides: synthesis and applications. Carbohydrate Research 402:158–171
[253] Román Galán E, Galbis Pérez JA, Arévalo Arévalo MA (1983) New C-nucleoside analogs by dehydration of 1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(D-galacto-pentitol-1-yl)-indol-4-one. Carbohydrate Research 116:255–262
[254] Gonzalez MA, Jimenez Requejo JL, Palacios Albarran JC, Gabis Perez JA (1986) Facile preparation of C-glycosylbarbiturates and C-glycosylbarbituric acids. Carbohydrate Research 158:53–66
[255] Wulff G, Clarkson G (1994) On the synthesis of C-glycosyl compounds containing double bonds without the use of protecting groups. Carbohydrate Research 257:81–95
[256] Kozikowski AP, Lin GQ, Springer JP (1987) An approach to bi-tetrahydrofurans from glucose and a correction of the literature. Tetrahedron Letters 28:2211–2214
[257] Rodrigues F, Canac Y, Lubineau A (2000) A convenient, one-step, synthesis of β-C-glycosidic ketones in aqueous media. Chem Commun 0:2049–2050
[258] Philippe M, Semeria D (2002) Novel c-glycoside derivatives and use thereof. WIPO Patent WO/2002/051803A2
[259] Hersant Y, Abou-Jneid R, Canac Y, Lubineau A, Philippe M, Semeria D, Radisson X, Scherrmann M-C (2004) One-step synthesis of β-C-glycolipid derivatives from unprotected sugars. Carbohydrate Research 339:741–745
[260] Foley PM, Phimphachanh A, Beach ES, Zimmerman JB, Anastas PT (2011) Linear and cyclic C-glycosides as surfactants. Green Chem 13:321–325
[261] Ranoux A, Lemiègre L, Benoit M, Guégan J-P, Benvegnu T (2010) Horner-Wadsworth-Emmons Reaction of Unprotected Sugars in Water or in the Absence of Any Solvent: One-Step Access to *C*-Glycoside Amphiphiles. European Journal of Organic Chemistry 2010:1314–1323
[262] Ranoux A, Lemiegre L, Benvegnu T (2010) Synthesis and evaluation of *C*-glycosides as hydrotropes and solubilizing agents. Science China Chemistry 53:1957–1962
[263] Werpy T, Petersen G (2004) Top Value Added Chemicals from Biomass: Volume I -- Results of Screening for Potential Candidates from Sugars and Synthesis Gas. National Renewable Energy Lab., Golden, CO (US)
[264] Bozell JJ, Petersen GR (2010) Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. Green Chem 12:539–554
[265] Rosatella AA, Simeonov SP, Frade RFM, Afonso CAM (2011) 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. Green Chem 13:754–793
[266] McElhanon JR, Zifer T, Kline SR, Wheeler DR, Loy DA, Jamison GM, Long TM, Rahimian K, Simmons BA (2005) Thermally Cleavable Surfactants Based on Furan−Maleimide Diels−Alder Adducts. Langmuir 21:3259–3266
[267] Stensrud K, Wicklund L (2016) Synthesis of non-ionic surfactants from 5-hydroxymethyl-2-furfural, furan-2,5-dimethanol and bis-2,5-dihydroxymethyltetrahydrofurans. WIPO Patent WO2016028845A1.
[268] Park DS, Joseph KE, Koehle M, Krumm C, Ren L, Damen JN, Shete MH, Lee HS, Zuo X, Lee B, Fan W, Vlachos DG, Lobo RF, Tsapatsis M, Dauenhauer PJ (2016) Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans. ACS Cent Sci 2:820–824
[269] Hanemann T, Schumacher E, Haase W, Lichtenthaler FW (1997) Some novel disaccharide-derived liquid crystals. Liquid Crystals 22:47–50
[270] Lichtenthaler FW, Martin D, Weber T, Schiweck H (1993) Studies on Ketoses, 7 – 5-(α-D-Glucosyloxymethyl)furfural: Preparation from Isomaltulose and Exploration of Its Ensuing Chemistry. European Journal of Organic Chemistry 1993:967–974
[271] Müller C, Diehl V, Lichtenthaler FW (1998) Building blocks from sugars. Part 23. Hydrophilic 3-pyridinols from fructose and isomaltulose. Tetrahedron 54:10703–10712
[272] Tan J-N, Ahmar M, Queneaua Y (2014) Isomaltulose Oxidation and Dehydration Products as Starting Materials Towards Fine Chemicals. Current Organic Chemistry 18:1768–1787
[273] Tan J-N, Ahmar M, Queneau Y (2015) Glucosyloxymethylfurfural (GMF): a creative renewable scaffold

towards bioinspired architectures. Pure and Applied Chemistry 87:827–839
[274] Tan J-N, Ahmar M, Queneau Y (2013) HMF derivatives as platform molecules: aqueous Baylis–Hillman reaction of glucosyloxymethyl-furfural towards new biobased acrylates. RSC Adv 3:17649–17653