Carbohydrate-Derived Surfactants

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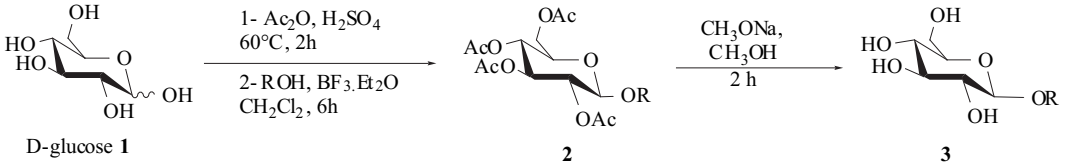
Abstract: The constant need for products obtained from natural raw materials instead of non-renewable petroleum feedstocks has led to a lot of effort on developing new "natural" surfactants. Most important among these are surfactants derived from carbohydrates and plant oils such as coconut or palm kernel. These compounds find applications in cosmetics, food manufacture, biology, etc, and some of them are studied for their liquid crystalline properties.

INTRODUCTION

Surfactants are amphiphilic molecules which are widely used in many industries. Natural surfactants are abundant in both plants and animals in small quantities. The cost of the isolation of these compounds led to the development of cheaper synthetic surfactants, mainly derived from petroleum. The increasing need for products less toxic and highly biodegradable led to numerous studies of new sugar-based surfactants, also considered "natural surfactants" [1], as they can occur in nature [2,3] or may be prepared from natural raw materials [4,5]. These compounds possess a carbohydrate hydrophilic part, which can be a mono- or oligosaccharide, and a hydrophobic tail, usually derived from a fatty acid. The two moieties can be directly linked *via* a functional group (ester, ether, hydrazine, amino group, etc) or separated by a spacer (gemini surfactants). Bola-amphiphile sugar surfactants are composed of two hydrophilic heads, linked by an hydrophobic spacer.



D-glucose **1** **2** **3**

Scheme 1.

Sugar surfactants are of great interest because they are biodegradable and are not noxious for the environment [5,6]. They can be used in several areas, such as food industry [7,8] (they have good functional properties such as emulsion stabilization, foaming, etc), biology [9] (extraction and purification of membranes proteins) [10,11], molecular recognition in glycobiology [12] or immunology [13] and detergents.

An important property of surfactants is the formation of aggregates, when they are dissolved in water at a concentration which exceeds the critical micellar concentration (CMC). These structures are known as micelles, in which the polar head groups are in contact with water, and the nonpolar hydrocarbon tails are inside the micelle [14].

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MONOMERIC SURFACTANTS

In this review, we are considering as monomeric surfactants, amphiphilic compounds obtained from one monosaccharide (glucose, galactose) or one disaccharide (saccharose, lactose, maltose).

ETHERS

O-alkyl Glycosides

Alkyl glycosides are a class of nonionic surfactants which have been described for the first time by Fisher in 1893, who prepared β-hexadecyl-D-glycoside [15]. These compounds have been on the market for almost 30 years, and their preparation and properties have been well described in the literature [16-23]. They are usually produced from D-glucose **1** and fatty alcohols, in the presence of an acidic catalyst [24-27] in a glycosylation reaction (Scheme **1**).

Goethals and its group prepared glucidoamphiphiles, in which the glucidic moiety and the hydrophobic alkyl chain were separated by a spacer arm [27]. Three series were prepared, derived from D-glucose, D-galactose and xylitol. 3-*O*-(3-*O*-Alkyl-glycer-1-yl)-D-glucopyranoses **7a-d**, in which the alkyl chain and the glucose moiety were separated by the glyceryl spacer arm, were synthetized from the allyl derivative **4** (Scheme **2**). After epoxidation and reaction with an alcohol and potassium hydroxide, ethers **6a-d** were obtained as diastereoisomeric mixtures. Deprotection with trifluoroacetic acid gave the products **7a-d** as anomeric mixtures (α/β 2:3).

6-*O*-[2-*O*-n-dodecylpoly-(α-propyleneglycol)-diethylen-glycol]- α-D-galactopyranose **12** was prepared as described in Scheme **3**. Protected galactose **8** was reacted with the diethylene tosylate **9** in the presence of potassium hydroxide. The activated compound **10** was then condensed with alcohol **11**. Compound **12** was obtained after deprotection in trifluoroacetic acid.

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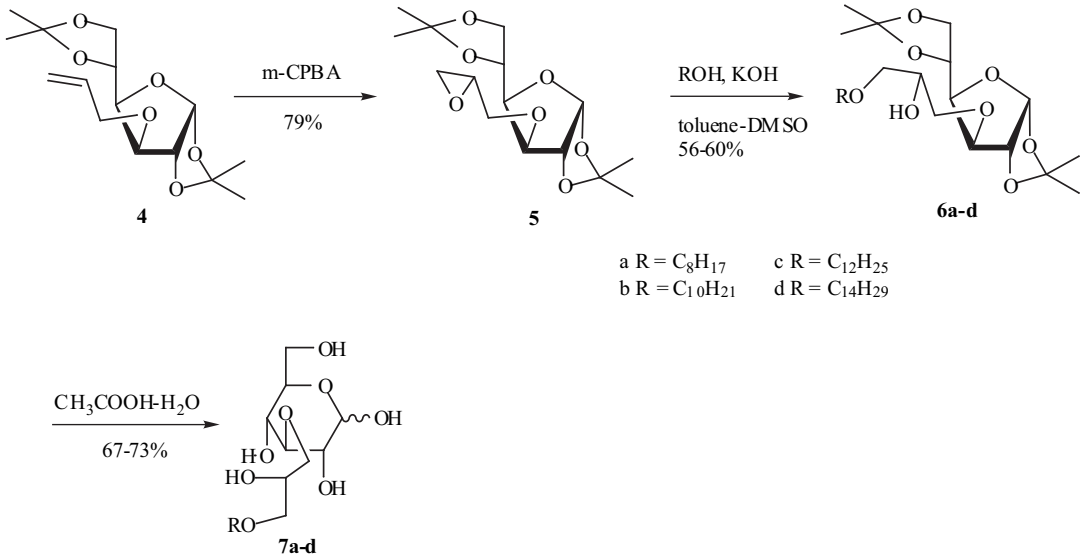
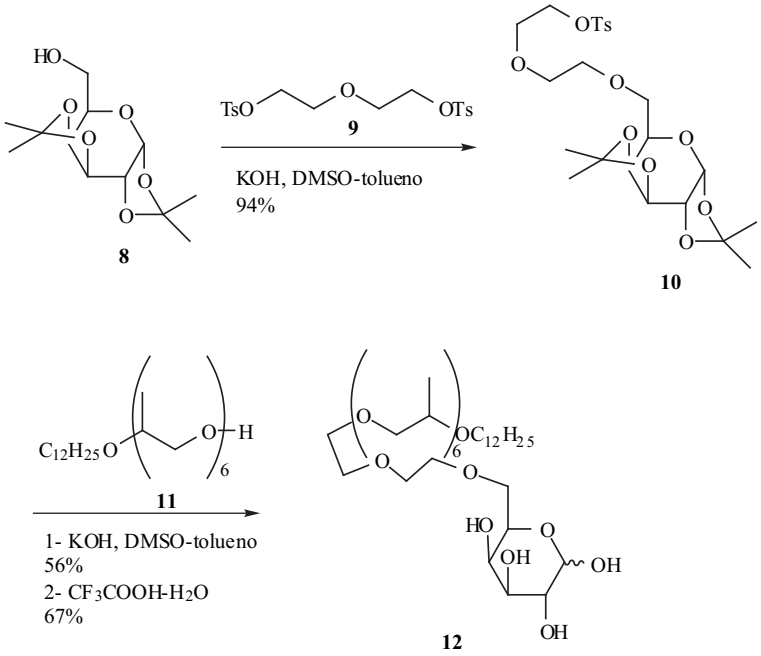


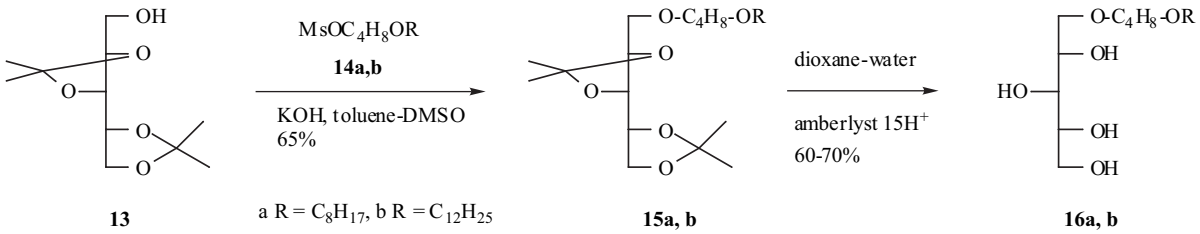
Scheme 2.



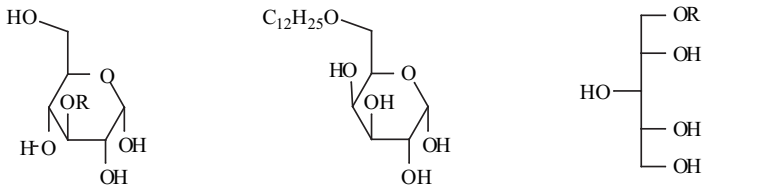
Scheme 3.

