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## Scientific information about sugar-based emulsifiers: a comprehensive review

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The instantaneous demand for foods, detergents, cosmetics, and personal care products that can be commercialized with value-added benefits including natural origin, environmental friendliness, and sustainability is increasing day by day. Accordingly, the associated industries are trying to identify bioactive ingredients that may be natural alternatives to synthetic ones. This review article is mainly aimed at the classification of natural saccharide-based emulsifiers (which are mainly bio-surfactants), their methods of preparation and their various types of applications in daily life activities. Different routes of production of mono and polysaccharide-based emulsifiers and their industrial advantages are exclusively highlighted. The readers can get an approach on how sugar-based emulsifiers are synthesized and used in the pharmaceutical, food, and personal care industries to contribute excellent physicochemical properties and feature excellent functional characteristics. Many of the synthetic procedures are associated with the use of natural ingredients to prepare emulsions concerning "eco-friendly" selective materials. In this report, an endeavour has been made towards contextual examples for the production methods of some saccharide-based emulsifiers and their advantages in various fields.

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### 1. Introduction

The development of science and technology is mainly focused on the security and safety of the environment, people, and ecosystem.<sup>1</sup> The diverse and conventional chemistry requires convenient alterations that promote the applied aspect of 'green chemistry' in the daily life activities of our community. Natural resources have been proved to be the most effective and dependable alternatives to accelerate the 'green chemistry' worldwide. In this context, species having properties such as

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## Review

lesser toxicity, chemical stability, biodegradability, environmental safety, efficient solubilisation, and of course, recycling facility are of key interest.

Emulsions are normally thermodynamically very unstable colloidal systems.<sup>2</sup> They consist of small oil droplets suspended in an aqueous phase. An emulsion is a colloidal substance whose dispersion medium and dispersed phase both are liquid. By adsorbing onto droplet surfaces and lowering the interfacial tension, emulsifiers tend to produce an emulsion.

Once it gets produced, it turns into a facile breakup of the droplet. Simple emulsions may exist as either oil-in-water (o/w) or water-in-oil (w/o) systems.<sup>3</sup> Emulsions are illustrated as fine colloidal systems containing emulsion droplets with a size larger than the dimension referred for a colloidal system, *i.e.* diameter > 1  $\mu\text{m}$ . The investigations over several studies enable us to explore that oil and water emulsions are prepared as well as stabilized utilizing nano- or micro-solid particle adsorption at the interfacial juncture. It also supports that protein could

stabilize solid- or semi-solid-like lipid materials such as structured emulsions and oil-in-water (o/w) emulsions. Some naturally available and readily found emulsifiers are polysaccharides, phospholipids, and proteins.<sup>4</sup> Almost regularly consumed milk, which is an important constituent of our diet, is a good example of the emulsion of fat in water. The electrostatic repulsions caused by a charged oil-water interface can suppress the aggregation between oil droplets, thereby developing emulsion stability. An emulsion is an unstable system from a thermodynamic viewpoint since a liquid/liquid system has a natural tendency to separate and diminish its interfacial area, as well as its interfacial energy.<sup>5</sup> To stabilize the emulsion, addition of an emulsifying agent or emulsifier is usually essential. The emulsifier plays an important role, as it exacerbates the stability of an emulsion by enhancing the kinetic stability.<sup>6</sup> Inspired by the momentous applications of environmentally benign emulsifiers, the present report has focussed on the production and utilization of such important 'green chemical', the sugar-based emulsifiers collectively.

Before discussing polysaccharide-based emulsifiers,<sup>7</sup> it is rational to interpret and discuss the reasons behind emulsion instability or, more specifically, why we need emulsifiers to stabilize emulsions. An emulsion should be stable until it achieved its purpose. A higher energy gradient is needed to stabilize the emulsion by preventing the fusion of droplets.<sup>8</sup> Based on the droplet size and different densities of the droplets and the medium, emulsions may break down in many ways (Scheme 1).

