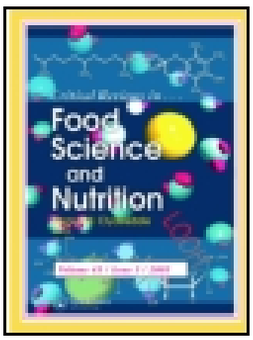

Critical Reviews in Food Science and Nutrition

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/bfsn20

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To cite this article: Yinglai Teng , Scott G. Stewart , Yao-Wen Hai , Xuan Li , Martin G. Banwell & Ping Lan (2020): Sucrose fatty acid esters: synthesis, emulsifying capacities, biological activities and structure-property profiles, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2020.1798346

To link to this article: https://doi.org/10.1080/10408398.2020.1798346

Published online: 04 Aug 2020.

CRITICAL REVIEWS IN FOOD SCIENCE AND NUTRITION
https://doi.org/10.1080/10408398.2020.1798346

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REVIEW

Sucrose fatty acid esters: synthesis, emulsifying capacities, biological activities and structure-property profiles

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ABSTRACT

The notable physical and chemical properties of sucrose fatty acid esters have prompted their use in the chemical industry, especially as surfactants, since 1939. Recently, their now well-recognized value as nutraceuticals and as additives in cosmetics has significantly increased demand for ready access to them. As such a review of current methods for the preparation of sucrose fatty acid esters by both chemical and enzymatic means is warranted and is presented here together with an account of the historical development of these compounds as surfactants (emulsifiers). The somewhat belated recognition of the antimicrobial, anticancer and insecticidal activities of sucrose esters is also discussed along with a commentary on their structure-property profiles.

KEYWORDS

Biological activities; chemical and enzymatic synthesis; emulsifying properties; esterification and transesterification; structure-property profiles

Introduction

The disaccharide sucrose (*β*-D-fructofuranosyl α-D-glucopyranoside), commonly called table sugar, is obtained from various plant sources, is easily refined and is marketed world-wide. Global production of this compound reached *ca*. 180 million metric tons in 2016/2017 (Canadian Sugar Institute 2019a). Direct consumption (as a food) accounted for most of the demand but sucrose is also employed as a starting material in the production of emulsifying agents, detergents, artificial sweeteners and various other derivatives (Human Metabolome Database 2019). Sucrose, which is photosynthesized by almost every green plant but is most readily derived from sugarcane and sugar beet (Canadian Sugar Institute 2019b), is also exploited in the production of ethanol and certain fine chemicals (Deneyer, Ennaert, and Sels 2018) including sucrose fatty acid esters (Neta, Teixeira, and Rodrigues 2015).

Sucrose fatty acid esters, as with esters more generally, are formally derived from the constituent alcohol (*viz*. sucrose) and (naturally occurring) fatty acid. Notable commercially available forms of such esters include the mono-esters derived from, *inter alia*, steric acid, palmitic acid, lauric acid, oleic acid, erucic acid and myristic acid. These esters, which frequently come as admixtures with various of their di-, tri- and tetra-acylated counterparts (Mitsubishi Chemicals 2019; Sisterna 2019a; Sisterna 2019b), have excellent emulsifying properties as well as a range of other useful physical properties that follow from their amphipathic nature (Szuts et al. 2010; Farrán et al. 2015; Soultani et al. 2003). Importantly, such nonionic surfactants are considered green because they are both nontoxic and biodegradable. Furthermore, both the constituent sucrose and fatty acid residues are inexpensive and renewable agricultural products (Szuts et al. 2010; Farrán et al. 2015; Soultani et al. 2003). These various attributes mean that sucrose esters have become profoundly important commodity chemicals in the food (common ingredient number E473, according to Food Standards Agency 2018), nutraceutical, cosmetic, dental and pharmaceutical industries (Szuts et al. 2010; Farrán et al. 2015; Soultani et al. 2003). Even a decade ago, the world production of sucrose esters was estimated to be above 6000 t/year and these were selling for 4 to 20 USD/kg. While mainly employed as food additives, they also feature in the manufacture of cosmetics, pharmaceuticals and detergents (Otomo et al. 2009). In 2015 the global sucrose ester market was valued at USD 55.7 million and projected to reach USD 74.6 million in 2020 (MarketsandMarkets 2019b). Key manufacturers of these now much sought-after community chemicals include Mitsubishi-Kagaku, Croda, Dai-ichi-Kogyo Seiyaku, Goldschmidt, Sisterna, Weixi Spark, Evonik Industries and BASF (Hill and Rhode 1999; Cruces et al. 2001; MarketsandMarkets 2019a; Parker, Khan, and York 1973).

The methods of synthesis of sucrose-based esters was the subject of a concise review in 2001 (Polat and Linhardt 2001) and surveys of enzymatic approaches have followed (Shi, Li, and Chu 2011; Gumel et al. 2011). In the present article we delineate both industrial and laboratory-based

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Table 1. Composition of commercial sucrose esters as determined by Plou and coworkers (Cruces et al. 2001).

		Composition (by wt.%)		
Compound	Source	Sucrose	Mono-esters	Di-esters
Sucrose caprylate	Calbiochem	2	95	3
Sucrose caprate	Sigma	5	93	2
Sucrose laurate	Fluka	2	95	3
Sucrose laurate L70-C	Sisterna	11	50	39
Sucrose laurate L-1695	Mitsubishi-Kagaku	2	77	21
Sucrose laurate L-595	Mitsubishi-Kagaku	0	27	43
Sucrose myristate M-1695	Mitsubishi-Kagaku	1	77	22
Sucrose palmitate P-1670	Mitsubishi-Kagaku	0	64	22
Sucrose palmitate P-1570	Mitsubishi-Kagaku	0	59	29
Sucrose palmitate P-170	Mitsubishi-Kagaku	2	88	10
Sucrose palmitate	Sigma	9	65	26
Sucrose stearate S-1670	Mitsubishi-Kagaku	0	54	20

processes for the formation of the title esters that have emerged in the intervening period. In addition, a commentary on the emulsifying properties as well as the antimicrobial, antitumor and insecticidal activities of these important esters is provided. Structure-property profiles arising from an examination of these follows.

Chemical synthesis

Many simple esters are prepared by esterification under Fischer-type conditions from the relevant acid and alcohol but sucrose esters are not readily formed by such direct means (Parker, Khan, and Mufti 1976). This is because sucrose undergoes glycosidic bond cleavage under the necessary conditions (*viz.* at pH 2–3 and 70–80 °C) and so producing a mixture of glucose and fructose (which is called inverted or invert sugar) (Soares et al. 2019). Accordingly, the industrial production of sucrose esters normally involves the transesterification of fatty acid esters with sucrose and so circumventing the need to employ strongly acidic conditions (Parker, Khan, and Mufti 1976).

Establishing a single-step, inexpensive and regioselective chemical synthesis of sucrose fatty acid esters is particularly challenging given there are eight distinct hydroxyl groups associated the parent carbohydrate (Queneau et al. 2008). The per-ester sucrose octaacetate was prepared as early as 1880 by Herzfeld (1880) and in 1939 Cantor (1939) patented a method for forming sucrose fatty acid esters from starch factory by-products and simultaneously claimed that such products could be used as emulsifying agents or fats. Of course, there are many possible esters (255 in fact) available by combining, through esterification, any given acid with sucrose, including 8 mono-esters, 28 di-esters, 56 tri-esters and so on (Weiss et al. 1971). Given the mono-esters of sucrose are the most desirable as emulsifiers because of their generally more appropriate HLB values (see below) (Polat and Linhardt 2001), methods for the selective production of these have been the focus of considerable attention. Of the eight distinct hydroxyl groups embodied within sucrose it has been established, unsurprisingly perhaps, that acylation occurs preferentially at the primary ones and with some selectivity being observed between these, *viz.* at the 6-OH (glucose unit), then at the 6′-OH (fructose unit) and, finally, at the 1′-OH (fructose unit) positions (Haines 1976). However, the difference in reactivity of these centers is not such that mono-esterification is readily achieved and a detailed evaluation of the composition of sucrose esters from various commercial sources (Table 1) emphasizes this point (Cruces et al. 2001). In this study a large variation in mono- and di-ester ratios was observed, a feature that reflects the differing synthetic protocols used to make these compounds as well as the potential for equilibration between certain of them. Related studies are notable for their use of quantitative GC and HPLC techniques to achieve the separation of the component esters and the often effective detection of these using evaporative light scattering (ELS) and/or refractive index techniques (Moh, Tang, and Tan 2000).

Current industrial syntheses

Methods for the large (industrial) scale production of sucrose esters traditionally involves the transesterification of sucrose using a suitable triglyceride, a process normally conducted in the presence of a catalyst such as potassium carbonate or a potassium soap. *N*,*N*-Dimethyformamide (DMF) is the often used solvent (Parker, Khan, and York 1973) but given its cost, toxicity and other safety issues, reactions employing DMSO have also been explored. Under favorable circumstances, mixtures comprising greater than 50% sucrose mono-ester can be obtained with the remaining components being other esters and the starting materials (Figure 1) (Polat and Linhardt 2001). Challenges remain, however, since removal of these high-boiling solvents (153 °C for DMF and 189 °C for DMSO) (Royal Society of Chemistry 2019) is a non-trivial matter and compounded by the relatively low thermal stability of the product esters. The necessary separation of by-products, so as to raise the mono-ester component to levels acceptable to the market (Gutiérrez et al. 2018), is problematic and also creates waste streams and so increasing production costs. Sucrose mono-esters have also been produced industrially from fatty acid methyl esters using reversible transesterification process with attendant removal of co-produced methanol so as to drive the reaction forward. Under the optimal conditions this protocol can provide material containing upwards of 70% of the mono-ester (Polat and Linhardt 2001).