1-*O*-(4-*O*-alkylbutyleneglycol-1-yl)-D,L-xylitols **16a,b** in which the alkyl chain and the xylitol moiety were separated by the butyleneglycol spacer arm, are described in Scheme **4**. Condensation of ethers **14a,b** with protected xylitol **13** gave the correspondent ethers **15a,b**, which were deprotected with acidic amberlyst resin.

The CMC of the compounds containing a spacer arm was measured (Table **1**) and compared to that of 3-*O*-alkyl-D-glucopyranose **17a-d**, 6-*O*-alkyl-D-galactopyranose **18** and 1-*O*-alkyl-D,L-xylitols **19a,b** (Fig. **1**) [28,29]. The results of physico-chemical studies showed that the spacer arm influences the solubility and the aggregate organization of the compounds, such as liquid crystals and micelles.



Scheme 4.



17a-d **18** **19a,b**

a R = C_8H_{17} c R = $C_{12}H_{25}$
b R = $C_{10}H_{21}$ d R = $C_{14}H_{29}$

a R = C_8H_{17}, b R = $C_{12}H_{25}$

Fig. (1).

Table 1.

Compound	CMC (mM)
7a	1.04
7b	0.12
7c	0.09
7d	0.05
12	0.05
16a	0.28
16b	0.03
17a	1.20
17b	0.78
17c	0.23
17d	0.18
18	no micelle
19a	6.7
19b	no micelle

The Fisher's method requires protection and deprotection steps, limiting its use for industrial purposes. This problem is being solved by the use of new synthetic methods.

Gagnaire and collaborators prepared amphiphilic hydroxyalkylsucrose ethers from unprotected sucrose in water [30] (Scheme **5**). Among the monosubstituted products, the 2- and 1'-regioisomers accounted for 60% of the mixture. Side reactions could be reduced by the addition of an ammonium surfactant such as CTAB (cetyl trimethylammonium bromide).

Another method is the enzymatic glycosylation, which allows the stereoselective preparation of alkylglycosides with no protection/deprotection steps of the hydroxyl groups [31-39]. The first step is a condensation between the enzyme and the carbohydrate, followed by a step of transglycosylation, as shown in Scheme **6**.

Other researchers showed that alkylglycosides could be synthesized directly using heterogeneous catalysts, such as macroporous sulfonated resins, acid clays and zeolites [40-44].

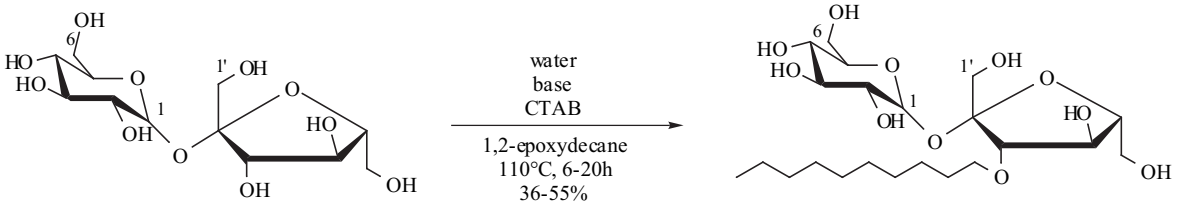
In the last years, alkylglycosides have been studied mainly because of their liquid crystal behavior [28,29,44-46].

Fluorinated *O*-alkylglycosides

Numerous fluorocompounds were synthesized, using two strategies: the first one is a convergent synthesis, in which the F-alkyl chain is first prepared and then is glycosylated. The second is a linear synthesis, involving the preparation of glycosides with a hydrocarbon chain containing a double bond, on which the F-alkyl chain can be grafted. To be stable, F-alkyl glycosides require a spacer between the sugar head and the fluorinated alkyl chain [47]. In Scheme 7 is illustrated a linear synthesis of *O*-(F-alkyl) glycoside **26** [48-52].

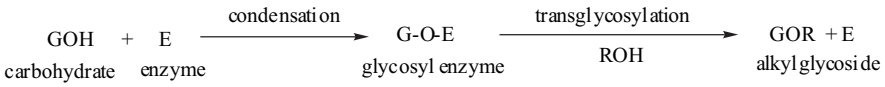
Thioethers

6-alkylthio- and 6-alkylsulfonyl-6-deoxy glycosides were prepared *via* carbohydrate halides, without protection of the

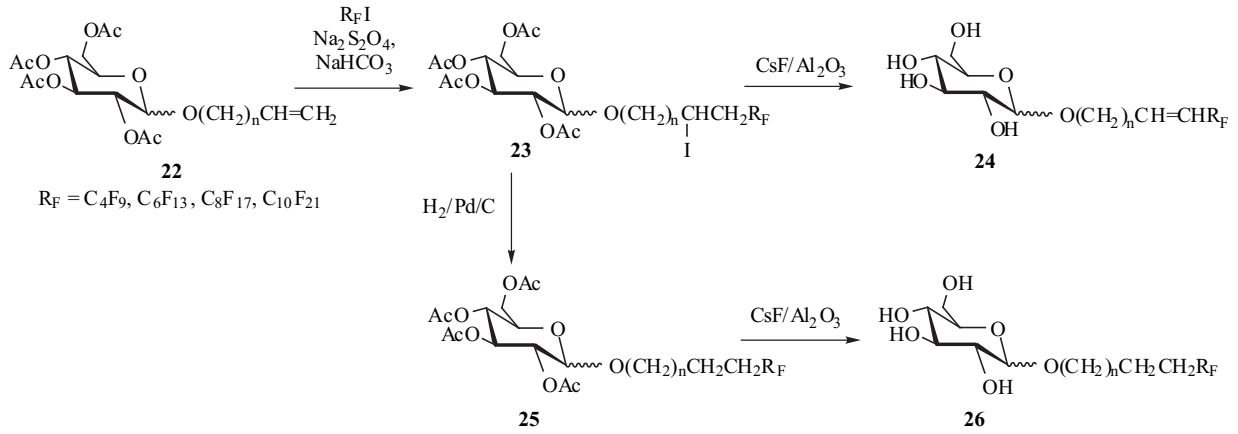


20 **21**
+ regioisomers
+ disubstituted products

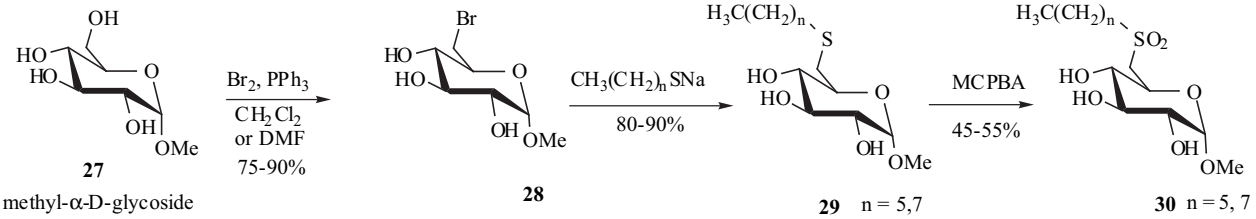
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

secondary hydroxyl groups (Scheme **8**) [53]. The starting carbohydrates used were methyl α-D-glycoside **27** and methyl α-D-mannoside. The CMC was not determined.

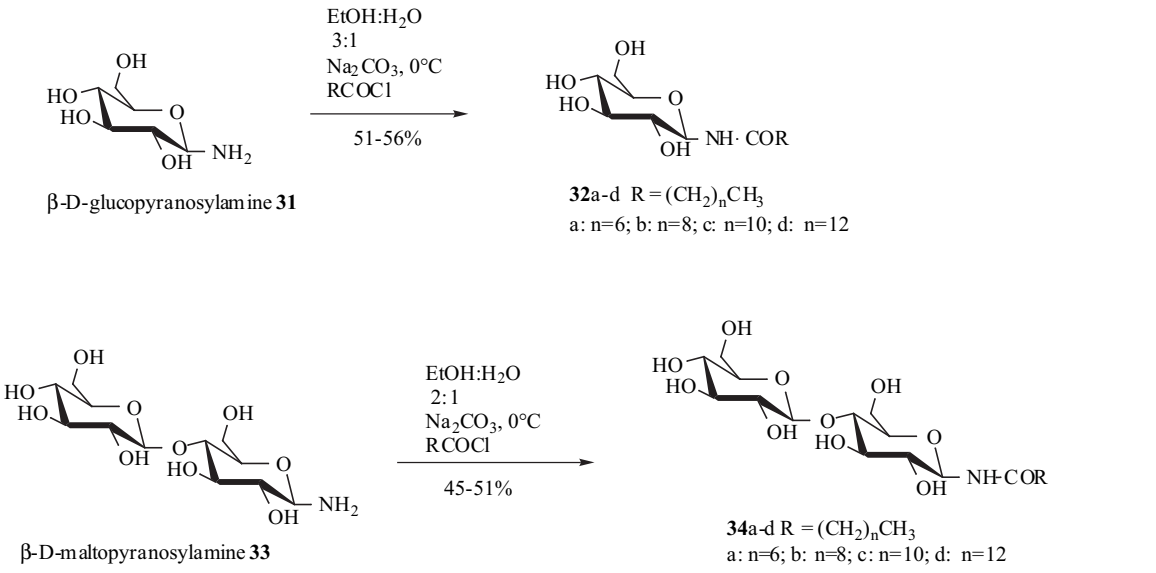
NITROGEN CONTAINING SUGAR SURFACTANTS

Amides

N-acyl carbohydrates derivatives were obtained, reacting a lyophilized glucopyranosylamine or maltopyranosylamine dissolved in water and ethanol with acyl chlorides (Scheme **9**) [54]. The amino carbohydrates were prepared from the corresponding sugars by reaction with ammonia in an ammonium hydrogen carbonate solution, and subsequent concentration and lyophilization of the reaction. The CMC of compounds **32a**, **34a** and **34b** was determined (Table **2**).