Sedimentation occurs when particles in suspension are settling out of the medium in which they entrain and come to rest against a barrier.<sup>9</sup> This is due to external forces such as gravity, centrifugal acceleration, or electromagnetism. An emulsion could be stabilized by preventing such aggregation since the aggregate of droplets could sediment faster than individual tiny droplets. Flocculation occurs when floc-like



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Scheme 1 Different mechanisms of emulsion breakdown. This scheme is reproduced from ref. 13, with permission from Springer, Berlin, Heidelberg, copyright 2015.

colloids appear from the suspension.<sup>10</sup> This process may be spontaneous or it may also be observed by adding a clarifying agent. In the case of flocculation, because of weak van der Waals attraction, the repulsive force is not adequately strong to keep the droplets apart. To prevent flocculation, it needs to overcome the attractive force acting between droplets. This can be done by introducing a repulsive force *via* the formation of the electrical double layer using an ionic surfactant. Ostwald ripening is best described by the alteration of the size of droplets over time in solid particles or liquid mediums.<sup>11</sup> In Ostwald ripening, larger droplets of poly-dispersed emulsion have lower solubility than smaller ones. Smaller droplets recombine with larger droplets and become invisible over time. Ostwald ripening may be prevented by using a stabilizer which can reduce the interfacial tension between solid solutions and liquid sols. There's a process called coalescence that occurs when two or more droplets join together.<sup>12</sup> This is because of the surface or film fluctuation which makes the droplets come close to each other. Coalescence can be reduced by using polysaccharides and polypeptides as weighting agents, which also coat the individual droplets. In phase inversion, dispersed phase and dispersion medium are interchanged, *i.e.* water-in-oil emulsion changes into oil-in-water emulsion and *vice versa*.<sup>13</sup>

It is legitimate to indicate here that a natural polymer like polysaccharides is composed of similar or different kinds of monosaccharide units bound together by two or more glycosidic linkages.<sup>14</sup> Physicochemical properties of polysaccharides especially depend on their molar masses, electric charge, hydrophobicity, degree of branching, and polarity. The emulsification performance of polysaccharides enhances when glycoproteins or glycolipids are covalently bonded with them.<sup>15</sup> However, several polysaccharides are amphiphilic and thus they can stabilize emulsions, being adsorbed onto the surface of oil droplets. In this review, we will discuss some natural emulsifiers which are polysaccharide-based bio-surfactants<sup>16</sup> such as alkyl poly-

glycosides, sorbitan esters, and sucrose esters.<sup>17–19</sup> Bio-surfactants are categorized into two classes based on their molecular masses by Rosenberg and Ron.<sup>20</sup> Surface-active agents fall into two categories: low-molecular-weight (such as glycolipids, lipopeptides, and phospholipids) and high-molecular-weight (such as polymeric and particulate surfactants).<sup>21</sup> Now, considering a surfactant having amphiphilic properties, it is a very difficult task to substitute polyethylene glycol with a carbohydrate molecule for fatty alcohol or fatty acid.<sup>22–25</sup> Though there are various ways of preparing a large number of carbohydrates, only very few of them satisfy the criteria for being raw material in the industrial aspect because of their cost, quality, and availability. For instance, glucose from starches, sucrose from sugarcane, and sorbitol from hydrogenation glucose derivatives are possible to prepare (Table 1).<sup>26</sup> Nowadays, remainders of straw and hemicelluloses processing are used for making the derivatives of lactose, xylose, and other carbohydrates.

## 2. Classification of polysaccharide-based emulsifiers

Surfactants are mostly derivatized using fats, oils, amino acids, *etc.*<sup>28</sup> Production of surfactants especially bio-surfactants (BSs)

Table 1 Accessibility of carbohydrate raw materials

	Volume of production [t a <sup>-1</sup> ]	Prices on average <sup>a</sup> [€ kg <sup>-1</sup> ]
Sorbitol	650 000	1.80
Glucose	30 000 000	0.30
Sucrose	150 000 000	0.25

<sup>a</sup> Several factors cause agricultural commodities to be highly volatile on the market. Hence, the figures shown can only be indications. Table is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.



is still not on a bigger industrial scale though researchers around the globe are emphasising these alternatives. The most important topic in the category of BSs nowadays is sugar-based BSs.<sup>29</sup> or particularly polysaccharide-based BSs.<sup>30</sup> There are a various types of polysaccharide-based BSs synthesized, such as alkyl polyglycosides, sorbitan esters, and sucrose esters.<sup>31</sup> Here, a chart has been represented for different polysaccharide-based surfactants (Scheme 2). This information would help the readers to understand the huge variety of such emulsifiers. The classification is solely based on the types of substrates used for the production of such surfactants.