Solvent-free processes have also been developed and used in industry. So, for example, in 1970, Feuge et al. (1970) found that the so-called interesterification of a suitable fatty acid methyl ester with molten sucrose in the presence of catalytic quantities of soap (usually a potassium soap) at 170–185 °C can produce the required mono-esters. However, this approach has drawbacks since at the required (elevated) temperatures sucrose only remains a liquid for brief periods (several minutes) and when reduced pressures are applied to remove the co-formed methanol then degradation of the sugar occurs as evidenced by the significant darkening of the reaction mixture. This impacts on both throughput and product quality while the need to remove the catalyst adds further technical difficulties (and attendant financial burdens). Another solvent-free and large-scale process was developed by Parker, Khan, and York (1973) and wherein

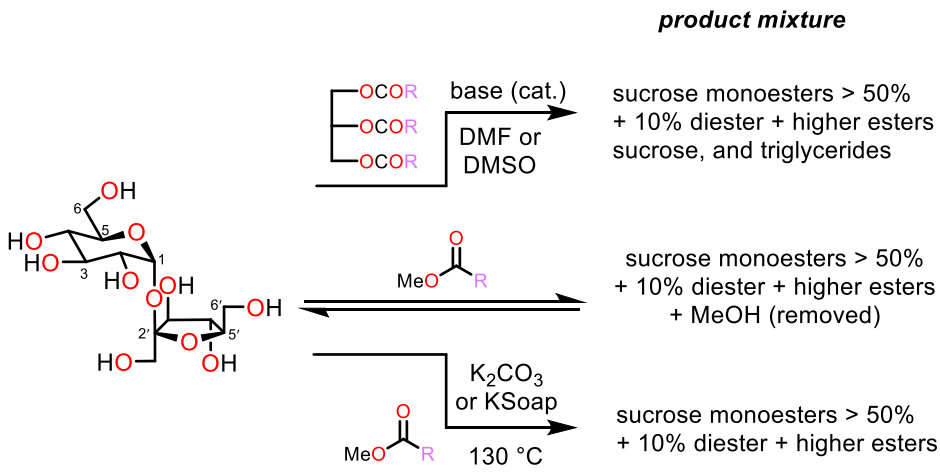

Figure 1. The most common methods used for the industrial preparation of sucrose mono-esters (Parker, Khan, and York 1973; Polat and Linhardt 2001).

fine particles of sucrose are reacted with triglycerides (in the form of oils such as tallow, palm oil or coconut oil) in the presence of catalytic amounts of potassium carbonate. In this way, the reaction can be performed at atmospheric pressure and temperatures of around 125 °C. Furthermore, the reaction can be accelerated by adding emulsifiers (*e.g.* a diglyceride). However, under such conditions a mixture of sucrose esters and glycerides is formed. While attractive in principle, the challenges (as mentioned above) attending the solvent-free production of sucrose mono-esters mean that DMF continues to be employed, as a matter of course, in many commercial processes.

Laboratory-scale syntheses

Nature and selectivity of acylating agents

Approaches to sucrose esters that avoid traditional and normally ineffective (see above) Fischer esterification approaches (Figure 2a) abound but it is clear that pure mono-ester formation cannot be achieved by simply controlling the fatty acid ester stoichiometry in transesterification reactions (Figure 2b). Furthermore, acyl group migration can occur during the course of such reactions and/or during isolation and thus introducing additional components into the product mixture (Queneau, Fitremann, and Trombotto 2004). Sucrose ester syntheses using acyl chlorides (Figure 2c) have been studied with, for example, the esterification of sucrose by octanoyl chloride at pH 10 shown to provide mixtures of mono-octanoates, di-octanoates and tri-octanoates. By employing 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as an acylation catalyst under dilute conditions, and by exploiting hydrophobic effects, greatly enhanced proportions of mono-octanoates can be obtained (Thévenet et al. 1997). However, the need to strictly control the water content of the reaction medium while using such protocols as well as the high cost of catalysts such as DMAP mean they are likely to be less attractive in industrial settings (Kea, Walker, and Kline 1987; Thévenet et al. 1999).

A range of replacements for acid chlorides as the acylating agent, including acid anhydrides and enol esters, has been explored. So, for example, the Plusquellec Group effected regioselective acylation at the 6′-OH group of sucrose using various 3-acyl-5-methyl-1,3,4-thiadiazole-2(3*H*)-thiones (Figure 2d) in conjunction with diazobicyclo-[2.2.2]octane (DABCO) (as base) at low temperature and DMF as solvent (Chauvin and Plusquellec 1991). Intriguingly, the same group found that by using 3-acyl-thiazoledine-2-thiones in the presence of NaH then a higher yielding reaction took place and now at the C2-OH group of sucrose (Chauvin, Baczko, and Plusquellec 1993). The Queneau Group completed a detailed study on the distribution of sucrose mono-acylation products obtained on using *N*-decanoylthiazolidinethione (Figure 2d) and various homologues as electrophiles (Molinier et al. 2003). Dipotassium hydrogenophosphate proved to be an effective base in these cases and it was concluded that *N*-acylthiazolidinethiones are better acylating agents than cyanoethyl-, methylthioethyl- and methyl-esters. In another study, 6-*O*-acylated sucrose derivatives were accessed in a highly selective manner through reaction (in DMF) of the parent sugar-derived dibutylstannylene acetal dimers with fatty acid anhydrides (Vlahov, Vlahova, and Linhardt 1997; Bazin, Polat, and Linhardt 1998). Subsequently the same sorts of intermediates were used to regioselectively produce 6-*O*-acylsucroses and 6,3′-di-*O*-acylsucroses (Wang, Zhang, and Yang 2007) but such attractive outcomes are offset by the possibility of product contamination by toxic tin residues. The three-fold benzoylation of sucrose using benzoyl chloride in the presence of pyridine has been shown to occur selectively at the 6-*O*, 1′-*O* and 6-*O* positions although various other tri-benzoates and certain tetra-benzoates are also produced (Clode et al. 1985).

Irreversible transesterification reactions involving vinyl esters (Figure 2d) provide a unique approach to the formation of sucrose mono-esters with vinyl acetate having been used to acetylate sucrose. This reaction was reported to take place in water under basic conditions at slightly elevated temperatures although the regioselectivity of the process is not clear (Smith and Tuschhoff 1957). In 2001, Plou et al. reported the transesterification of sucrose using vinyl caprylate, laurate, myristate or palmitate under strictly anhydrous conditions in DMSO with Na_2HPO_4 serving as the catalyst (Cruces et al. 2001). By such means, remarkably high yields

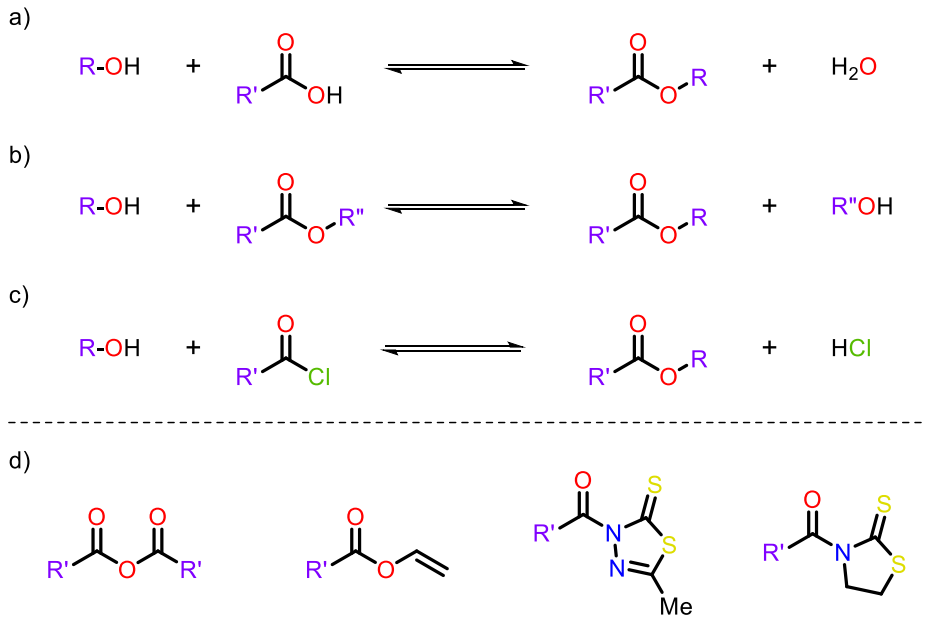

Figure 2. Procedures used for the production of sucrose esters: (a) esterification; (b) transesterification; (c) acyl chloride-based esterification and d) examples of traditional and modern acylating agents (Chauvin and Plusquellec 1991; Chauvin, Baczko, and Plusquellec 1993; Molinier et al. 2003).

(86–97%) of product mixtures rich in mono-esters (90–94 wt.% as determined by HPLC) were realized, an outcome that compared favorably with industrial processes in operation at the time. The predominant product of such reactions was the 2-*O*-acylated material but the co-production of its 3-*O*-acyl counterpart, arising through acyl group migration, could not be avoided.

Much research into "solvent-free" transesterification reactions has focused on the "solubility" of sucrose in the product ester over the temperature range of 40–140 °C with substrate decomposition only becoming evident above this upper limit. Notably, the solubility of sucrose in the methyl esters of various fatty acids was observed to increase from 0.25 to 1.40 g/100 g following addition of 2.5 wt.% sodium stearate and even more so in presence of the surfactant S1570 (Zhao et al. 2014).

Selective di-esterification at the 6-*O* and 6′-*O* positions of sucrose can be achieved using gallic acid as the nucleophile under Mitsunobu conditions (Potier et al. 1999). In these cases it is assumed that the surcrose-derived oxyphosphonium ion, prepared using PPh_3 and DIAD, undergoes nucleophilic displacement (and the product esters were examined for their capacities to serve as antioxidants). Other Mitsunobu-based approaches have provided 6-*O*-palmitoylsucrose (47% yield) (Bottle and Jenkins 1984) and the corresponding 6-*O*-polyfluoroalkanoates (Abouhilale, Greiner, and Riess 1991). 6-*O*-Acyl-3′,6′-anhydro- and 6-*O*-acyl-3′,4′-anhydro-sucroses have been formed as by-products during the esterification of unprotected sucrose by related means (Molinier et al. 2004). These epoxide-containing compounds can also be formed deliberately by using Mitsunobu protocols (Guthrie, Jenkins, and Yamasaki 1980).

The esterification of sucrose and certain of its congeners through coupling with activated sulfonic acid derivatives has also been the subject of several studies and variations in the reaction conditions provide complementary outcomes in terms of regioselectivity (Bazin, Polat, and Linhardt 1998; Kowalski, Cmoch, and Jarosz 2014; Wuts and Greene 2006; Buchanen and Cummerson 1972; Teranishi 2002). Thus, sucrose 2-*O*-*p*-toluenesulfonate can be obtained under one set of conditions, while modest changes to these provides access to the 6-*O* or 6′-*O* regioisomers (Teranishi 2002).

The effect of bases

As suggested by the outcomes of certain of the reactions described above, the choice of base employed in sucrose esterification reactions can have a significant influence on the yield of such processes. While both NaOH and KOH can be useful for such purposes, in water and other protic solvents their use leads to saponification of the desired ester. As such they are only effective under strictly anhydrous conditions, a requirement that limits their utility in industrial settings. The milder potassium carbonate is a more suitable catalytic base with a recent study of its application in the esterification of sucrose using coconut esters in DMF focusing on quantitating the most effective molar ratio of sucrose to fatty acids, catalyst concentration, solvent volume, reaction temperature and viscosity (Deshpande et al. 2013). Sonication has been explored as a means for promoting the esterification of sucrose and under appropriate conditions good yields of mixtures of sucrose mono-esters can be obtained. For example, the (trans)esterification of sucrose in DMSO at 70 °C using ethyl palmitate and K_2CO_3 was achieved in 73% yield to give a product mixture containing 92% of a *ca.* 2.5:1 mixture of the 6-*O*- and 6′-*O*-acylated mono-esters (Huang et al. 2010a). Related transesterifications employing K_2CO_3 in methanol have been reported (Vassilev et al. 2016).