Table 2.

Compound	CMC (mM)
32a	40
34a	51
34b	4,1
n-octyl-β-D-glucopyranoside (as reference)	19



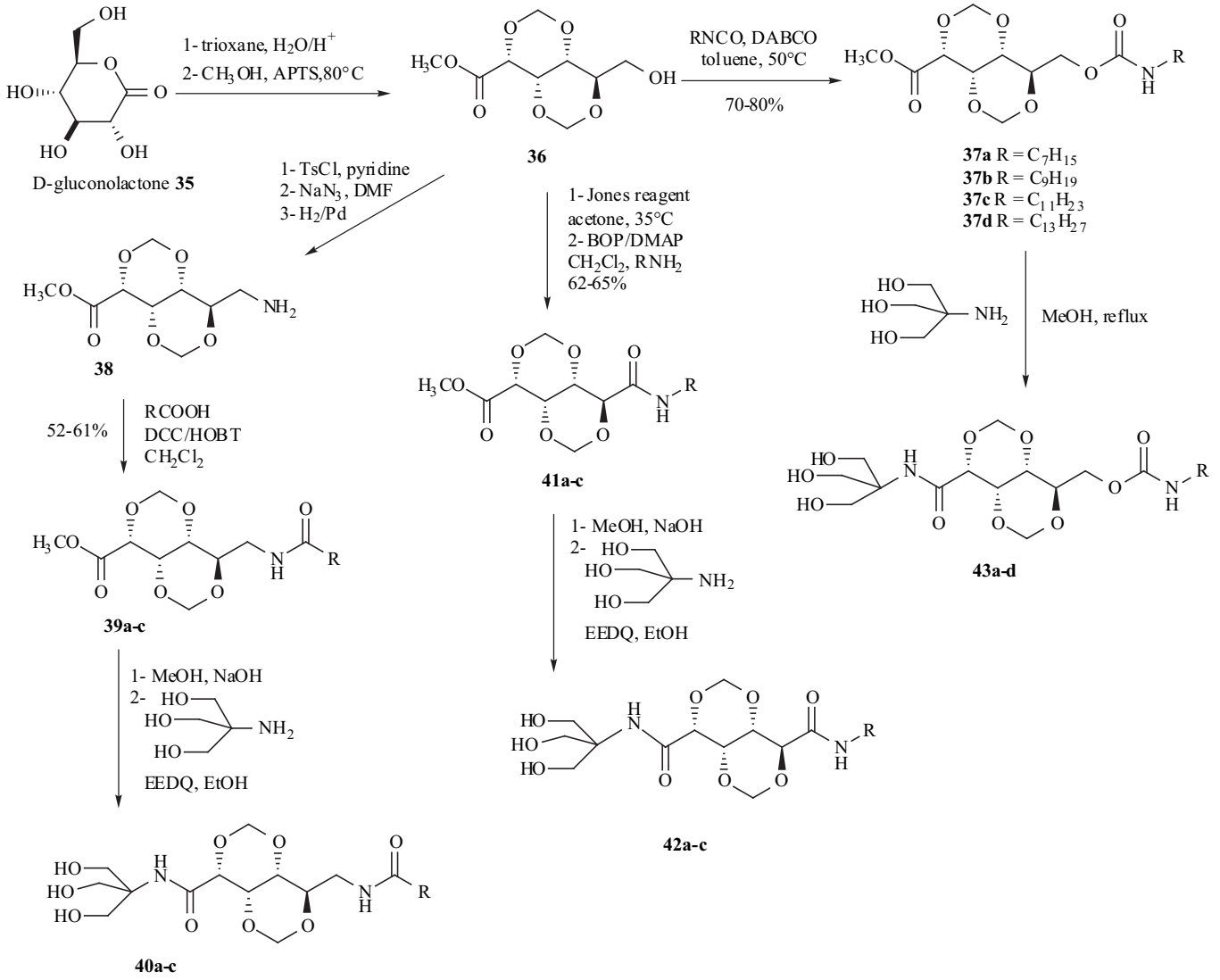
Scheme 9.

Abert and collaborators [54] used D-gluconolactone **35** as starting material for the preparation of non-ionic amphiphilic compounds, using 3 different functional groups to link the sugar moiety and the hydrophobic part: carbamate, amide or "inverse amide" functionality (Scheme **10**). D-gluconolactone **35** was first hydrolyzed and protected. The resulting compound was then esterified to give ester **36**, intermediate for the preparation of the three series of derivatives. Carbamates **37a-d** were obtained by reaction of **36** with alkyl isocyanates, in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane), in 70-80% yield. Amides **39a-c** were prepared *via* tosylation and substitution by an azide group. Subsequent hydrogenation and reaction with fatty acids using DCC (dicyclohexylcarbodiimide) and HOBT (1-hydroxybenzotriazole), lead to compounds **39a-c** in 52-61% yield. A third series was synthesized by oxidation of **36** and condensation of the resulting carboxylic acid with fatty amines. This reaction was performed in the presence of BOP (benzotriazol-1-yloxy-tris(dimethylamino)-phosphonium hexafluorophosphate) with a catalytic amount of 4-dimethylaminopyridine (DMAP), yielding compounds **41a-c** (62-65%).

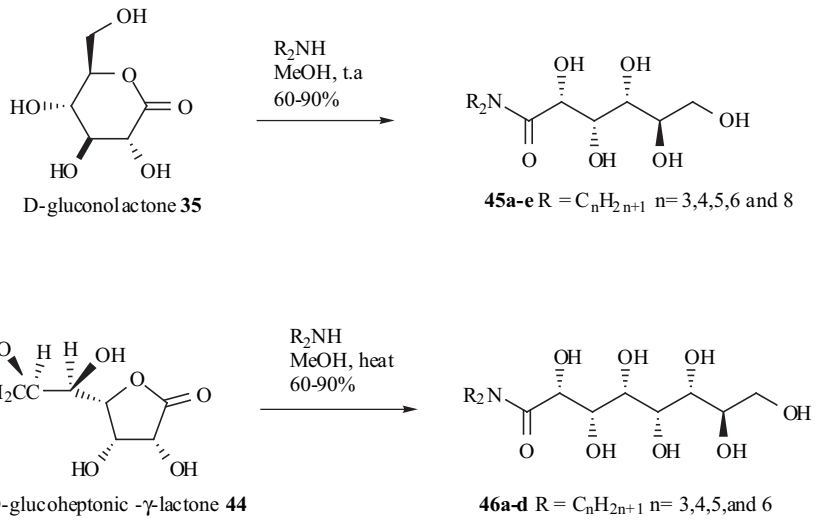
As the water solubility of intermediates **37a-d**, **39a-c** and **41a-c** was not sufficient for physico-chemical studies, the ester groups of the compounds were hydrolized. The resulting intermediates were coupled to TRIS [tris(hydroxymethyl)methylamine] in ethanol, in the presence of 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ), yielding **40a-c** and **42a-c**. Compounds **37a-d** were directly coupled to TRIS by refluxing in methanol (Scheme **10**).

The CMC of compounds **43b-d**, which presented better water solubilities than **40a-c** and **42a-c**, were compared to those of two comercial surfactants SILWET L77 (trisiloxane methyl esters S77) and RHODASURF 860P (polyethoxylated fatty alcohol R860P) (Table **3**). These results, and static and dynamic surface tension measurements showed that carbamate derivatives of gluconic acid may be attractive as wetting agents. They could be useful in adjuvant blends used in the phytosanitary domain.

Pilakowska-Pietra and collaborators also used D-gluconolactone **35** and D-glucoheptonic-γ-lactone **44** to obtain *N*,*N*-di-*n*-alkyl-substituted amides (Scheme **11**) [55]. This type of surfactants, with two long-chain alkyl residues,



Scheme 10.



Scheme 11.

possess better solubility than the related compounds with one alkyl chain [56,57], and can be applied as cell or membrane units and modifiers [58,59].

Table 3.