Surfactant is itself a class of chemical especially known for its wide range of applications and variety of production. BSs are a type of surfactant which has been introduced a few decades ago. As this review article is solely focused on only polysaccharide-based BSs, we have given the details of different types of polysaccharide-based BSs in the above diagram.

### 3. Production and utilization of saccharide-based BSs

This review article is a dedicated endeavour to collectively present different polysaccharide-based emulsifiers with the aim of gathering scientific knowledge on polysaccharide-based BSs, their production, and their application in different chemical

and industrial fields. We have decided to provide acquired scientific knowledge of different classes of polysaccharide-based BSs, their production, and scientific information regarding them.

#### 3.1. Sorbitan esters

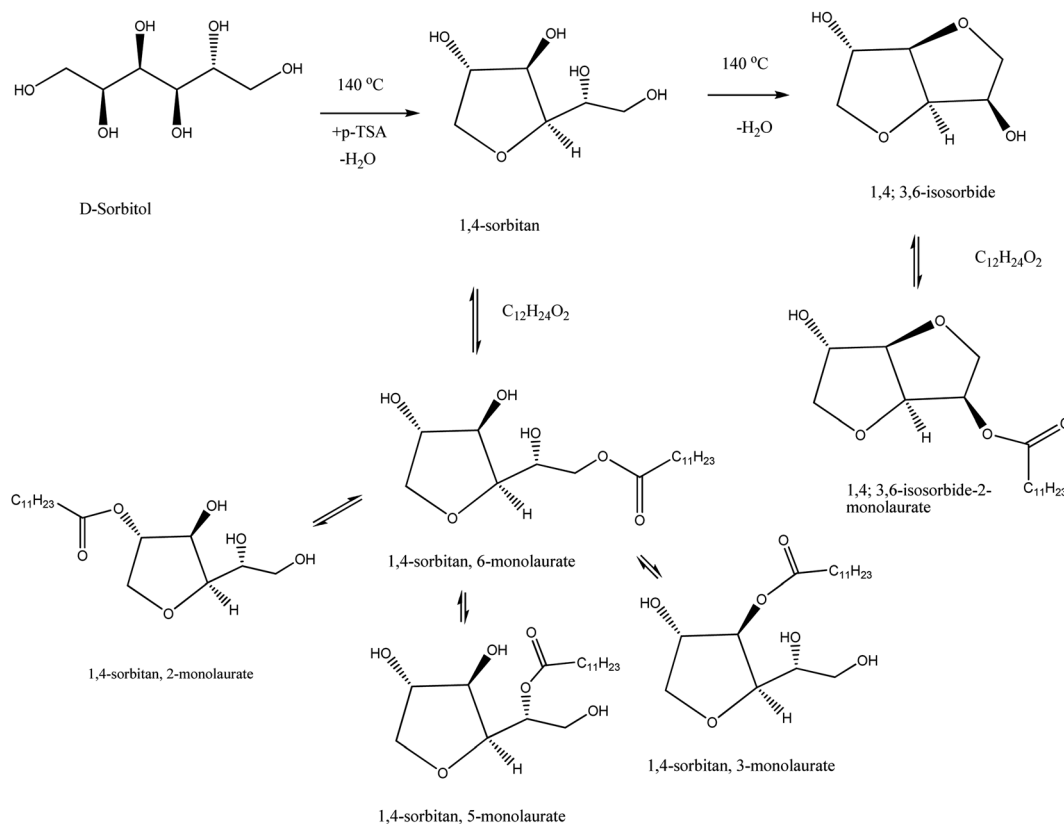
In the process of preparation of polysaccharide-based bio-surfactants, the first synthesized emulsifying agent was sorbitan ester. It is prepared by direct acid<sup>32</sup> and base-catalyzed reactions of sorbitol containing a fatty acid at high temperatures. Stockburger<sup>33</sup> explains how to produce sorbitan ester *via* acid-catalyzed anhydridization of anhydro sorbitol (a combination of sorbitans, isosorbide, and unreacted sorbitol). At a temperature less than 215 °C, the anhydro sorbitol is reacted with a fatty acid in the presence of a base. Sorbitan emulsifiers typically have a low HLB (hydrophilic lipophilic balance) value of about 1–8. More dedicated researchers are needed in association with modified technologies to improve the HLB value. It has been established that if these esters are reacted with ethylene oxide, a compound like sorbitan ester ethoxylate is produced with a higher value of HLB about 10–17.<sup>34</sup> A schematic diagram of sorbitan emulsifier production is given in Scheme 3.