Combinations of the acetylating agent *N*-decanoylthiazolidinethione and various carbonates such as K_2CO_3, Li_2CO_3 and Cs_2CO_3 or phosphates (*e.g.*, K_2HPO_4) have been trialed

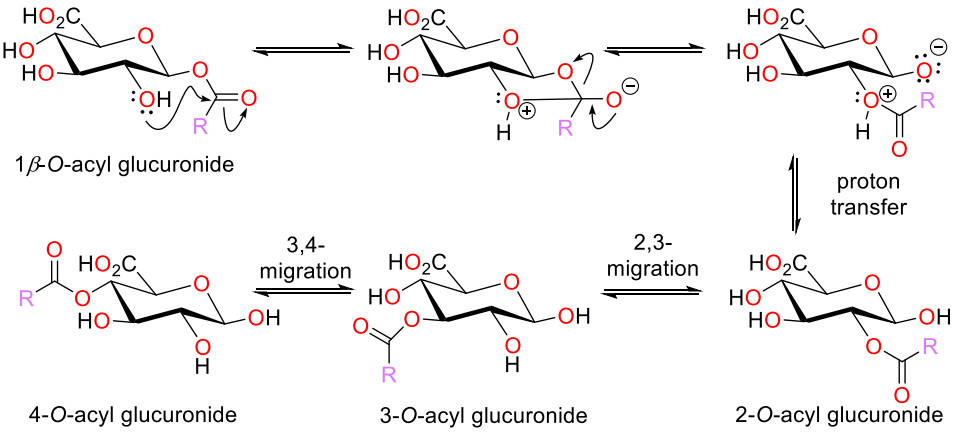

Figure 3. Acyl migration processes observed within the glucuronide framework (Akira et al. 1998).

at ambient temperatures for effecting the esterification of sucrose. A 71% yield of the 2-*O*-acylated mono-ester was achieved using two equivalents of K_2HPO_4 while various mixtures of the 3-*O*, 3′-*O* 4-*O* (diester), 2-*O*, 4′-*O*, 6-*O* and 1′-*O*, 6′-*O* congeners were also observed with the precise distribution being dependant on the base used (Molinier et al. 2003). Some preference for formation of the 2-*O*, 3-*O*-, and 6-*O*-alkanoyl sucroses was seen. So when, for example, lithium carbonate was employed selective esterification at the 2-OH group was observed.

Acyl migration methods and sucrose ester stability

Both inter- and intra-molecular acyl migration protocols, *viz*. transesterifications, play a pivotal role in the derivatization of carbohydrates including sucrose. NMR techniques involving ^{13}C-labeled substrates have been used to study acyl group migrations within 1β-*O*-acyl glucuronides (Figure 3) (Akira et al. 1998) and, as might be expected, such migrations most likely involve intramolecular nucleophilic attack by the adjacent hydroxyl group at the carbonyl moiety and, thereby, formation of a tetrahedral intermediate that itself collapses to form the migrated product. Depending upon its strength, added base can facilitate migration through acceleration of one or other of the discrete steps shown in Figure 3 and under suitable conditions such acyl migrations can provide a useful means for obtaining single regioisomeric forms of carbohydrate mono-esters. Since 6-*O*-acylated sucroses and their 1′-*O* and 6′-*O* counterparts are the most stable of the eight possible mono-esters (Molinier et al. 2003), these can be prepared by treating, for example, the isomeric 2-*O*-acylsucroses with a (hindered) organic base and so effecting *O*-acyl migration in up to 60% yield. Such processes have been exploited to prepare both 6-*O*-octanoylsucrose and 6-*O*-stearoylsucrose (Baczko et al. 1995). In an extensive study of the isomerization of 3-*O*-monolaurate sucrose acyl under basic conditions, the rate of migration from the 3- to the 6-position was found to accelerate in the presence of water both during the aqueous workup and under the HPLC conditions used for analysis (Molinier et al. 2003). Notably, no significant isomerization of the substrate occurred when this was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the absence of water.

While acyl migrations from the 2-*O* to the 3-*O* positions are reversible, at equilibrium the 3-*O*-ester is normally favored (Cruces et al. 2001; Baczko et al. 1995). Migration from the 3-*O* to the 6-*O* position can be observed and a detailed study involving the use of various acylating agents, including acid chlorides and alkyl chloroformates, established that a range of factors, including steric ones, impact on mono-ester product distributions (Thévenet et al. 1999). If appropriate control of various physical and chemical parameters is attained then pure mono-esters can often be generated.

Summary

While various laboratory-scale protocols have been established for the reliable and selective production of sucrose mono-esters, the translation of these into industrial settings is challenging, not least because solvents such as pyridine cannot be used in the food industry while acylating agents such as acyl chlorides and vinyl esters are prohibitively expensive and/or are environmentally disadvantageous. Such issues have attracted the recent attention of various academic groups who acknowledge industrial imperatives and have thus pursued the use of enzymes to prepare sucrose esters. The nature and outcomes of such studies are now discussed.

Enzymatic syntheses

Enzyme-catalyzed syntheses of sucrose esters offer a pathway to higher purity forms of these products as a result of their enhanced regioselectivities. Furthermore, these biocatalytic processes are generally environmentally-friendly ones because of the mild conditions involved and the nontoxic nature of the (often aqueous) media involved (Franssen et al. 2013). To date, however, no commercial sucrose ester production process appears to exploit this enzyme-based approach, not least because of the associated costs and the need for these to be run in batch rather than flow mode (Satyawali, Vanbroekhoven, and Dejonghe 2017). Both lipases and proteases can be used for the esterification of sucrose (Chang and Shaw 2009). The associated processes have also been employed extensively for the production of

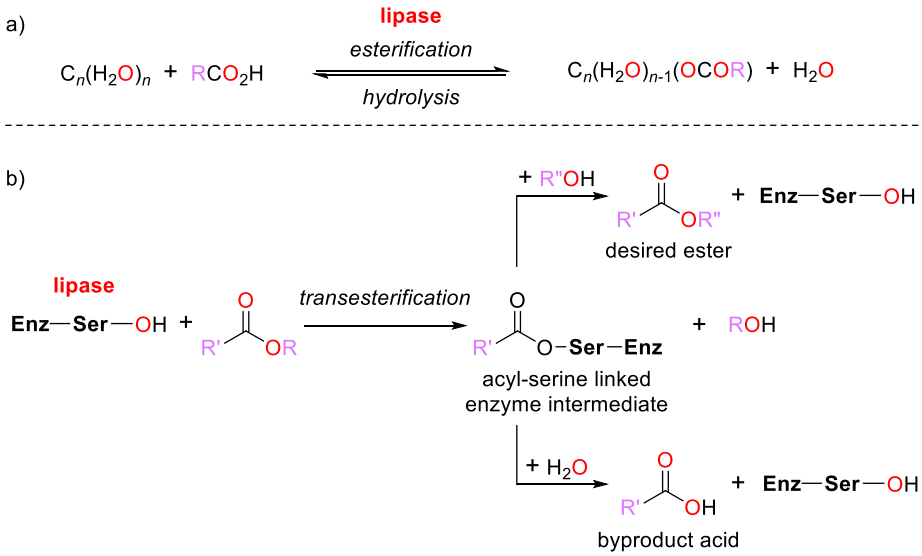

Figure 4. (a) Lipase esterification of carbohydrates and hydrolysis of carbohydrate esters (Neta, Teixeira, and Rodrigues 2015); and (b) the "bi-bi ping-pong" transesterification mechanism (Reyes-Duarte et al. 2005).

other sugar esters, including lactose monolaurate (Walsh et al. 2009). Detailed studies of such transformations, some outcomes of which are discussed in the following sections, reveal that the nature of the solvent, the water content of the medium and the temperature as well as the method of mixing are often crucial. Such requirements are dictated by the need to retain/preserve/protect the enzyme active site (*viz*. to avoid denaturing of the enzyme).

Lipases

Lipases are a group of esterases that catalyze the hydrolysis of lipids and such enzymes are comprised of several subclasses including phospholipases and acylglycerol lipases (Schomburg et al. 2017). In the present context, the most important lipases are, arguably, the triacylglycerol lipases (EC 3.1.1.3) that selectively hydrolyze insoluble triacylglycerols at the substrate-water interface (BRENDA 2019b). As such these lipases, especially immobilized forms, have found a multitude of applications in industry particularly for flavor and biodiesel production as well as in the treatment of waste water (Filho, Silva, and Guidini 2019). Various lipases have also been used for the laboratory-scale preparation of sucrose esters, including certain commercially available and immobilized ones such as Lipozyme TL IM (a lipase derived from the thermophlic fungus *Thermomyces lanuginosus*, formally *Humicola lanuginosa*) (Ferrer et al. 2005) and Novozym 435 (derived from the yeast *Candida antarctica* B) (Shao et al. 2018; Ye, Hayes, and Burton 2014).

Generally, when a lipase is hydrated then only small amounts of water need be present in the reaction medium so as to ensure its catalytic viability (Goderis et al. 1987). On the other hand, since lipases function in equilibrium (Figure 4a), hydrolysis of the product ester can occur even when anhydrous (organic) solvents are employed (Gumel et al. 2011). Thus, determining the optimal water content of the reaction medium is a major consideration in any associated methodological studies (Chamouleau et al. 2001; Gumel et al. 2011). Unlike many enzymes that follow Michaelis–Menten kinetics, lipase acyl-transfer reactions are thought to proceed through a "bi-bi ping-pong mechanism" (Figure 4b) with competitive substrate inhibition being caused by the alcohols used as acyl acceptors (Martinelle and Hult 1995; Reyes-Duarte et al. 2005).

Solvent effects

Lipases remain viable at low concentrations in a range of organic solvents including *n*-hexane, DMSO, methanol, xylene and cyclohexane (Salihu and Alam 2015). So, for example, Novozym 435 has been deployed in the preparation of long-chain long fatty acid esters by treating sucrose with the relevant acylating agent in a mixture of DMSO and 2-methyl-2-butanol as so to produce sucrose palmitate (Reyes-Duarte et al. 2005). While the use of DMSO facilitates dissolution of the sugar, it can impact negatively on the enzyme activity although this can be overcome by using higher concentrations of the acyl donor and/or by employing, for example, vinyl palmitate as a reactant and thereby rendering esterification irreversible. This last tactic significantly broadens the applicability of such enzymes across a range of reaction and substrate types.