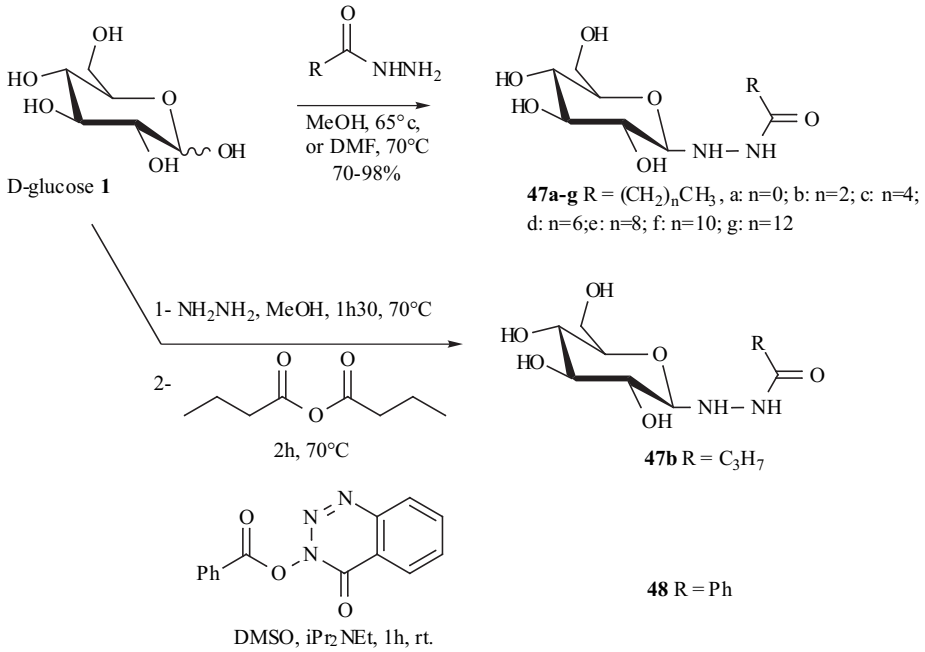
Compound	CMC (mM)
43b	0.8
43c	0.33
43d	0.011
S77	0.12
860P	0.19

N,*N*-di-*n*-alkyl-gluconamides **45a-e** were synthesized by reaction of di-*n*-alkylamines with D-gluconolactone in methanol at room temperature. The products were obtained after evaporation of the solvent and repetitive washes with acetone or hexane, with yields from 60 to 90%. To obtain *N*,*N*-di-*n*-alkyl-heptonamides **46a-d** , heating was necessary to improve the yields.

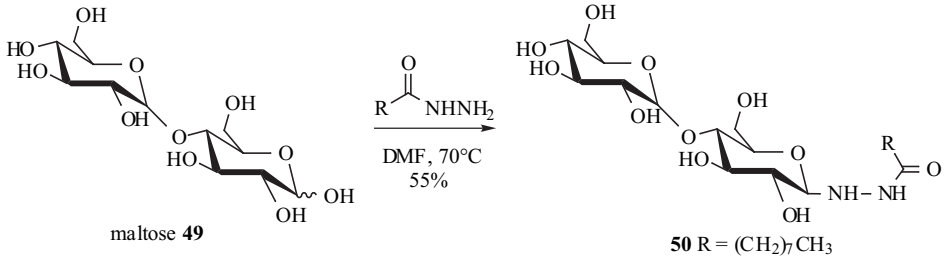
Physico-chemical studies of these compounds showed that they do not form micelles in aqueous solutions, but have a good ability to lower surface tension.

Acylhydrazine (Hydrazide)

1-glycosyl-2-acylhydrazines were prepared from D-glucose **1**, condensing it with acylhydrazines (hydrazides) derived from fatty acids, in methanol or DMF (Scheme **12**) [60]. The corresponding glucosylhydrazides **47a-g** were obtained in 70-98% yield after chromatography. The same reaction was performed using maltose **49** and octanoylhydrazine, furnishing **50** (Scheme **13**).



Scheme 12.



Scheme 13.

Glucose was also allowed to react first with hydrazine monohydrate, and then with butanoic anhydride in methanol, or 3-hydroxy-1,2,3-benzotriazin-4(3H)-one in DMSO, affording compounds **47b** and **48** in 58% and 53% yield, respectively.

Glucosylhydrazides are soluble in water for alkyl chains up to 14 carbon atoms. The CMC of compounds **40b-g** and **44** were determined and are given in Table **4**.

Table 4.

Compound	CMC (mM)
47b	252
47c	23
47d	13
47e	1.2
41f	0.22
47g	0.04
47a	3.55

N-(Fluorinated Alkyl)-Surfactants

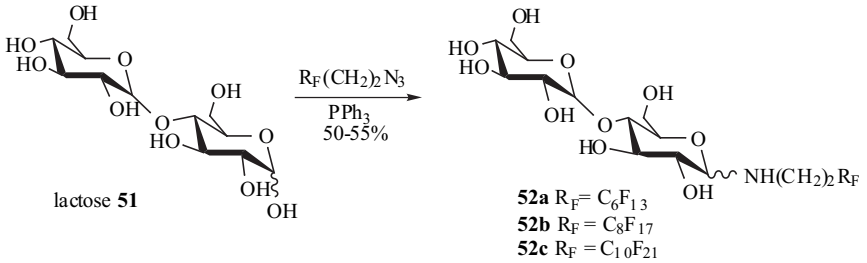
Fluorinated surfactants, also named fluorosurfactants, are surfactants with one or more perfluoroalkylated hydrophobic chain. The investigation of carbohydrate derived fluorinated amphiphiles has been expending in the recent years [61]. These compounds could be used in pharmaceuticals and drug delivery systems [62,63].

The synthesis of *N*-[2-(F-alkyl)ethyl]lactosamine **52a-c** was described by the reaction of a 2-(F-alkyl)ethyl azide with lactose **51** without protection, *via* an iminophosphorane intermediate (Scheme **14**) [64,65].

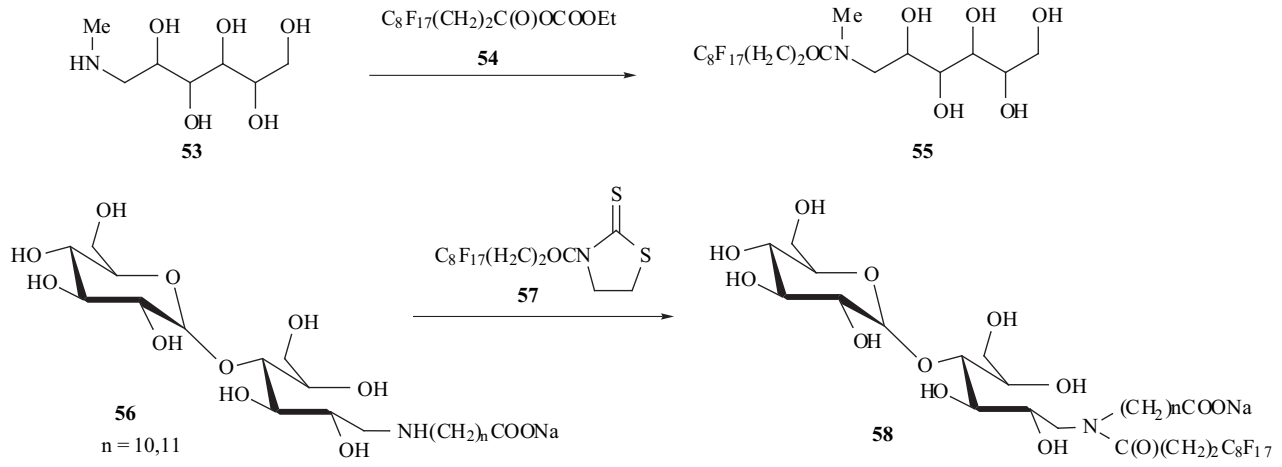
Several works describing the preparation of fluorinated alkyl amides [66-73], ureas [74,75] or carbamates [76-80] derived from carbohydrates have been published.

N-[3-(F-octyl)propanoyl]-*N*-methyl-D-glucamide **55** was obtained from *N*-methyl-D-glucamine **53** in 60% yield, using compound **54** as the acylating reagent [66] (Scheme **15**). Treatment of 1-amino-1-deoxy-lactitol derivative **56** with the fluorinated acylating reagent **57** gave compound **58** (yield 20%) [72].