The interesting information about sorbitan esters is that approximately 20 000 tons of these surfactants are produced and utilized in the market every year. The main use of sorbitan



**Scheme 2** Different types of polysaccharide-based surfactants. The scheme is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Germany.





**Scheme 3** Esterification reactions hypothetically leading to sorbitan monolaurate. The scheme is reprinted with permission from ref. 35 copyright 2019 Carl Hanser Verlag GmbH & Co. KG.

ester is an emulsifier in food processing, cosmetics, polymerization, and pharmaceutical industries.

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### 3.2. Sucrose esters

Unlike sorbitan esters, sucrose esters are very mild and their sole application is based on dermatological products. In many countries, it is an approved edible food processing emulsifier.<sup>36,37</sup> Sucrose-fatty acid esters are widely accepted non-ionic

surfactants usually applied as emulsifiers in food products and beverage industries. Sucrose is a very temperature-sensitive molecule and thus its esterification needs an optimum method and perfect control. For such reasons, sucrose emulsifier production is very difficult compared to sorbitan esters. Here also mixtures of mono-, di-, tri-, tetra- or penta-esters are observed. These emulsifiers were first introduced in the market by the Dai-Nippon manufacturing company in the late 1960s. The application of DMSO and DMF as solvents is of great concern for such emulsifier production as both DMSO and DMF have established health hazards. Industrial-scale productions of

**Table 2** Potential uses of sugar-based surfactants and approximated production capacities

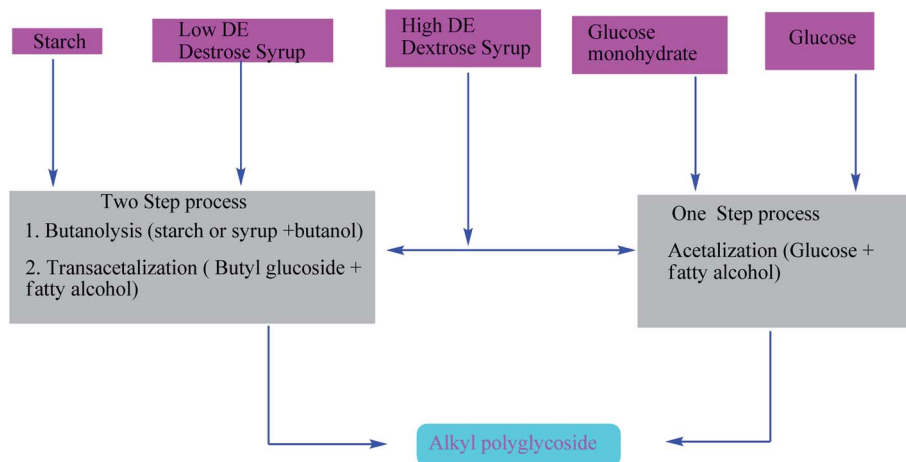
	Specified suppliers	Fields of utilization	Production ability, world <sup>a</sup> [t a <sup>-1</sup> ]
Sorbitan esters	Akzo Nobel, Cognis, Kau, Dai-Ichi Kogyo Seiyaku, SEPPIC, Riken Vitamin	Pharmaceuticals, personal hygiene, foodstuffs, fiber, agrochemicals, platings, bombs	20 000
Sucrose esters	Jiangsu Weixi, Cognis, Evonik/Goldschmidt, Croda, Mitsubishi-Kagaku, Dai-Ichi Kogyo Seiyaku	Pharmaceuticals, personal care, food	<10 000
Alkyl polyglycosides	Cognis, Akzo Nobel, China BASF, Dai-Ichi Kogyo Seiyaku, Research Institute for Daily Chemical Industry, LG, and SEPPIC	Personal care, agrochemicals, detergents	85 000
Anionic alkyl polyglycoside derivatives	Cognis, Cesalpina	Personal care, pharmaceuticals	<10 000

<sup>a</sup> Estimated figures are based on private communications and literature data, references given in the text.









**Scheme 7** Manufacturing process for alkyl polyglycosides. The scheme is reprinted with permission from ref. 57 copyright 2001 American Oil Chemists' Society (AOCS).

or dyeing effect.<sup>56</sup> It is clear from Table 3 that the wetting time of alkyl polyglycosides reduced with the increase in the length of the alkyl chain. Because of the higher penetration and wetting powers, alkyl polyglycosides are broadly used in crop protection formulation.<sup>57</sup>

The information in Table 3 is reprinted with permission from ref. 57 copyright 2001 American Oil Chemists' Society (AOCS).