The capacities of ionic liquids (ILs) to solubilize both polar and non-polar species provides unique possibilities for simultaneously dissolving both sucrose and fatty acid esters and thereby facilitating reaction between them. Given their green "credentials" (Otomo et al. 2009; Anastas and Warner 1998), thermal stabilities, salt-like properties in the liquid state (and that often occurs at room temperature) (Welton 1999), good specific conductivities and negligible vapor pressures, ILs have been exploited in a multitude of settings (Johnson 2007). They are noted for their abilities to dissolve biomass components (Singh 2019) and have been employed as solvents in reactions involving lipases (Itoh 2017) and so exploited in the preparation 6-*O* and 6α-*O*-linoleyl-α-D-maltose (Fischer et al. 2013).

There have been various reports of the enzyme-catalyzed synthesis of sugar fatty acid esters in ionic liquids (Yang and Huang 2012). However, only a few of these have focused on sucrose ester formation, probably because of the low solubility of sucrose in conventional ILs and/or the enzyme denaturing properties of such solvents (Shi, Li, and Chu 2011). As part of efforts to circumvent these difficulties, the Sheldon group (Liu et al. 2005) established that the solubility of sucrose in [BMIm][dca] is 195 g/L at 25 °C and 282 g/L at 60 °C. Furthermore, they revealed that this IL can be used in the Novozym 435-catalyzed acylation of sucrose by dodecanoic acid at 55 °C. In related work, Huang et al. studied the enzymatic preparation of 6-*O*-lauroylsucrose by reaction of sucrose with lauric acid vinyl ester and concluded that by deploying Lipozyme TL IM in [BMIM]BF_4 the target ester could be obtained in 50% yield (Huang et al. 2010b). Shao et al. (2018) reported a synthesis of the same sucrose mono-ester in a 1.5:1 v/v mixture of [3CIM(EO)][NTf_2] and 2-methyl-2-butanol and so affording the product in 66% yield, a pleasing outcome attributed to the capacity of this IL to maintain the high activity of the lipase and to enhance the solubilities of the substrates.

Supercritical CO_2 has also been exploited as a solvent in various lipase-catalyzed biotransformations (Knez 2018). So, for example, an immobilized lipase from *Candida antarctica B* (EC 3.1.1.3) was used in supercritical CO_2 at 10 MPa to produce sucrose palmitate and sucrose laurate (Habulin, Šabeder, and Knez 2008). The addition of molecular sieves to that reaction affording sucrose laurate from equimolar amounts of the fatty acid and sucrose at 60 °C resulted in a 74% conversion. The non-toxic and non-flammable nature of CO_2 means these types of reactions are considered amenable to the industrial preparation of food additives.

Yields and selectivity

Recent reports have revealed that the regioselective production of sucrose esters can be effected in 40–90% yield using the lipases derived from *Bacillus thermoproteolyticus*, *Candida antarctica*, *T. lanuginosus*, *Bacillus pseudofirmus AL-89* and *Bacillus subtilis*. However, in order to realize these outcomes acylating agents such as vinyl esters and anhydrides are required. Interestingly, essentially quantitative yields of a product sucrose ester were achieved using 2,2,2-trifluoroethyl butyrate as the acyl donor in conjunction with the *Bacillus* protease *Bioenzyme 240*. When pyridine was used as the solvent this combination of reactants produced 1′-*O*-butyryl sucrose (Patil, Rethwisch, and Dordick 1991). Lipases were less effective. Significantly, lipases derived from *Rhizomucor miehei* have been used to effect the high-yielding formation of sugar mono- and di-esters with simple carboxylic acids serving as the acyl donors (Dang, Obiri, and Hayes 2005; Ye, Pyo, and Hayes 2010).

The selective acylation at the 6-*O* and 6′-*O* positions of sucrose is often observed when lipases are employed for this purpose (Shi, Li, and Chu 2011) although other less-common enzymes allow for alternative outcomes. Plou's group reported the preparation of 6-*O*-lauroylsucrose and 6-*O*-palmitoylsucrose (Ferrer et al. 1999) through acylation of sucrose using mixed-solvent combinations and lipases derived from various species but most notably an immobilized form obtained from *Humicola lanuginosa Candida rugosa* lipase (CRL) has also been used in transesterification studies for the formation of sucrose-6-*O*-acetate with various reaction parameters, including temperature, concentration and pH, being examined and so leading to the identification of an effective two-phase system comprising 2-butanol and Tris-HCl buffer at an initial pH of 8.60 and a temperature of 47 °C. Under such conditions the target mono-acetate was obtained in 57% yield (Zhong et al. 2013).

Reaction parameters

The Hayes' group has reported detailed studies on the use of the immobilized lipase derived from *Rhizomucor miehei* (*viz.* Lipozyme IM *ex.* Novozymes) for preparing sucrose esters and by such means a 9:1 mixture of mono- and di-esters was obtained in 80–93% combined yield when oleic acid was employed as the acyl donor (Dang, Obiri, and Hayes 2005). Notably, only small quantities of solvent (*tert*-butanol) were required during the early stages of the reaction and after a 25% conversion had been realized the product sucrose ester served as the reaction medium. The same enzyme and protocols were used for the esterification of sucrose and fructose with oleic acid. The reaction took 6 days and led to a liquid phase consisting of an 11.5:1 mixture of mono- and di-esters in 88% combined yield (Ye, Pyo, and Hayes 2010). Similarly high yields were realized using acetone or methyl ethyl ketone (butanone) instead of *tert*-butanol or, alternatively, using carefully defined mixtures of oleic acid and fructose or sucrose.

Both *Rhizomucor miehei* and *Candida Antarctica*-derived lipases have been used in esterifications under conditions involving high-speed homogenization and high-intensity ultrasonication of the reaction mixtures. These conditions were found to be effective in reducing the size of sucrose particles in a solvent-free synthesis of sucrose oleate (Ye, Hayes, and Burton 2014). It has also been observed that pre-incubation of *C. Antarctica* lipase B (CALB) in oleic acid at 60 °C for 24 h enhances the initial rate of enzymatic esterification. Moreover, the synthesis of sucrose esters using either acrylic resin or chitosan immobilized CALB in conjunction with oleic acid, sodium sulfate and ethanol, delivered product yields of 56 and 55%, respectively (Neta et al. 2012).

A lipase derived from *T. lanuginosus* and its immobilized form, Lipozyme TL IM, have also been used to produce 6-*O*-lauryl sucrose from vinyl laurate. Thus, Ferrer et al. (2002b) prepared a silica-granulated lipase (particle size around 0.3–1 mm) obtained from *T. lanuginosus*, and this so immobilized enzyme allowed for the synthesis of sucrose mono-laurate in > 95% yield when a mixture 4:1 v/v *tert*-amyl alcohol and DMSO was deployed as the solvent system at 40 °C and sucrose added to the reaction mixture in portions. The capacity to recycle this enzyme is highlighted by its ability to continue to effect this reaction in 80% yield over 20 cycles, each of which lasts *ca.* 6 h (Ferrer et al. 2005). The regioselective synthesis of 6-*O*-palmitoylsucrose

Table 2. Commercial enzymes used in the preparation of sucrose esters.

Enzyme	Other Names
Lipase (*Thermomyces lanuginosus*, previously *Humicola lanuginosa*) (Ferrer et al. 2005)	Lipozyme® TL IM (Shao et al. 2018)
Lipase (*Candida Antarctic* B)	Novozym 435® (Ye, Hayes, and Burton 2014)
Lipase (*Rhizomucor miehei*)	Lipozyme IM® (Dang, Obiri, and Hayes 2005; Ye, Pyo, and Hayes 2010)
Lipase (*Candida rugosa*)	CRL (de Maria et al. 2006)
Serine protease subtilisin (*Bacillus licheniformis*)	ChiroCLEC-BL (Polat, Bazin, and Linhardt 1997); Protex 6L (Wang et al. 2012); Subtilisin A, Subtilopeptidase A, Novozymes Alcalase® (Rawlings et al. 2018); Subtilisin Carlsberg (Delange and Smith1968)

catalyzed by Lipozyme TL IM in a continuous flow microreactor has been reported (Du and Luo 2012) and involves using silicone tubing (inner diameter 2.0 mm) with a Y-shaped junction at the start point that is packed with silica spheres (0.3–0.9 mm) carrying surface-adsorbed enzyme. To carry out the reaction, solutions of sucrose (in 2-methyl-2-butanol and DMSO) and vinyl palmitate (in 2-methyl-2-butanol) were injected into the junction for mixing then flushed through the microreactor. At 40 °C (and using a flow rate of 20.8 μL/min that resulted in a residency time of 0.5 h), a high conversion ($\geq$ 95%) of sucrose into the corresponding 6-*O*-acyl mono-ester was realized. This outcome is attributed to the favorable surface area-to-volume ratio of the Lipozyme TL IM presenting on the silica particles.

Proteases

While most reports on the enzymatic preparation of sucrose esters involve the use of lipases, deploying proteases (Rawlings et al. 2018) for the same purpose has also been explored in the ongoing efforts to achieve ever higher regioselectivities and yields within useful timeframes. An attractive feature of proteases is their relative stabilities and good activities when used in conjunction with organic solvents such as DMF and DMSO (Plou et al. 2002). In general, proteases selectively acylate at the 1′-*O* position of sucrose in such solvents as well as in pyridine (Riva et al. 1988). Thus, an examination of the effectiveness of subtilisin conducted by Riva et al. (1988) established that this enzyme is catalytically active in anhydrous DMF and allows for the production of 1′-*O*-monobutyrylsucrose in 85% yield and with 90% selectivity. Using a stabilized, insoluble and commercially available polymer of substilisin called ChiroCLEC-BL Linhardt et al. were able to produce a range of 1′-*O*-acyl sucrose esters that were accompanied by minor amounts of the corresponding 1′,6-di-*O*-acylated (di-ester) derivatives (Polat, Bazin, and Linhardt 1997). The most effective reaction conditions employed dry pyridine as the solvent and vinyl esters as the acyl donors. More recently, Protex 6 L, a commercially available and alkaline protease derived from *Bacillus licheniformis*, was used to synthesize sucrose monolaurate (Wang et al. 2012). In this process, vinyl laurate dissolved in a 15:1:4 v/v/v mixture of *tert*-amyl alcohol/DMSO/water was treated with fine particles of sucrose ($\leq$ 0.2 mm). By such means 98% of the sucrose was converted, regioselectively, into 1′-*O*-lauroylsucrose after 9 h and so establishing that Protex 6 L is superior to many commonly used enzymes including the immobilized lipase Novozym 435.