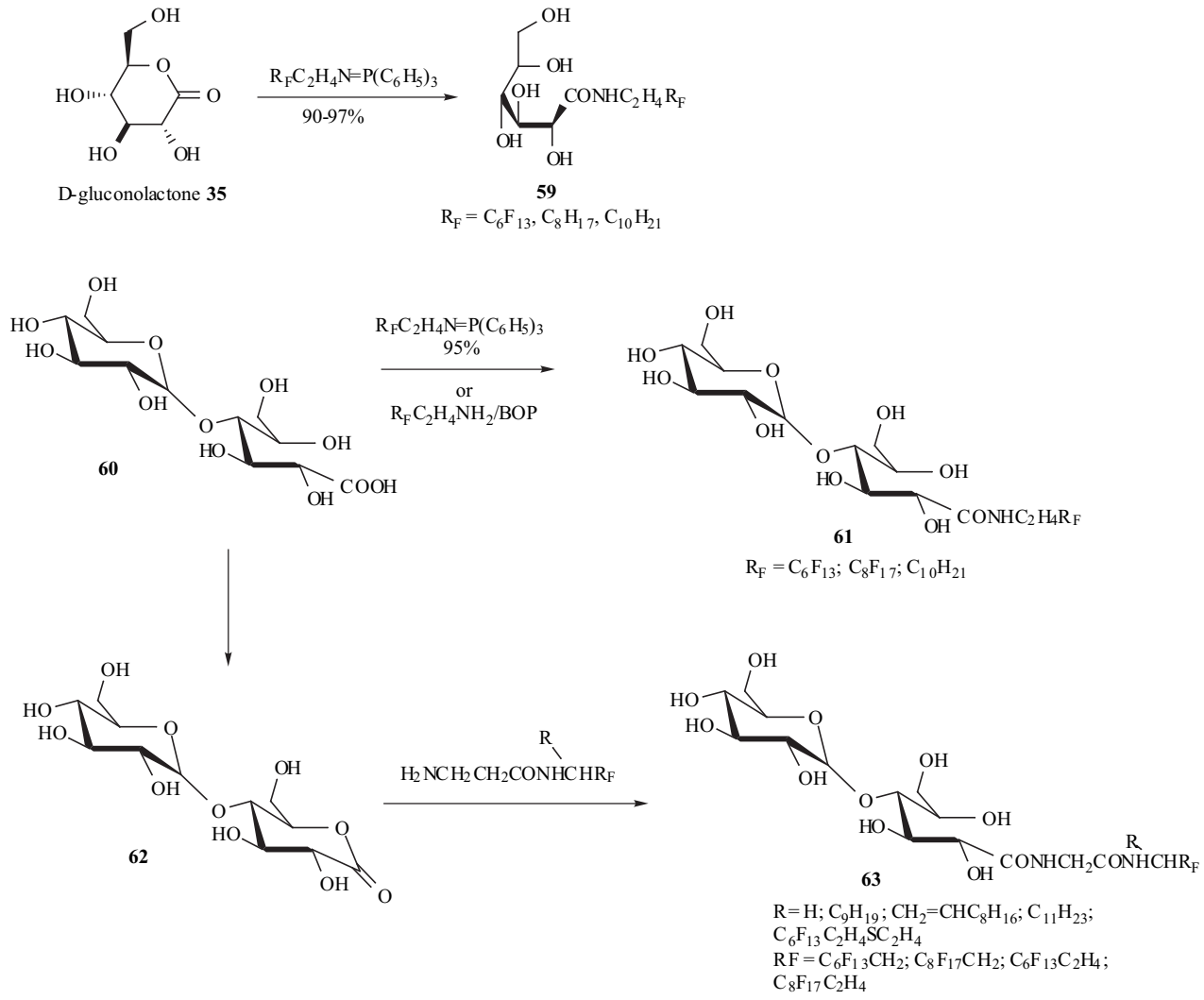
F-alkyl-D-gluconamides **59** [68,72] and F-alkyl-D-lactobionamides **61** and **63** [65,68-73] were obtained from



Scheme 14.



Scheme 15.

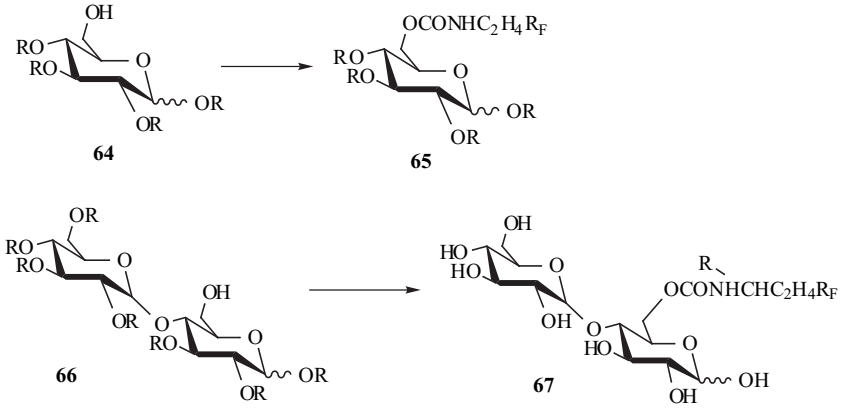


Scheme 16.

D-gluconolactone **35** and lactobionic acid **60**, respectively, using three methods: aza-Wittig-type reaction, activation by BOP, and reaction of 1,5 biolactone **62** with amines in the presence of a base (Scheme **16**). All products were obtained without protection of the carbohydrate.

Fluorinated surfactants derived from lactose showed good surfactant properties, with CMC from 4.3 x 10^{-2} mM to 1,9 mM, and low surface tensions at CMC. But, owing to their instability, these compounds cannot be used in biocompatible formulation. Lactobionic derivatives have good CMC (~0.1 mM), but the surface tension at the CMC is not good enough to make them good surfactants [28].

F-alkylated sugar carbamates **65** and **67** were obtained, condensing protected carbohydrates on fluorinated



Scheme 17.

isocyanates, in the presence of DABCO, followed by deprotection (Scheme **17**) [76].

SUGAR ESTERS

Sugar esters can be prepared either by enzymatic synthesis, using a lipase catalyst, or by an organic chemical route. The organic synthesis requires the use of protecting groups to obtain a good selectivity, but allows variations in the sugar unit. Using the bio-organic route, the esterification occurs almost exclusively at the C6-position of the sugar moiety.

Dimeric and trimeric sugar ester surfactants have been synthesized by a combination of enzymatic and organic chemical methods, and an impressive series of products have been prepared with different spacer units between the sugar rings [79-85].

Sucrose and glucose based surfactants were the first alternatives to those derived from petroleum. Drummond's group relates the synthesis of octyl (C8), dodecyl (C12) and hexadecyl (C16) fatty acid mono-esters of lactose **51** and lactitol **68** (Scheme **18**) [86]. The CMC of the mono-octanoate, mono-dodecanoate and mono-hexadecanoate esters of lactose and lactitol were determined (Table **5**). The results were similar to those of sucrose ester surfactants. The interfacial tensions above the CMC showed that the mono-esters could be good emulsifiers.

Table 5.

Compound	CMC (nM)
69a	2.63
70a	2.75
69b	0.427
70b	0.427
69c	9.55×10^{-3}
70c	7.59×10^{-3}

Pinna and co-workers synthesized 1-*O*-lauryl-D-mannitol **73** from 1,2:4,5-di-*O*-isopropylidene-D-mannitol **71** and vinyl laurate, using the immobilized *Candida antarctica* lipase B (Novozym 435) as catalyst [87]. After deprotection, pure compound **73** was obtained without the occurence of unwanted isomers (Scheme **19**).

Alkyl-6-*O*-acyl-glycopyranosides **74** and **75** were prepared by a chemoenzymatic procedure, for the study of their liquid crystalline properties (Fig. **2**).

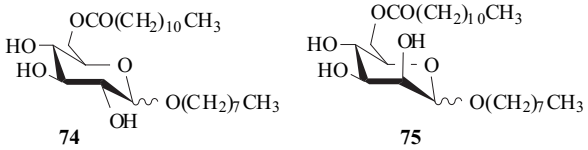
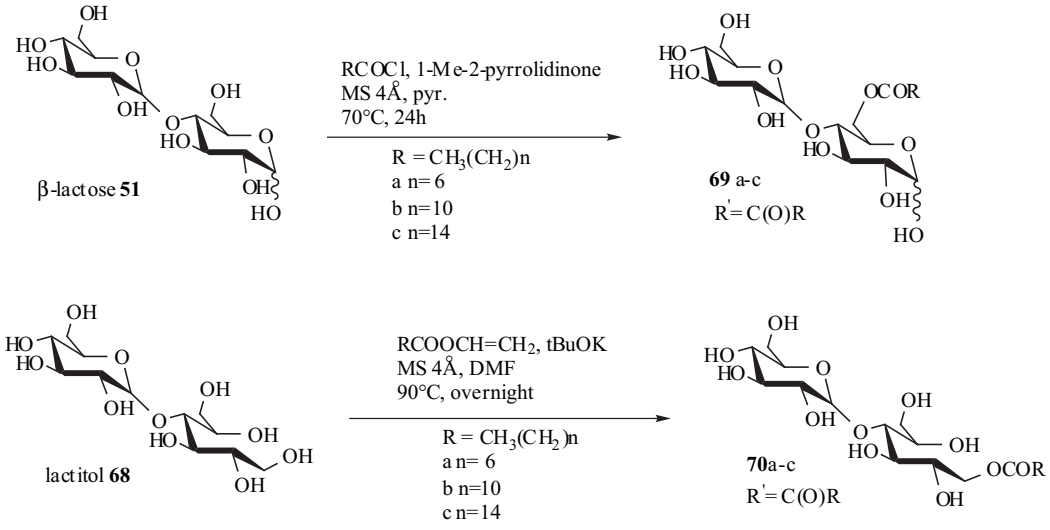
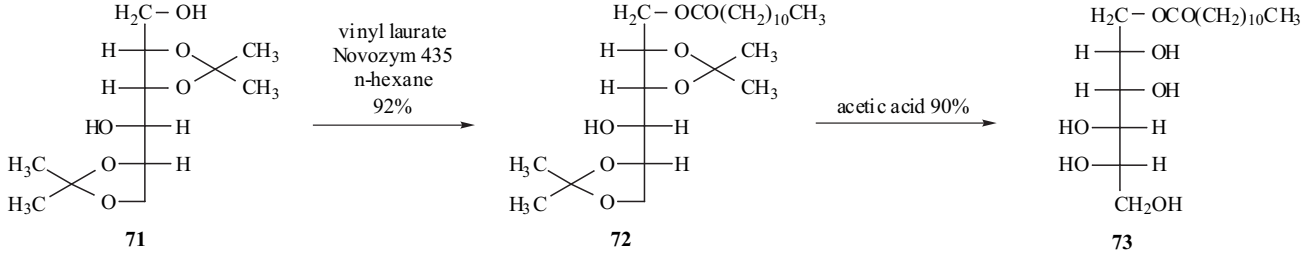