For the manufacturing of high-quality products, we have to develop the industrial process. The crucial point for this is to establish reaction conditions which must be secure and economically adaptable. This may be achieved by adjusting the reaction parameters such as pressure, temperature, reaction time, and the glucose-to-fatty-alcohol ratio.<sup>58,59</sup> At present, alkyl polyglycosides are directly manufactured by a special method that includes a smooth distillation technology for removing the excess fatty alcohol *via* bleaching and stabilization (Scheme 7).<sup>60-63</sup>

Mid-chain ( $C_{12/14}$ ) alkyl polyglycoside was first industrially introduced by Cognis. Currently, Cognis has the largest capacity worldwide in case of supply. Other manufacturers are listed in Table 2.

A large amount of non-ionic surfactant is produced by using vegetable oils and sugar. This process is completely based on renewable resources.  $C_{12/14}$  alkyl polyglycoside is used as a dishwasher agent, detergent, and cosmetic. Hard surface cleaners, agrochemicals, and products for institutional and industrial cleaning are the principal applications for  $C_{8/10}$  (or branched C8) alkyl polyglycosides (Table 2). According to Anastas and Warner, basic features of method and product and the environmental consequence for Glucopon, Plantaren, and Plantacare types by applying '12 principles of green chemistry' are represented in Table 4.<sup>64</sup>

Alkyl polyglycoside is present in the market in an adequate amount. Therefore, it is used as a starting component for the production of the main surfactant. Currently, by using these raw materials the properties of surfactants are also modified with great commitment.

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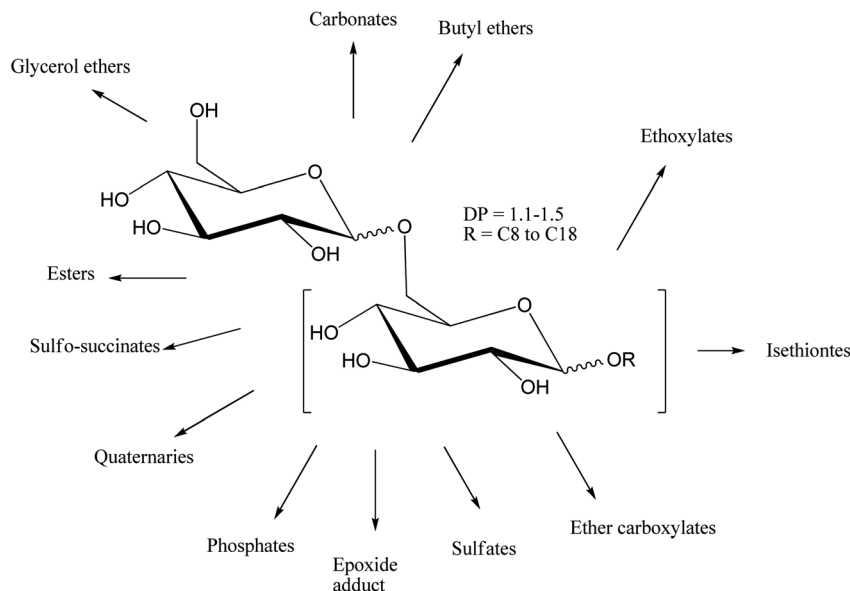
Alkyl polyglycoside derivatives are prepared by an easier mechanism such as nucleophilic substitution. Along with esterification or ethoxylation of alkyl polyglycosides, ionic

**Table 4** Green chemistry: twelfth principles applied to polyglycosides (Glucopon, Plantacare, and Plantaren types)

(1) Prevention	Optimistic reaction procedure with re-usage of excess fatty alcohols
(2) Atom economy	Highest utilization: reaction 100% – water >90%
(3) Less hazardous chemical synthesis	The method is secure; proven suitable tox and ECOTOX information
(4) Designing safer chemical	Replacement of ethylene oxide by glucose
(5) Safer solvent and auxiliary	No solvent rather than water
(6) Design for energy efficiency	Distillation of excess fatty alcohols under atmospheric condition; minimize the requirement of energy
(7) Usage of renewable feedstock	Starting compounds (glucose and vegetable fatty alcohol) are completely reusable
(8) Minimize derivative avoid blocking	No uses of the protection group
(9) Catalysis	Acids are applied in a catalytic amount
(10) Design for degradations	Aerobic and anaerobic degradations proven
(11) Pollution prevention through real-time analysis	Process management <i>via</i> process information system PI
(12) Accident-prevention based on inherently safer chemistry	The use of less fugitive raw material makes the process safe