The alkaline soda lakes of Ethiopia have proven to be interesting sources of proteases including one derived from *Bacillus pseudofirmus AL-89* that functions within the pH range 7–10 in the presence of 7.5% v/v water (Pedersen et al. 2003). Under such conditions vinlyl laurate can be used to effect sucrose esterification at the 2-position rather than its 1′ or 6-counterparts. Another 2-*O*-selective acetylation of sucrose is achieved using the neutral metalloprotease thermolysin (E.C. 3.4.24.27) in DMSO. This catalytic process relies, as confirmed by EDTA binding and other studies, on the presence of zinc in the active site (Pedersen et al. 2002; Lie, Meyer, and Pedersen 2014).

Liao's group has reported regioselective acetylation at the 4′-*O* position of sucrose using a purified serine protease derived from *Serratia* sp. SYBC H and thus providing sucrose-4′-*O* mono-acetate in more than 90% yield (Li et al. 2011a). In contrast, when a crude alkaline protease obtained from the same source was used then exhaustive and high yielding peracetylation of sucrose was observed (Li et al. 2011b).

Other enzymes

A 2016 study focused on the preparation of sucrose 6-*O* acetate employed *Aspergillus oryzae* fructosyltransferase (E.C. 2.4.1.9 or, as recommended by BRENDA, inulosucrase) (BRENDA 2019a) that was originally isolated from a sample of root soil associated with the growth of sugarcane (Wei et al. 2016). This enzyme, which has been shown to transfer a fructosyl unit from one sucrose residue to another (Wei et al. 2014), was deployed in various IL/buffer combinations with sucrose and glucose 6-*O* acetate as substrates. The best medium for the reaction proved to be a 1:4 v/v [Dmim][PF_6]/phosphate buffer system and under optimal conditions 88% conversion of glucose 6-*O* acetate was observed and the product sucrose 6-*O* acetate obtained in 77% yield. In 2017, a novel, chemoenzymatic route to a new class of sucrose esters was reported (Possiel, Bäuerle, and Seibel 2017). The enzyme used in this case was *Bacillus subtilis* levansucrase (EC 2.4.1.10, a member of the glycoside hydrolases family of 68 enzymes) that is known to hydrolyze sucrose as well as effect transfer of the fructosyl moiety of sucrose (Ortiz-Soto et al. 2017). By such means, the glucose residue of sucrose was substituted for various *D*-glucuronic or D-galacturonic acid ester residues to form the corresponding β-*D*-fructofuranosyl-(2,1)-α-*D*-glucuronic or galacturonic acid esters.

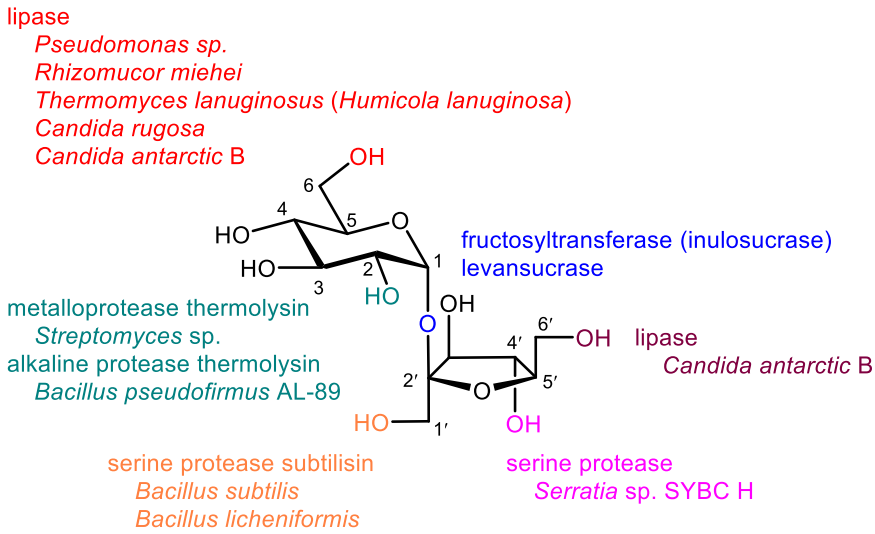

Figure 5. The regioselectivities exhibited by various enzymes available for the formation of sucrose esters and certain derivatives.

Table 3. Brief comparison of various methods available for the synthesis of sucrose esters.

Synthesis Method	Advantages	Disadvantages
chemical preparation methods in general	catalyst cost is usually low; some economical processes have been industrialized	are generally less selective and so yield a mixture of esters; complicated product purification; generation of waste streams
transesterification in solvents (typically DMF)	providing >70% of monoester; preferred industrially	solvents are often toxic and difficult to remove
solvent-free	inexpensive raw material and catalyst cost; can be industrialized	forms a mixture of esters; degradation of sucrose leads to darkening
with acid chlorides	enhanced proportions of mono-esters	strict control of water content required; high catalyst cost; unfavorable in industry
with fatty acid vinyl esters (also applicable with enzymes)	the irreversible reaction affords high yields and high mono-ester content; often preferred in lab settings	high cost of acylation reagent and hence unfavorable in industry
with other acylation agents (*e.g.*, acid anhydrides and enol esters)	can achieve high selectivity	complicated reaction procedures makes it unfavorable in industry
under Mitsunobu conditions	preparation of functional esters (*e.g.*, gallic acid ester) in lab	complicated reaction procedures make it unfavorable in industry
enzymatic preparation methods in general	high selectivity; green processes and purer products	high catalyst cost; industrialization is challenging
in organic solvents	facilitates dissolution of sugar	organic solvents can deactivate enzymes
in ionic liquids	can dissolve both substrates and thus facilitate the reaction	low solubility of sucrose in conventional ionic liquids; enzyme denaturing
in supercritical CO_2	solvent is non-toxic and non-flammable	high production cost
reduced solvent and solvent-free system	avoids massive use of solvents	small sucrose particles are needed; homogenization or ultrasonication is often needed to promote reaction

Summary

Certain of the commercially available enzymes used for the preparation of sucrose esters are listed in Table 2 and their selectivities are summarized in Figure 5. Further, and as outlined above and emphasized in Table 3, enzymes can provide greener and more selective methods for obtaining sucrose esters, including ones that are often inaccessible by other means. Nevertheless, much remains to be done within this promising area of sucrose mono-ester synthesis, both for the purposes of making "customized" and essentially pure forms of such systems in "boutique" quantities as well as in the production of such systems at commercial scales for the food industry. The use of, *inter alia*, protein engineering, directed evolution and gene shuffling techniques for the production of dedicated enzymes capable of meeting industry demands for superior sucrose-ester production processes will certainly be a focus of ongoing efforts in this area.

Sucrose esters as emulsifiers

Sucrose esters are of great interest as surfactants. For more than fifty years the food industry has been developing methods for preparing various sucrose esters with a "tunable" range of surface activities (Tucker and Martin 1958; Roshdy, Horst, and Herbert 1967). As a result, a large number of

Table 4. Parameters commonly used to characterize the emulsifying effects of surfactants.

Parameter and formula	Definitions of variables
Hydrophilic-lipophilic balance (HLB) value (Zhang et al. 2014): $HLB = 20 \times \frac{M_h}{M}$	M_h:molar mass of the hydrophilic moiety. M:molar mass of the surfactant molecule.
Foamability (Zhang et al. 2014): $FA = \frac{H_T - H_0}{H_0} \times 100\%$	H_0:height of surfactant solution before foam formation. H_T:total height of foam and solution measured immediately after foam formation.
Foaming stability (Zhang et al. 2014): $FS = \frac{H_t}{H_i} \times 100\%$	H_i:foam height measured immediately after foam formation. H_t:foam height after the sample was rested for some time.
Emulsifying ability (Zhang et al. 2014): $EA = \frac{H_1}{H_0} \times 100\%$	H_0:height of surfactant solution and an oil phase (*e.g.*, equal volume of soybean oil) H_1:height of the emulsion layer measured immediately after homogenization.
Emulsion stability (Zhang et al. 2014): $ES = \frac{H_2}{H_1} \times 100\%$	H_1:height of the emulsion layer measured immediately after homogenization. H_2:height of the emulsion layer after the emulsion was rested for some time.
Emulsion stability index (Ren and Lamsal 2017; Pearce and Kinsella 1978): $ESI = A_0 \times \frac{t}{A_0 - A_t} \times 100\%$	A_0:initial absorbance obtained immediately after homogenization and dilution. A_t:absorbance obtained after the test sample was rested for certain time. t: time that the test sample was rested (*e.g.*, 20 min).
Size distribution (McClements 2015): $S_n = \int_0^\infty x^n F(x)dx \approx \sum_{i=1} n_i x_i^n$ $x_{ab} = \left(\frac{S_a}{S_b}\right)^{1/(a-b)}$ $c_n = \left(\frac{S_n S_{n+2}}{S_{n+1}^2} - 1\right)^{1/2}$	S_n: the nth moment of the distribution. x_{ab}: the mean particle size. a,b: integers (usually between 0 and 6). c_n: relative standard deviation weighted with the nth power of x. n: the nth moment of the distribution. n_i: the number of droplets in a size-class.

sucrose esters is now available commercially for satisfying diverse needs in a wide range of areas. Various parameters have been used to characterize and calibrate their properties as surfactants (Table 4) and so assisting with their commercial success (Griffin 1949; Griffin 1954; Ren and Lamsal 2017; Pearce and Kinsella 1978; McClements 2015).

The emulsifying capacity of surfactants can be very clearly determined/demonstrated by measuring the particle/droplet sizes and their distributions associated with the emulsions formed using them. In order to examine droplet size, various devices, including laser diffraction particle-size analyzers, can be employed and a plot of continuous size distribution is then generated by the software packages normally associated with such instruments. In general, a smaller mean value and narrow standard deviation of the distribution signifies a better emulsifying capacity (Walstra 2002). McClements (2015) suggested that droplet size will influence a range of properties of the emulsions including stability, optical behaviors, rheology and even sensory attributes (Ren and Lamsal 2017; Pearce and Kinsella 1978).