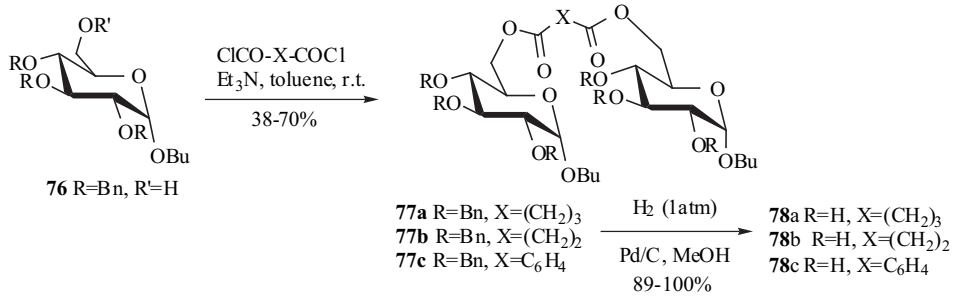
Fig. (2).



Scheme 18.



Scheme 19.



Scheme 20.

DIMERIC SURFACTANTS

Dimeric (or gemini) surfactants are defined as surfactants made up from two identical amphiphilic moieties connected at the level of the head groups, or of the alkyl chains but still very close to the head groups, by a spacer group which can be hydrophobic or hydrophilic, flexible or rigid. They form structures and have dynamic properties drastically different from those of single-chain surfactants, including aggregation behavior and micelle shape.

The synthesis of dimeric surfactants from butyl-α-D-glucopyranoside was reported, using three different spacers (glutaryl, succinyl and terephtaloyl) to link the sugar moieties through *O*-2 or *O*-6 [88]. Protected compound **76** was treated with different diacyl dichlorides, furnishing after hydrolysis of the benzyl groups, the desired compounds **78a-c** (Scheme **20**).

The CMC for these new compounds was ten-fold smaller than that of their monomeric counterpart (Table **6**).

Compounds **80a-c**, linked through *O*-2 were also prepared from stannylene **79**, using the same diacyl dichlorides as linkers (Scheme **21**). Compound **79** was obtained from butyl-α-D-glucopyranoside which was first protected to form 4,6-*O*-benzylidene acetal, and then heated with dibutyltin oxide in toluene.

Table 6.

Compound	CMC (mM)
78a	8.0
78b	6.0
80a	7.0
80b	1.5
80c	6.0

BOLA-AMPHIPHILES

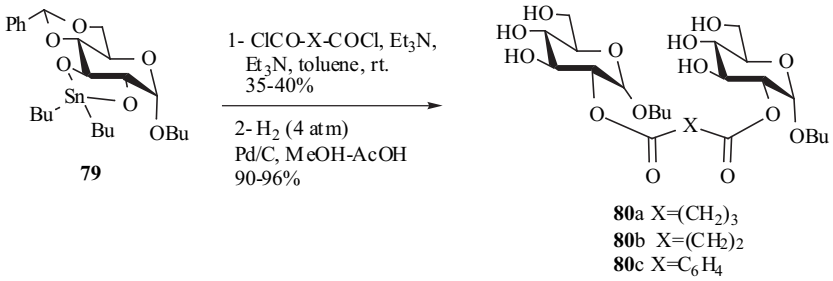
Bola-amphiphile are molecules in which two or more hydrophilic heads are connected by one or two hydrophobic chains. Over recent years, there has been an increasing interest in such surfactants because of their ability to form vesicles and supramolecular arrangement, and because of their potential application in pharmacy and chemistry. The use of the sugar as the polar head can offer greater potential for interaction at the cell surface by molecular recognition.

Gouéth and collaborators [89] prepared bis(glycosyl)ethers in which the hydrophilic heads are D-glucose, D-galactose and xylitol, or the corresponding protected derivatives. The protected carbohydrates were first condensed with dibromo- or dimesyl-alkanes in basic medium (Scheme **22**). Changing experimental conditions allowed the preparation of monosubstituted alkyl derivatives, bis-substitution products or elimination products.

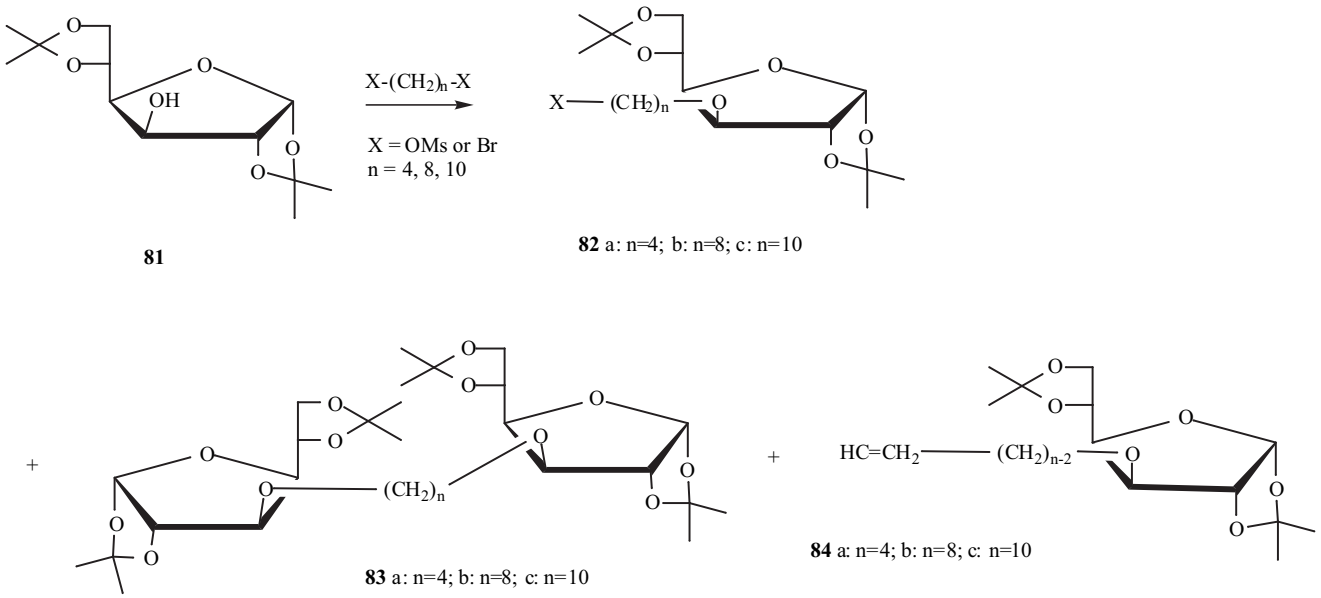
Monosubstituted compounds **82a-c** could be condensed with a second protected carbohydrate in a Grignard reaction (Scheme **23**). The resulting compounds were then totally deprotected or derivatized (partial deprotection and esterification) (Scheme 24). CMC values were determined for compounds **85a**, **87c** and **90c** (Table **7**).

A variety of compounds with polar head derived from D-glucose or D-galactose was prepared by Prata's group, in order to determine the relationship between molecular structure and the nature of the aggregates [90].