**Scheme 8** Overview of alkyl polyglycoside derivatives. The scheme is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

products of sulphate, as well as phosphate, may also be prepared (Scheme 8). But till now, only a few products, such as methyl glucoside ester and some selective ionic derivatives of alkyl polyglycoside are established in the market.<sup>65-68</sup>

**3.3.2 Methyl glucoside esters.** We can get our desired products by treating methyl glucoside (which we can get from glucose or starch or methanol) with methyl esters or stearic or oleic acids and the corresponding polyethylene glycols, methyl glucoside esters are produced by subsequent ethoxylation (Scheme 9).

Unlike alkyl polyglycoside, methyl glucoside ester with the identical hydrophobic chain length is barely dissolved due to its lipophilic nature. However, they show excellent emulsification properties.<sup>36,69</sup> It is used as an emollient, emulsifying agent, thickener for cosmetic applicants, and moisturizer also. A

useful method for manufacturing methyl glucoside ester and its ethoxylated derivatives is treating Lubrizols with their Noveon lines. There are heavy market sizes of methyl glucoside including the ethoxylated products, *i.e.* around 10 000 tons per year (Table 2).

### 3.4. Alkyl polyglycosides with anionic derivatives

Chemicals, a division of Lamberti Spa in Italy, released three non-ionic polyglycoside esters – citrates, sulfosuccinates, and tartrates – for use in personal care products a few years ago.<sup>70</sup>

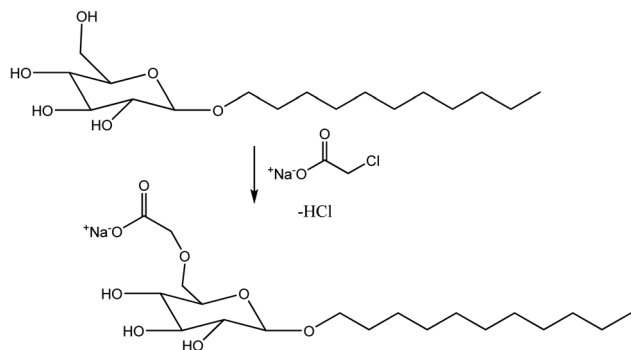
For their synthesis, alkyl polyglycosides are first prepared and then treated with citric acid, maleic anhydride, and tartaric acid, respectively.<sup>71</sup>

After the production of non-ionic polyglycoside esters, alkyl polyglycoside carboxylate, a new anionic surfactant, which is



**Scheme 9** Synthesis of methyl glucoside esters. The scheme is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.





**Scheme 10** Synthesis of alkyl polyglycoside carboxylate. The scheme is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

used in personal care cleansing applications, has been introduced to the market by Cogins. It is seen that this anionic derivative of alkyl polyglycosides shows better performance in personal care products than those non-ionic derivatives. The anionic surfactants have a relatively high tendency to form foam than non-ionic sugar-surfactants in shampoo and shower bath formulations. The sensorial effects are also better in body wash