HLB values and their utility

Sucrose esters have unique surface-active properties arising from their amphiphilic nature that itself derives from the presence, within the molecular framework, of the hydrophilic hydroxyl groups associated with the sucrose moiety and hydrophobic characteristics associated with the fatty acyl side-chain. The hydrophilicity or lipophilicity of a surfactant is often measured by the so-called hydrophilic-lipophilic balance (HLB) that ranges in value from 0 (completely lipophilic/hydrophobic) to 20 (completely hydrophilic/lipophobic) (Griffin 1949; Griffin 1954). In the case of sucrose esters, a wide range of HLB values can be achieved by controlling the type of associated fatty acids and the degree of esterification of the carbohydrate framework (Plou et al. 2002). As would be expected, longer acyl chains or higher degrees of esterification will increase the hydrophobicity and thereby decrease the HLB value. In practice, the HLB values of commercial sucrose esters range between 1 and 16 (Mitsubishi Chemicals 2019; Sisterna 2019a). It is also possible to blend sucrose esters with other surface active compounds (often glycerides) to meet different needs (Gupta, James, and Smith 1983). As noted by Ye and Hayes (2014), sucrose esters with HLB values $\leq$ 5 are used in chocolates to form water-in-oil emulsions while those with intermediate HLB values (8–10) are best used in, for example, chewing gum for their more balanced lipophilicity and hydrophilicity. Those esters with HLB values $\geq$ 11 are widely used in ice cream and cake batter to form oil-in-water (an opposed to water-in-oil) emulsions. The type of fatty acid residue involved also impacts of the utility of the sucrose esters. For example, when the HLB value of the surfactant is between 11 and 16, as seen in sucrose esters with 12, 14, 16, 18 and 18:1 carbon-containing acyl groups (*viz.* in laurate, myristate, palmitate, stearate and oleate esters derivatives), these are used as detergents, in ice cream, in milk beverages, in cake batter, and in sauces or dressings, respectively (Ye and Hayes 2014). A great deal of information about the surface-active properties and applications of sucrose esters is provided in the scientific literature (Otomo et al. 2009; Ye and Hayes 2014) and/or on manufacturers' websites (Mitsubishi Chemicals 2019; Sisterna 2019a).

Various new studies relating to the HLB values of sucrose have been reported. So, for example, Jiang et al. (2019) investigated the competitive interfacial adsorption of commercial emulsifiers such as Mitsubishi's lipophilic sucrose stearate (S-370, HLB = 3) and its more hydrophilic counterpart (S-1670, HLB = 16). They found that, overall, the former was superior in producing well-textured frozen aerated emulsions. These same authors claimed that lipophilic emulsifiers accelerated crystallization of fat, promoted interfacial heterogeneous nucleation as well as partial coalescence of fat droplets, enabled strong aeration activity, and allowed a short melting starting time. Sucrose ester S-1170 (HLB = 11) was also added (in up to 6% w/w) into a high amylose starch-based wood adhesive so as to improve bonding/shear

strength (in both dry and wet states), mobility, storage and thermal stability as well as rheological and degradation resistant properties. At the micro-level, the addition of this sucrose ester was found to hinder the aggregation of latex particles as well as their dispersion (Zia-Ud-Din et al. 2017; Zia-Ud-Din et al. 2019). Sucrose esters were also added to tobacco shred so as to improve their humectant and moisture resistant properties. Similarly, the hydrophobic portion of the sucrose ester S-5 (HLB = 5), as supplied by the Zhejiang Synose Tech Co., Ltd., was shown to play an important role in reducing the interaction of tobacco shred with water (Lin et al. 2020). Likewise, sucrose esters, together with other small molecular emulsifiers, were found to reduce the degradation of starch in food products like pancake mixtures (Yamashita et al. 2020). This reduction was attributed, in the main, to emulsifier-starch complex formation and so reducing the leaching of starch molecules from product granules. The degree of such complexation was, in turn, influenced by the HLB values of the emulsifiers involved.

The development of synthetic methods (in particular enzymatic ones) has enabled the preparation of high purity sucrose mono-esters and these have allowed for in-depth comparative studies of their surface-active properties (Ferrer et al. 2002a). So, Zhang et al. (2014) have reported that a longer acyl chain (C8–12) results in a reduction of HLB (14.5 to 13.1) and CMC (0.78–0.45 mM) values while the associated $^{\gamma}_{CMC}$ values increase (32.36–34.54 m/Nm). By comparing fatty acid sugar mono-esters incorporating C12–18-containing acyl chains, it was found that those involving the longer ones decrease the CMC values while for those embodying the same length of acyl chain the order of CMC values was: sucrose > maltose > leucrose > maltotriose (Ferrer et al. 2002a). All in all, most studies of the surface properties of sucrose esters reveal that they are good surfactants with a wide range of practical applications.

Foaming properties

Much confectionery, including ice cream, mousses and marshmallow, use food emulsifiers to provide a satisfying texture, attractive appearance and long shelf-lives. As such, the so-called foamability of these emulsifiers as well as the stability of the derived foams (foam stability) are of vital importance (Hutzler et al. 2011). Surfactants stabilize the foams by preventing bubbles from coalescing (Belhaij and Al-Mahdy 2015) so foamability, which is defined as the surfactants' capacity to form foams, and foam stability (a metric derived by determining variations in foam height or volume as a function of time), are important metrics used to define the foaming properties of food emulsifiers (Husband et al. 1998).

At the early stage, Husband and coworkers demonstrated that a 4:1 molar ratio of sucrose mono- and di-esters can display superior foaming properties as a result of interactions between these constituents (Husband et al. 1998). It is also widely recognized that the stability of foams derived from sucrose octaacetate decreases on standing (Petkova et al. 2017). Tual et al. (2006) have suggested that the destabilization of fat droplet interfacial layers in dairy products can be caused by the presence of sucrose esters meaning that optimal concentrations of these must be established so as to produce the most stable and high-quality dairy foams. Furthermore, when the concentration of the sucrose ester is too low to support foam formation then adding small amounts (often just 0.050 wt.%) of β-lactoglobulin can retrieve matters (Garofalakis and Murray 2001). Although aqueous foams are more common than non-aqueous ones, more research on the latter has been reported due to their great potential (Fameau and Saint-Jalmes 2017). For example, the edible emulsifiers made from sucrose esters and lecithin contribute to the formation of stable oil foams involving high air volume fractions and thus showing interesting rheological and thermoresponsive properties likely to be of value in generating food products possessing novel textures (Patel 2017).

Emulsifying capacity

Sucrose esters are expected to provide emulsifiers suitable for deployment in various food products and cosmetics, not least because of their broad range of HLB values, their non-toxic nature and their degradation to readily digestible sucrose and fatty acids. As such, several methodologies and metrics have been developed so as to quantitate their emulsifying capacities (Otomo et al. 2009). For example, Ariyaprakai and coworkers have reported that sucrose esters could be employed as a promising replacement for Tweens in coconut milk emulsions since such substitutions provide more thermally stable systems (Ariyaprakai, Limpachoti, and Pradipasena 2013). This group also reported that edible oil-in-water emulsions derived from sucrose esters are particularly stable toward freezing then thawing (Ariyaprakai and Tananuwong 2015). Furthermore, Zhao, Chen, and Wu (2018) demonstrated that the addition of carefully selected cryogelling polysaccharides such as alginate can enhance the stability of the associated emulsions toward freeze-thaw cycles. Similarly, mixtures of polyglycerol monostearate (PGE) and sucrose esters have proven to be useful in the preparation of flavor oil emulsions (Ariyaprakai 2016). Other research has revealed that sub-micron-sized emulsions can be formed from sucrose esters *via* a so-called spontaneous emulsification process instead of employing higher-energy homogenization techniques (Ariyaprakai, Hu, and Tran 2019) and that, under simulated gastrointestinal conditions, sucrose ester-derived emulsions undergo coalescence while Tween80-based ones do not (Verkempinck et al. 2018).

Biological activities

While sucrose esters are considered to be safe for humans, a multitude of studies have reported their inhibitory effects on microbes, tumor cells and viruses as well as revealing their insecticidal potential. Such properties are now discussed.

Antimicrobial activity

Since sucrose esters have been widely used in food products, their antimicrobial activities (including antifungal and antibacterial effects) have been also been studied extensively as highlighted by the data presented in Table 5. Most early research in this area used commercially-derived sucrose esters but in recent years studies have been focused on more novel and enzymatically-derived systems (Ferrer et al. 2005).

It has been known for sometime that detergent molecules, such as polyoxyethyleneglycol, can bind to bacterial membranes and so destroying them (Le Maire, Champeil, and Møller 2000), and it is very likely that sucrose esters exert their antibacterial effects by the same basic mechanism. Indeed, as revealed by Shao et al. (2018), the antimicrobial activity (particularly against Gram-positive bacteria) of sucrose monolaurate is initiated through disruption of the integrity of the bacterial cell membrane. This triggers collapse of the cytoplasmic membrane, loss/leakage of intracellular enzymes and the release of K^+ from the cytosol, disruption of the subcellular localization of proteins and, thereby, bacterial inactivation.

Thanks to their antimicrobial properties, sucrose esters are considered to have a promising future as non-toxic food preservatives while also possessing unique emulsifying and/or foaming properties (Habulin, Šabeder, and Knez 2008). Yang et al. (2003) suggested that the use of sucrose mono-esters derived from lauric, myristic and palmitic acids in salad dressing will also inhibit the growth of microorganisms involved in spoilage. In fact, sucrose esters even show inhibitory effects on the growth of spores, prompting Shearer et al. (2000) to suggest using sucrose laurate for food applications where high-temperature processing is undesirable. Another interesting use of sucrose esters is in oral-care products like toothpaste. It has been reported that 6-*O*-lauroylsucrose completely inhibits the growth of the oral bacterium *Streptococcus sobrinus* and so suggesting that such compounds could be included in oral-hygiene products in order to disrupt plaque formation and thereby preventing (or at least reducing) dental caries (Devulapalle et al. 2004).

Given their increasingly broad deployment, the possible emergence of microorganisms resistant to sucrose esters has been investigated. As Sugimoto et al. (1998) discovered, while some commercial sucrose mono-esters inhibit the development of *Bacillus cereus* spores as well as the vegetative growth of cells, the germinated spores and growing cells can release esterases that promote ester degradation and so aiding their capacity to regenerate (*viz*. become resistant).

Antitumor activities

In 1971, Kato et al. showed that the water-soluble sucrose esters incorporating laurate, myristate, palmitate and linoleate residues exhibit strong *in vitro* antitumor activity against Ehrlich ascites tumors in mice. Subsequently, the Nishikawa group reported a series of studies on the chemical and biochemical properties of synthetic and commercially available carbohydrate esters including sucrose esters. The group first revealed that sucrose mono-esters of myristic acid (Nishikawa et al. 1976a) as well as elaidic and oleic acids (Nishikawa et al. 1976b) exerted marked inhibitory activities against Ehrlich ascites carcinoma in mice. Subsequently, they found that sucrose mono-esters of palmitic, stearic, hydnocarpic and ricinoleic acids exerted antitumor effects against this cancer as well (Nishikawa et al. 1977a). These studies have been extended to commercial sucrose esters as well as other tumor cell lines and so revealing that mono-ester-rich systems exhibit pronounced antitumor effects (Nishikawa et al. 1977b; Ikekawa et al. 1979). A consideration of the possible mechanisms of actions of these esters as cytotoxic agents suggested that they might not just act as detergents (and so disrupting tumor cell membranes) or as prodrugs for the associated fatty acids (Nishikawa et al. 1976a) but also have inherent antitumor properties themselves (Nishikawa et al. 1977a). Such a possibility is supported by the observation that as the HLB value of the sucrose monoester increased the associated ID_{50} value decreased (Ikekawa et al. 1979).