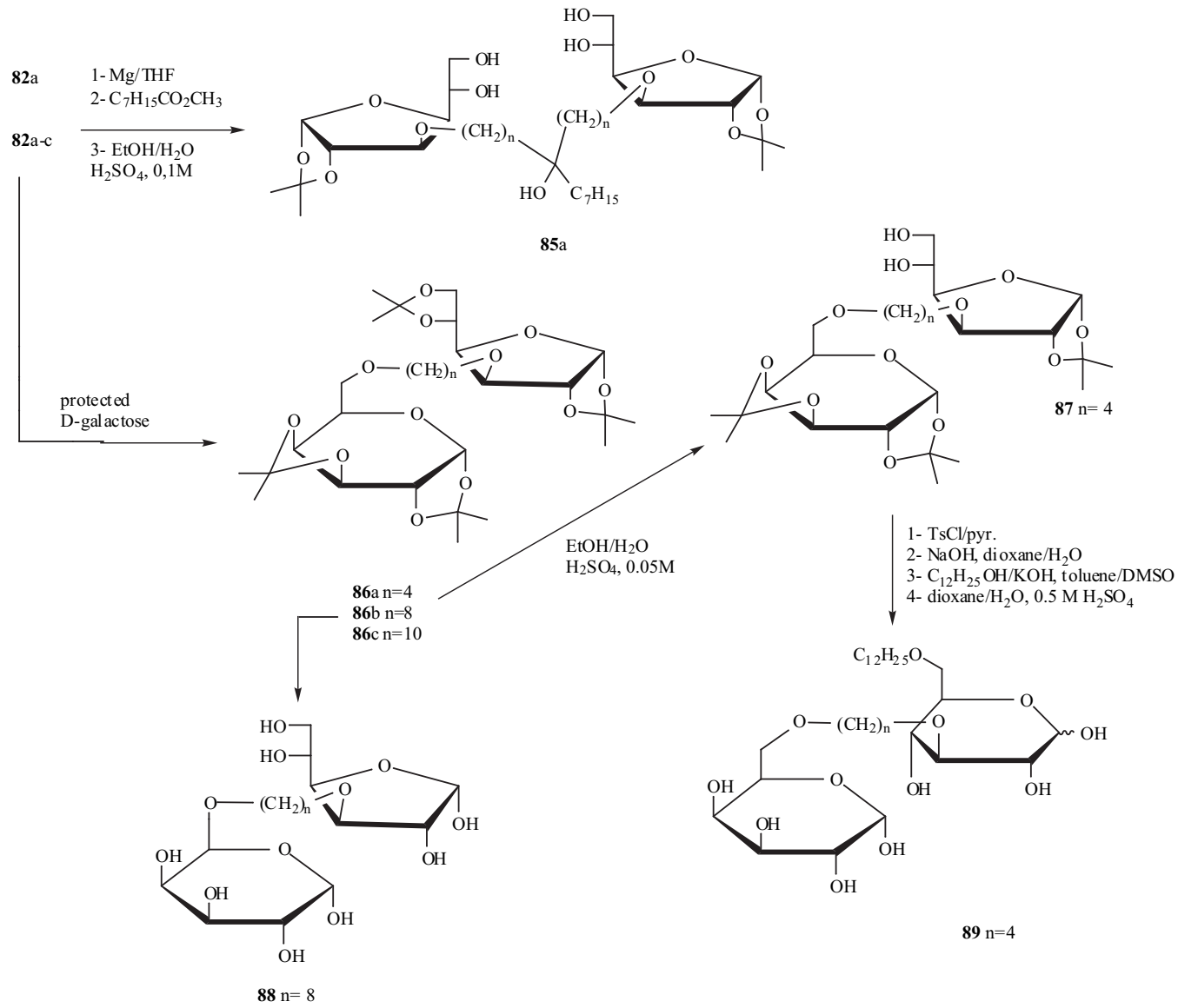
Bis(*O*-galactopyranosyl) and *bis*(*O*-lactosyl) bis(carbamate) **93-96** (Fig. **3**) were obtained by reaction of one molar equivalent of α,ω-polymethylene diisocyanate with two equivalents of 2,3,4,6-tetra-*O*-acetyl-D-galactopyranose or 2,3,6,2',3', 4',6'-hepta-*O*-acetyl-lactose. The reaction performed in toluene, in the presence of 1,4-diazabicyclo[2.2.2]octane allowed the obtention of β-anomer



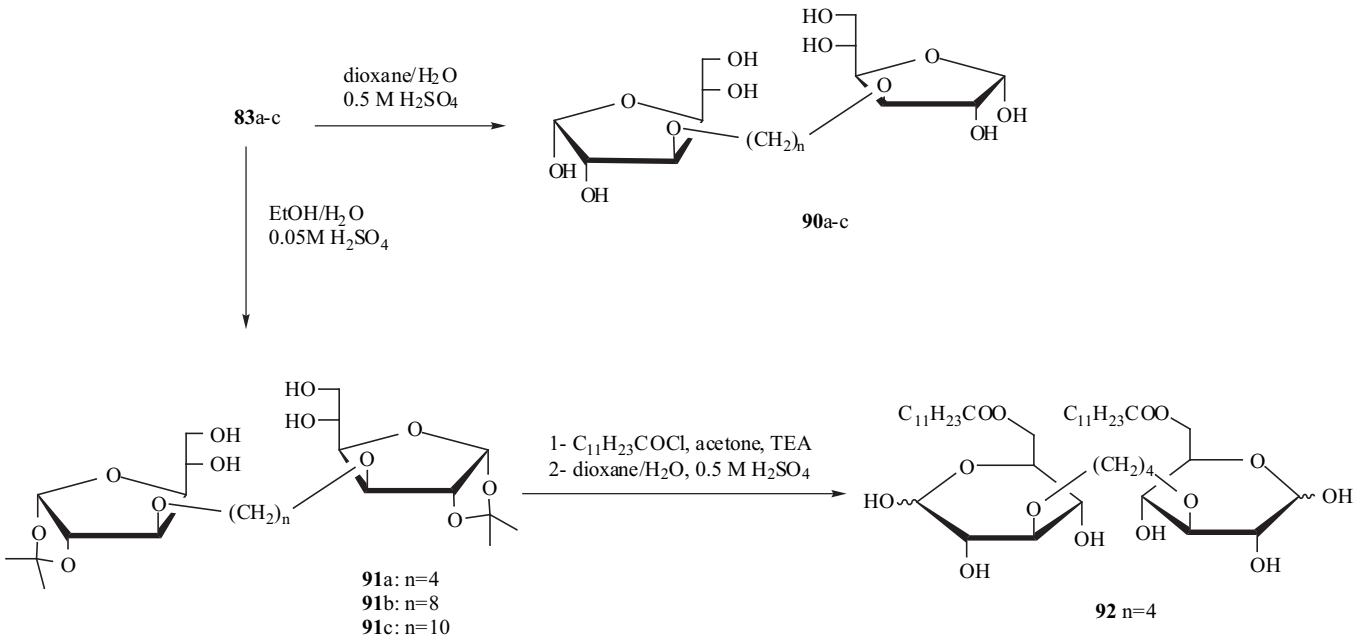
Scheme 21.



Scheme 22.



Scheme 23.



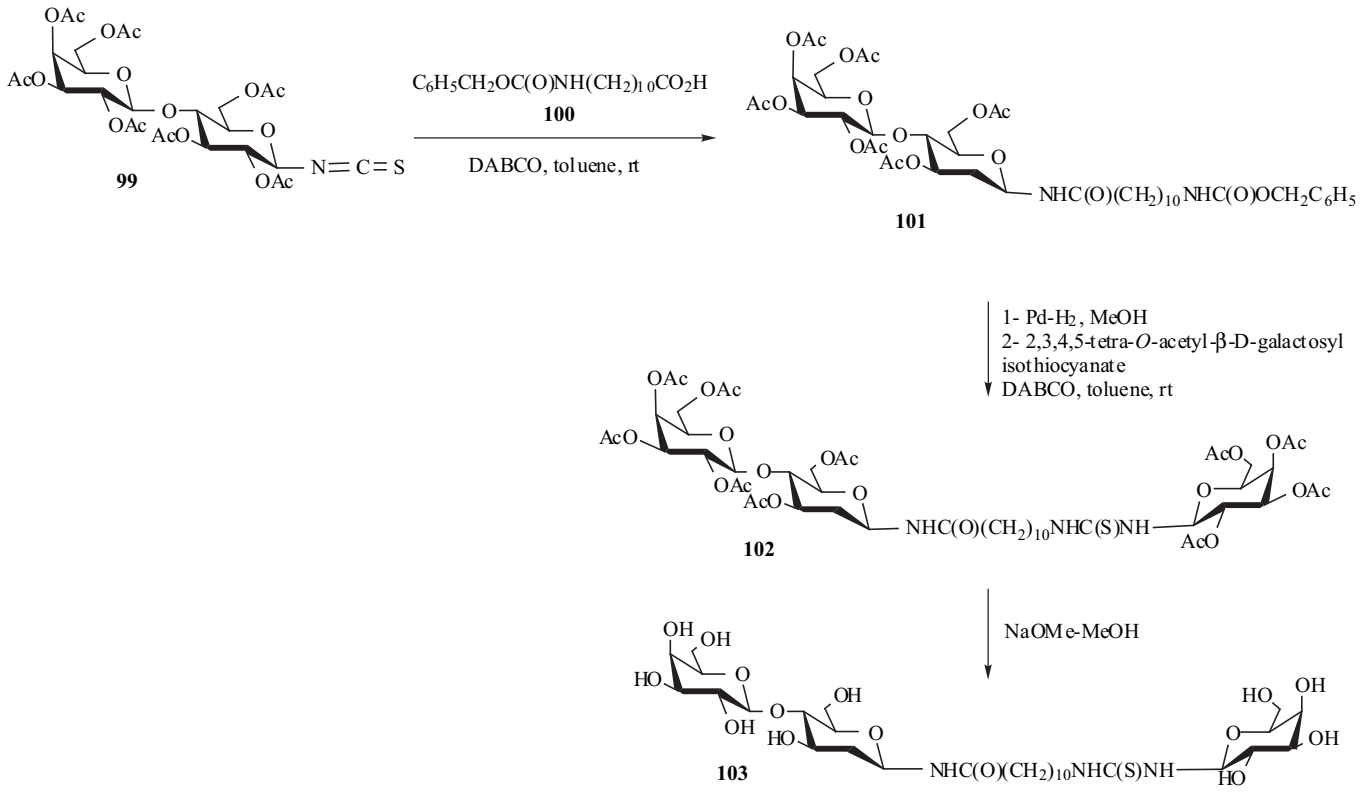
Scheme 24.

with complete diastereoselectivity. The acylated compounds were then quantitatively *O*-deacylated to give the desired compounds.