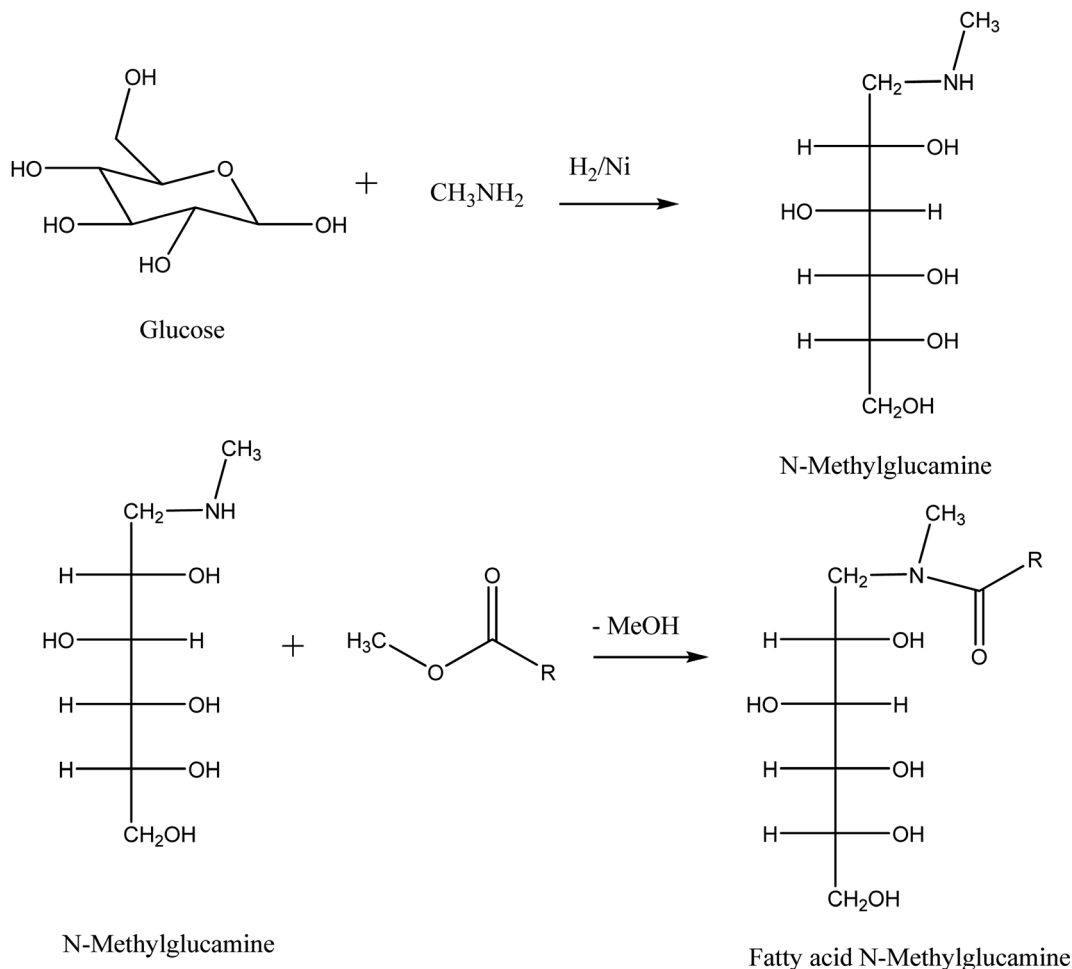
applications in the case of the anionic derivative. These advantages make the anionic derivative appropriate for many cosmetic products, for sensitive skin and hair. A new method is introduced by which these anionic derivatives can be made through an environment-friendly and cheaper procedure. This process is being carried out by treating sodium monochloroacetate with aqueous alkyl polyglycoside, and the speciality of the reaction is that it does not require any solvent (Scheme 10).<sup>72</sup>

### 3.5. Fatty acid glucamides

Fatty acid glucamides are produced *via* a two-step reaction. In the first step, glucose reacts with methylamine *via* reductive alkylation to produce *N*-methyl glucamine. A reaction with a fatty acid methyl ester converts *N*-methyl glucamine to the corresponding fatty acid amide in the second step.

Now, we have seen from the product that glucamides of fatty acids are made of one carbohydrate molecule linked with it.

This may be one reason for the less solubility of fatty acid glucamides and the tendency to crystallize smoothly from the aqueous solution. Scheme 11 depicts the manufacturing method for fatty acid glucamides. However, a problem arises



**Scheme 11** Synthesis of fatty acid glucamides in two steps. The scheme is reprinted with permission from ref. 27 copyright 1999 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.



during the process of manufacturing fatty acid glucamides. A large amount of *N*-methyl glucamine remains unreacted, which acts as precursors for nitrosamines.<sup>73</sup> To avoid this problem, Procter and Gamble have introduced an alternative method that deals with the reaction with acetic anhydride. By using acetic anhydride, secondary amines form corresponding acetates as the desired product.<sup>71,72,74,75</sup>

### 3.6. Carbohydrate raw materials used in the production of polysaccharide-based BSs

**3.6.1 Hemicellulose.** Recent progress of alkyl poly-pentosides has already been discussed. The product is associated with hemicelluloses, which when hydrolysed form a mixture of glycosides (exclusively pentose like arabinose and xylose). The pentoses react with fatty alcohol under suitable conditions and transform into desired alkyl poly-pentosides. It is reported that the products have similar properties to alkyl polyglycosides.<sup>76</sup>

**3.6.2 Inulin.** Inulin derivatives are examples of sugar-based polymeric surfactants, which act as emulsifiers in paint, coating, agrochemical, and also cosmetic industries. There are various polymers of fructose found in inulin. It is made up of chain-terminating glucosyl moieties and a repeating fructosyl moiety that are joined together by  $\beta$ -(2,1) bonds.