Interestingly, plant-derived sucrose esters can also exhibit antitumor activities. Thus, in 2017, Fang et al. reported the isolation of eight isovaleryl sucrose esters (named ainslosides A–H) from *Ainsliaea yunnanensis* Franch, and discovered that congener B (Figure 6a) exerted notable cytotoxic effects against the A549 (lung adenocarcinoma) cell line with an IC_{50} of 3.3 μM. This compound was found to arrest the cell cycle at the G_0/G_1 phase and induce cell apoptosis with the latter effect arising from a decrease in mitochondrial membrane potential and an attendant growth in the levels of growth of reactive oxygen species. In 2018, Petrova et al. synthesized a library of sugar esters with C3–5 unsaturated fatty acyl chains and found that 6-*O*-methacryloyl sucrose as well as 1′,2,3,3′,4,4′,6′-hepta-*O*-acetyl-6-*O*-methacryloyl sucrose (Figure 6b) were the most active against a range of food contaminating and clinically notable pathogens (MIC: 0.24–1.40 μM). The later ester also showed good antifungal activity (MIC: 0.28–1.10 μM). Synthetic, non-fatty-acid sucrose esters possessing antitumor activities have also been identified. For example, Bai (2009) prepared a unique sucrose selenite (Figure 6c) showing promise in treating cancers. This compound has a selenium content of 17.4% which is significantly higher than that of conventional selenium-containing nutrients and anticancer drugs (*ca*. 1.2%). It exhibited excellent antimutagenic bioactivity as evidenced by an inhibition rate of 97.4% when applied in a standard assay at a loading of 500 μg/dish.

Sucrose fatty acids esters have also been used in drug delivery systems (Abdel-Mageed et al. 2012; Guan, Chen, and Zhong 2019). For example, Guan, Chen, and Zhong (2019) recently reported that a sucrose fatty acid ester purchased from the Tokyo Chemical Industry Co. in Japan (Product No. S0112) could be used to nanoencapsulate caffeic acid phenethyl ester (CAPE), a natural product possessing anticancer activities but low water solubility. Such encapsulation is expected to enhance the capacity to deploy CAPE in the treatment of certain colon and breast cancers. Of course, the possible synergistic effects associated with the

Table 5. Summary of the literature reporting the antimicrobial activities of sucrose fatty esters.

Sucrose ester	Active Against	Comment	Ref.
6-*O*-lauroylsucrose	*L. monocytogenes*, *B. subtilis*, *S. aureus*, and *E. coli*.	Indicates significant antimicrobial activity against these bacteria, particularly Gram-positive bacteria.	Shao et al. 2018
Sucrose monolaurate (6-*O*-lauroylsucrose, from Sigma-Aldrich Co.)	Gram-positive bacteria	Exerted bacteriostatic and bactericidal effects against these bacteria.	Park et al. 2018
Physakengoses (natural sucrose esters isolated from *Physalis alkekengi* var. *franchetii*)	*Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli*.	Five out of seven natural sucrose esters isolated displayed potent antibacterial activity, and long chain fatty acid esters attached to sucrose were essential for this activity.	Zhang et al. 2017
Sucrose monocaprate (home-made)	*Bacillus cereus*, *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli*, and *Salmonella typhimurium*.	Displayed the strongest antibacterial activity against these bacteria, particularly Gram-positive bacteria.	Zhao et al. 2015
Octa-*O*-acetylsucrose	17 Microorganisms: Gram-positive and Gram-negative bacteria, yeasts, and fungi	Inhibited the growth of fungi *Penicillium sp.*, *Rhizopus sp.* and *Fusarium moniliforme*, and yeasts *Candida albicans*. Did not inhibit Gram-positive and negative bacteria.	Petkova et al. 2017
Sucrose esters with C8, C10, C12, C14 and C16 fatty acids (Mitsubishi-Kagaku Foods Co., Japan)	*Bacillus* species: *B. cereus*, *B. subtilis*, *B. megaterium*, and *B. coagulans*	Sucrose esters displayed bactericidal effects on these species at pH 6.0, but only showed an antibacterial effect on *B. coagulans* at pH 8.0 (better at 37 °C than 50 °C).	Nakayama et al. 2015
Sucrose monolaurate (from Sisterna, the Netherlands)	Gram-positive and Gram-negative bacteria	Most effective against the growth of Gram-positive bacteria (inhibited *Listeria* and greatly inhibited *S. suis*).	Wagh et al. 2012
Sucrose monolaurate (from AppliChem Inc., Darmstadt, Germany)	*Escherichia coli* O157:H7	The efficacy of chlorine (from NaOCl) sanitization was significantly improved by sucrose monolaurate which enables inactivation or removal of the microorganism.	Xiao et al. 2011
Commercial sucrose ester (sucrose palmitate, P-1670, from Mitsubishi-Kagaku Food Co., 80% mono ester), or enzymatically synthesized sucrose laurate (mono and diesters)	Gram-positive bacterium *B. cereus* (ATCC 11778)	At 9.375 mg/mL, commercial and enzymatically synthesized sucrose laurate inhibited 99.8% and 94.0% of the growth of *B. cereus* after 52 h. Mono-esters inhibit *B. cereus* to higher extent than di-esters.	Habulin, Šabeder, and Knez 2008
6-*O*-lauroylsucrose (2 mg/mL) 6,1′-di-*O*-lauroylsucrose (1 mg/mL) 6,6′-di-*O*-lauroylsucrose (0.25 mg/mL)	*Bacillus sp.*, *Pseudomonas fluorescens*, *Staphylococcus aureus*, *Escherichia coli*, and *Pichia jadinii*	Inhibited the growth of *Bacillus sp.*, *E. coli* and *L. plantarum*. But the antimicrobial activity of these diesters was negligible as a result of their limited solubility.	Ferrer et al. 2005
6-*O*-lauroylsucrose	*Streptococcus sobrinus*	In media supplemented with 2 mg/mL of the sucrose ester, bacterial growth was not observed.	Devulapalle et al. 2004
Sucrose monoesters of lauric, myristic, palmitic, and stearic acids.	*Zygosaccharomyces bailii*, and *Lactobacillus fructivoran*	The growth of *Z. bailii* was significantly inhibited by 1% sucrose monoesters of lauric, myristic and palmitic acid in salad dressing, but the inhibition of *L. fructivorans* lacks practical value.	Husband et al. 1998
Sucrose laurates, palmitate, and stearates (Mitsubishi Chemical Co., N.Y., U.S.)	Spores of *Bacillus sp.*, *Clostridium sporogenes* PA3679, and *Alicyclobacillus sp.*	In terms of sporeformer inhibition, sucrose laurates and palmitate were more effective than stearates.	Shearer et al. 2000
Sucrose palmitate (P-1570 and P-1670) Sucrose stearate (S-1570 and S-1670) (Mitsubishi-Kagaku Foods Co.)	*L. monocytogenes*, *Bacillus cereus* (both cells and spores), *Lactobacillus plantarum*, and *Stuphylococcus aureus*	Improved the antimicrobial activity of nisin (an antibacterial peptide used as a food preservative) against these strains. Inhibition of Gram-negative bacteria was not observed.	Thomas et al. 1998
Sucrose monolaurate (SE12), sucrose monopalmitate (SE16), and sucrose	*Bacillus cereus*	Inhibit the germination of spores, with the effectiveness of laurate > palmitate > stearate, and	Sugimoto et al. 1998

(*continued*)

Table 5. Continued

monostearate (SE18) (Mitsubishi-Kagaku Foods Co.)		the vegetative growth of cells. But the germinated spores and growing cells can release esterases to decompose these esters, causing loss of antimicrobial activity.	
Sucrose monocaprate, and Sucrose monolaurate	*Listeria monocytogenes*, and *Staphylococcus aureus*	The monocaprate (400 μg/mL) did not inhibit growth, while the monolaurate exhibited an inhibitory or lethal effect and this can be enhanced by EDTA.	Monk, Beuchat, and Hathcox 1996
Sucrose monolaurate	*Streptococcus mutans* NCTC 10449 (an oral bacterium)	Reduced acid production from sugar. This is due to altering of cell membrane permeability causing loss of important metabolites.	Iwami, Schachtele, and Yamada 1995
Six sucrose esters with fatty acid composition of *ca.* 70% stearic acid and 30% palmitic acid. (DKS International Inc., Tokoyo, Japan)	*Aspergillus*, *Penicillium*, *Cladosporium*, and *Alternaria*.	Antimycotic activity was detected against listed molds. The least substituted sucrose ester was the most active, and this inhibitory activity was not influenced by variations in pH.	Marshall and Bullerman 1986
Sucrose caprate, caprate, laurate, myristate and palmitate (Ryoto Co. Ltd., Tokyo, Japan.)	*Vibrio parahaemolyticus*	The minimum concentrations for inhibition by sucrose caprylate and caprate were 40 and 100 μg/mL, respectively. The rest of the esters studied were ineffective at 100 μg/mL.	Beuchat 1980

simultaneous deployment of two proven cytotoxic agents in such settings is worthy of investigation.

Insecticidal activities

A less studied aspect of sucrose esters properties concerns their insecticidal effects. In 1994, field and green house studies of *Nicotiana gossei* Domin plants led to the identification of an isolate, containing 2,3-di-*O*-acyl-1′-*O*-acetylsucrose and 2,3-di-*O*-acyl-1′,6′-di-*O*-acetylsucrose, that proved toxic to sweet potato whiteflies. The side-chains associated these esters were predominantly derived from 5-methylhexanoic and 5-methylheptanoic acids (Figure 6d) (Severson et al. 1994). Subsequent reports described the insecticidal activity of certain synthetic sugar esters, including sucrose-based ones, against a range of insects including *Bemisia argentifolii* (Liu, Stansly, and Chortyk 1996; Chortyk, Pomonis, and Johnson 1996). Synthetically-derived sucrose esters containing C_6–C_{12} aliphatic acid residues (Youngs 1958) and especially diheptanoyl, dioctanoyl and dinonanoyl-containing ones, were shown to be active against whiteflies and aphids (Chortyk 2003) and field tests of these (to protect various crops) were undertaken. The prospect of using *Nicotiana* species for producing sugar esters as "biorational" insecticides has also been pursued (Jackson et al. 1998).