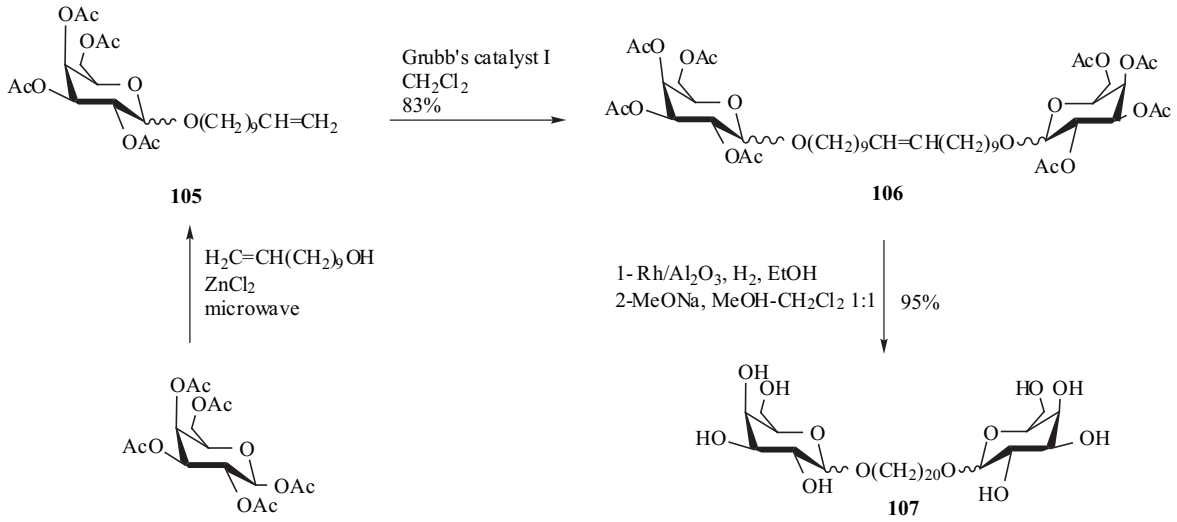
Compounds **97** and **98** [*O*-galactopyranosyl-*O*-lactosyl bis(carbamate)] were obtained in a one pot sequence, by successive addition of 2,3,4,6-tetra-*O*-acetyl-D-galacto-pyranose and 2,3,6,2',3',4',6'-hepta-*O*-acetyl-lactose to a long chain alkyl diisocyanate in toluene and *O*-deacetylation of the intermediates.

Table 7.

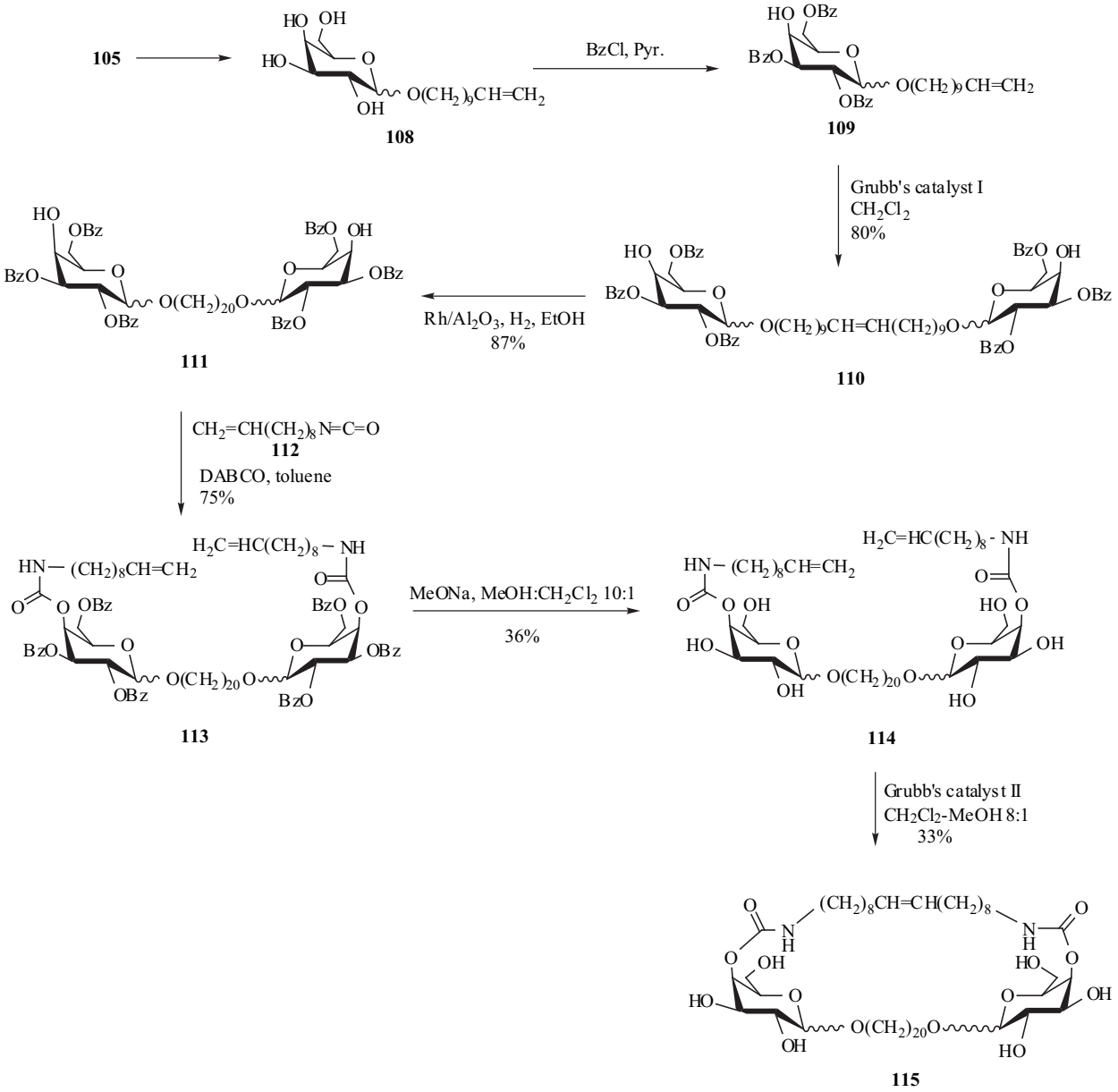
Compound	CMC (nM)
90c	0.65
87c	0.42
85a	0.47



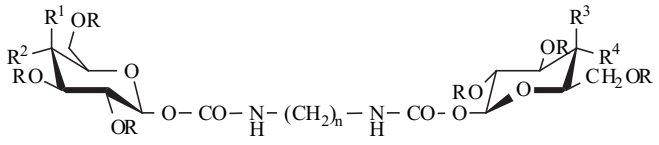
Scheme 25.



Scheme 26.



Scheme 27.



93 n=6, R = R^2=R^4=H, R^1=R^3=OH
94 n=12,R = R^2=R^4=H, R^1=R^3=OH
95 n=6, R=R^1=R^3= H; R^2=R^4=β-D-gal
96 n=12; R=R^1=R^3= H; R^2=R^4=β-D-gal
97 n=6; R=R^2=R^3=H, R^1=OH, R^4= β-D-gal
98 n=12; R=R^2=R^3=H, R^1=OH, R^4= β-D-gal

Fig. (3).

Galactopyranosylthiourea derivative **103** was also prepared (Scheme **25**). The amino group of 11-amino decanoic acid was first protected with a *N*-benzyloxycarbonyl group to afford compound **100**, and then reacted with per-*O*-acetyl-β-lactosyl isothiocyanate **99** in toluene, in the presence of 1,4-diazabicyclo[2.2.2]octane. Deprotection of the amino group and reaction with 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl isothiocyanate afforded intermediate **102**, which was *O*-deacetylated to furnish bola-amphiphile **103**.

Compounds **94**, **96** and **98** showed the absence of micellization. Compounds **95**, **96**, **98** and **103** showed the presence of vesicles.

Recently, Satgé and collaborators described the synthesis of bolaform and macrocyclic galactose-based surfactants, using a reaction of olefin metathesis [91]. Single-chain bolaform surfactants **107** were obtained by homodimerization of **105**, followed by catalytic hydrogenation of the olefinic disaccharides. The homodimerization occurred by olefin metathesis in the presence of Grubb's catalyst I, with an 83% yield. Catalytic hydrogenation of compounds **106** was catalysed with rhodium on alumina, yielding the saturated products **107** almost quantitatively (Scheme **26**).

Pseudomacrocyclic compounds **114** were prepared from benzoylated products **109** (Scheme **27**). The homodimerization reaction was carried out as described in the previous Scheme, leading to compounds **111** in 80 and 87% yield, respectively. Dicarbamates **113** were obtained by coupling **111** with isocyanate **112**. Removal of the benzoyl groups and ring closing metathesis of the resulting compounds gave the expected macrocycle **115**. This compound is an analog of archaeobacterial membrane component.

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