Chicory root is the main source of extraction for the commercial production of inulin. Researchers are also developing surfactant-type derivatives of it. Inulin derivatives are traded in the market as Inutec.<sup>77,78</sup>

### 3.7. Preparative/synthetic methods of sugar-based emulsifiers

**3.7.1 Sugar beet pectin.** Nowadays sugar beet pectin has been used to have good emulsification properties<sup>79–82</sup> and it has the potential to be utilized as a food emulsifier.<sup>83</sup> Hence, sugar beet pectin acts as a sugar-based emulsifier.

**3.7.2 Preparation of sugar beet pectin in the laboratory.** Fresh sugar beet pulp was utilized to extract pectin from sugar beets. To begin, cleaned roots of sugar beet (30.4 kg) were separated, hand-cut into strips, and chopped, then blanched for 5–10 min at 85 °C. During two hours of boiling at 60 °C, 20 l of water was suspended in the substance to recover its sugar content. Using a hydraulic piston press, the separated pulp was pressed at 15 bar, the press cake was swung in 40 liters of water at 70 °C, and the pH was lowered to 1.5 by adding diluted HNO<sub>3</sub>. After 2 hours of slow agitation at 70 °C, the extraction mixture was passed over the screen to separate the viscous liquid. Then, the pulp was washed 2 times with 8 l of water at 70 °C for 2 h each and pH 3 was achieved by adding 20% sodium carbonate solution to the filtrates, mixing, and centrifuging at 2500g for 15 min. A precoated vacuum plate filter was used to clarify the supernatant. Sodium cationic exchange resin was used to exchange the cations from the filtrate. Vacuum evaporation was used to concentrate the refined sugar beet pectin juice to ~2.5% pectin.

To isolate sugar beet pectin, three-volume portions of pure isopropyl alcohol were prepared and the mixture constant

agitation was carried out for one hour. The mixture was cleaned by separating sugar beet pectin from it using cotton canvas and then suspending it in 20% aqueous isopropyl alcohol. Overnight drying at 50 °C in a well-ventilated oven followed a second separation of the material. Using a 0.5 mm sieve, 335 g of sugar beet pectin was isolated after milling the dried pectin. Details about the various methods of preparation of sugar beet pectin can be found in the literature.<sup>84</sup>

## 4. Conclusion and future direction

Nowadays, it has been found that there is a tendency of consumers for claiming more plant-based natural cosmetics, food, and beverages. For this reason, scientists have focused on the classification, production, and application of natural emulsifiers such as bio-surfactants, mainly polysaccharides rather than synthetic ingredients. Some of those emulsifiers form tiny droplets of oil-in-water emulsions, which are stable in various circumstances and thus become appropriate for producing food and cosmetic products.

However, we still need to investigate and examine far more significant outcomes to successfully unveil several natural emulsifiers. The natural emulsifiers which have greater functionalities such as stability to freezing/thawing, protection of encapsulated components against the degradation of chemicals, or controlled release properties are very much effective in the food industry. From the above-mentioned points, we can conclude that a good natural emulsifier should be amphiphilic, so that it can stabilize emulsions, being adsorbed onto the surface of oil droplets. Therefore, each newly revealed natural emulsifier should be cautiously classified according to the above criteria.

It is noteworthy for this review that surface-active agents or surfactants are one type of emulsifier. Beyond this discussion, future scientific research is additionally needed to spot, isolate, purify, and characterize new forms of natural emulsifiers, and to check their efficacy in cosmetics, detergent, food, and other products.

## Author contributions

The project was conceived by Aniruddha Pal, Monohar Hossain Mondal, and Bidyut Saha. The manuscript was written by Aniruddha Pal, Monohar Hossain Mondal, Ajaya Bhattarai, and Bidyut Saha and edited by Achyut Adhikari. The manuscript was revised several times by Bidyut Saha, Achyut Adhikari and Ajaya Bhattarai.

## Conflicts of interest

The authors declare that there is no conflict of interest.

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