McKenzie and Puterka (2004) have studied the insecticidal activities of sucrose octanoate and in so doing found that nymphal and adult *Diaphorina citri* (Asian citrus psylla) as well as mites were both controlled to considerable effect (> 90%) by sucrose octanoate, albeit at rather high concentrations (8000 ppm). Given that sucrose octanoate is essentially nontoxic to many beneficial insects, this ester may prove to be a useful (selective) pesticide in commercial settings. Song et al. (2006), who prepared sucrose octanoate by transesterification of sucrose with ethyl octanoate under reduced pressure, have also evaluated the insecticidal activity of this compound. They reported that the contact toxicity of sucrose octanoate to first-instar larvae of *Lymantria dispar* was 72.5% after 36 h, and the insect reduction rate, after 5 days, of *Aphis glycines* was above 80% at application rates of 4 and 8 mg/mL. Considering the emulsifying properties and other advantages of sucrose esters (such as their biodegradability as well as lack of toxicity toward higher animals and crops), they represent promising leads for the development of commercial insecticides.

Puterka et al. (2003) studied the structure-activity profiles of various sugar esters in an effort to determine the origins of their insecticidal properties and claimed that changing the fatty acid and sugar residues in such systems resulted in unpredictable levels of insecticidal activity. Notably, their HLB values did not correlate with activity. So, for example, they observed that monoester-rich sucrose octanoate had higher activities than other esters embodying acyl chains of similar length (C6–12) and was toxic to a broader range of arthropod species. Interestingly, a comparison of the insecticidal activities of sugar esters and soaps led to the conclusion that more than one mechanism-of-action might be involved with one of these being suffocation caused by mechanical occlusions of body openings and another being desiccation of insect cuticles.

Structure-property profiles

In general, the overall surfactant and emulsifying properties of sugar esters are profoundly influenced by both the length of the associated fatty acid chain (*viz.* the hydrophobic tail) and the nature of the sugar residue (*viz.* the hydrophilic head) (Zhang et al. 2015). In the case of sucrose esters,

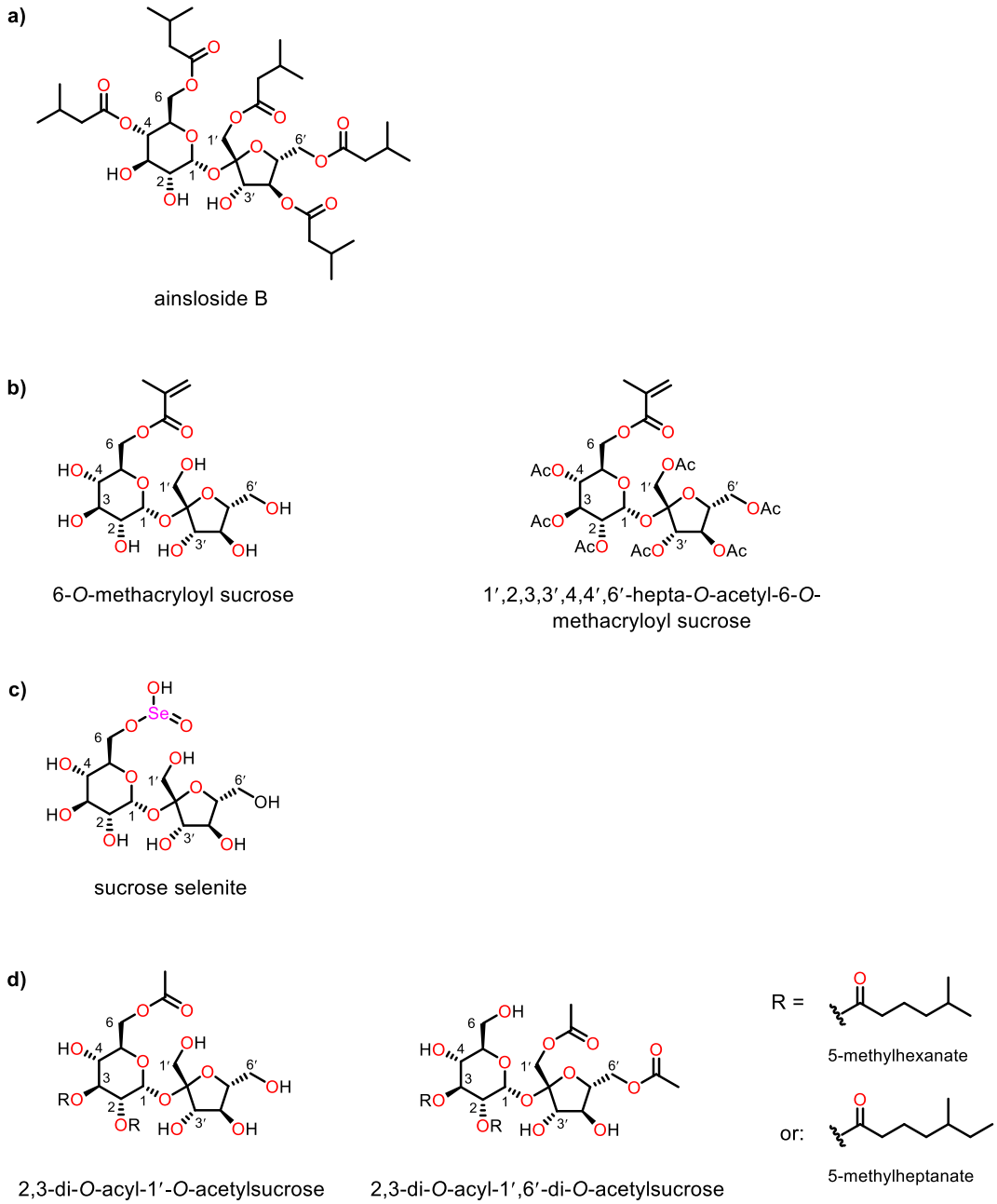

Figure 6. Selected sucrose esters showing biological activities: a) ainsloside B (Fang et al. 2017); b) sucrose esters of some unsaturated fatty acids (Petrova et al. 2018); c) sucrose selenite (Bai 2009); and d) the natural pesticides 2,3-di-*O*-acyl-1′-*O*-acetylsucrose and 2,3-di-*O*-acyl-1′,6′-di-*O*-acetylsucrose (the acid residues of which are mostly derived from 5-methylhexanoic and 5-methylheptanoic acids) (Severson et al. 1994).

precisely how their properties vary as a function of the length of the fatty acid residue (structure-property profiles) remains unclear. Zhang et al. (2015) have prepared and characterized three sucrose medium-chain fatty acid (octanoate, decanoate and laurate) mono-esters and found that increasing hydrophobic chain length enhances the emulsifying potencies of medium-chain fatty acid mono-esters. However, sucrose mono- and di-esters bearing longer (> 12 carbons) chain fatty acids have yet to be properly evaluated in this regard. As well as the acyl chain length, it can be expected that increasing the degree of acylation/esterification leads to a higher hydrophobicity and so decreasing surface activity. A more important issue is the associated decline in water solubility, a property that limits applications in the food industry (Ferrer et al. 2002a). In principle, the degree of unsaturation of the acyl chain should have limited influence on the surface properties, as it does not significantly alter the molar mass of the hydrophilic moiety and, hence, the HLB. Although the practical applications of sucrose esters in the food industry are guided, at least in a rudimentary sense, by their hydrophilic-lipophilic balance (HLB) values (Ye and Hayes 2014), the development of detailed structure-property profiles are wanting. Once established these would be expected to aid in the selection of the most relevant ones for any given practical application(s).

In terms of the bioactivities of sucrose esters, it seems that mono-esters rather than higher order ones play pivotal roles, and the influence of the acyl chain length may also be

involved. Thus, it has been shown that mono-esters are significant antibacterial entities with the corresponding di- and tri-esters displaying less notable activities possibly because of their low(er) aqueous solubility. The length of the fatty acid residue has a notable influence on activity (C12 > C10 > C8), almost certainly a result of its influence on the HLB that is involved in the inhibitory effect (Zhang et al. 2014). In terms of the antitumor activity, the Nishikawa group has concluded that mono-esters are most active and that there might often be an inverse correlation between HLB and the ID_{50} values (Nishikawa et al. 1977b; Ikekawa et al. 1979). Unsaturation within the fatty acyl chains (Nishikawa et al. 1976a, 1976b) has little impact on activity unless a Michael acceptor is involved (*e.g.*, Petrova et al. 2018). In terms of insecticidal activity, the impact of the fatty acid residue is unpredictable although a high mono-ester content sucrose octanoate exhibits high toxicity to a broad ranges of species (Puterka et al. 2003). Clearly, more research is required so as to fully reveal the mechanisms-of-action of such compounds and thereby establishing guidelines for their practical applications.

In our recent work on homologous series of glucose, maltose, lactose and raffinose esters (Liang et al. 2018a, 2018b; Ma et al. 2018; Li et al. 2019) we established that in order to maintain good foaming properties, fatty acid side chains of 10 or 12 carbons in length are required regardless of the nature of the sugar residue involved. So, while the incorporation of longer fatty acid side-chains results in better emulsifying potencies for glucose and raffinose esters, medium length ones are more effective when bonded to their maltose and lactose counterparts. Intriguingly, in the case of lactose esters, the longer the alkyl side chain the greater their cytotoxicities. However, determining analogous and unequivocal structure-property profiles for sucrose esters is complicated by the mixed nature of most commercially available materials that can often include seven or more types of fatty acid residues. Clearly further work in this important area is required.

Conclusion

In recent years, there has been a growing interest in the use of sucrose esters as emulsifiers because of their excellent properties, especially as these can be exploited in the food industry. An associated body of knowledge focused on their preparation has accumulated as a result and attendant, detailed studies of their emulsifying properties and various bioactivities have emerged. While rather conventional chemical methods dominate the industrial production of such systems, a more recent but largely academic focus has been on the enzymatic preparation of sucrose esters. There are distinct advantages associated with such approaches given that they are generally greener and less energy-demanding processes but the likely cost of the enzyme required in applying such protocols in industrial settings remains a challenge. The antimicrobial, antitumor and insecticidal activities of sucrose esters are important emerging areas of study, especially considering that such compounds are also likely to be useful as food additives, drug carriers and/or emulsifiers. Clearly, this is an evolving field of science where exciting new discoveries are being made.

Funding

The authors thank the Program for Guangdong Pearl River Introducing Innovative and Entrepreneurial Teams (grant 2017ZT07C571), the Program for Guangdong Yang Fan Introducing Innovative and Entrepreneurial Teams (grant 2016YT03H132), the Science and Technology Planning Project of Guangdong Province (grant 2016A010105010) as well as the National Natural Science Foundation of China (grant 21801094 and grant 31701525) for funding.

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