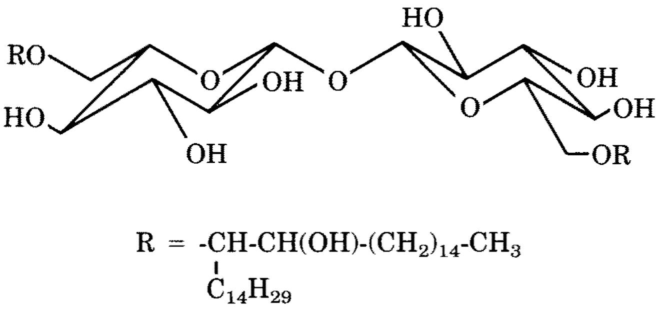
Sucrose Esters as Model Compounds for Synthetic Glycolipid Surfactants

M. J. Donnelly and J. D. Bu'Lock*
Department of Chemistry, University of Manchester, Manchester, M13 9PL, England

Some chemical and surfactant characterizations have been carried out on a range of sucrose esters varying in composition from predominantly mono- to diester. These compounds are proposed as simple models for more complex glycolipids (cord-factor analogues) which are representative of biosurfactants. The latter have potential application in enhanced oil recovery arising from their excellent surfactant properties.

Biosurfactants typically are produced when specific strains of microorganisms are grown on n-alkanes. Their outstanding surfactant properties have attracted growing attention for use in enhanced oil recovery (1). Representative effects are the lowering of the surface tension of aqueous salt solution to approximately 30 dynes/cm, and of interfacial tension against n-hexadecane to ca. 1-8 dynes/cm with cmc values of 0.02-0.0002% w/w (2-4).

Although the biosurfactants as a class encompass a very wide range of structures including glycolipids (5-7), cyclic lipopeptides (8) and polysaccharide/fatty acid ester/protein complexes (9), many of the most common structural features are encountered in the bacterial lipids known as "cord-factor" and its analogues. One such structure (10) is given in Figure 1.



$$R = \underset{\displaystyle C_{14}H_{29}}{-\underset{|}{CH}}-CH(OH)-(CH_2)_{14}-CH_3$$

FIG 1. Typical "cord factor" analogue structure.

At present, production of these compounds by fermentation suffers from the disadvantages of low yield (2,11) and difficulties associated with recovery of the product (11,12). Chemical synthesis of these molecules or their analogues would lead to greater availability, while studies relating structure to surfactant properties could lead to better understanding of why biosurfactants are so effective.

A preliminary stage in such a program would be to evaluate, in particular under conditions which simulate oil well salinities, simple analogues of relevant glycolipids. The most readily available of such models are the commercial sucrose esters (SE) of n-alkyl fatty acids. Though these are available commercially, surfactant data for preparations of characterized identity and structure are scarce; this paper presents some characterization and surfactant data on one series of these compounds.

MATERIALS

A range of sucrose esters was obtained from Croda Chemicals (Hull, England); these are produced from a palmitic:stearic (30:70) mixture and are mixtures of mono-, di- and triesters (14). Each sucrose ester mixture has a manufacturer's product code as follows: F10, F20, F50, F70, F110, F140 and F160.

Synthetic deposit water was made up from NaCl (100 g/l), $CaCl_2$ (28 g/l), $MgCl_2$ (10 g/l) in distilled water (2).

EXPERIMENTAL PROCEDURES

Saponification equivalents were determined by reaction with excess KOH in diethylene glycol (13). Acid values were obtained by titration of methanol/chloroform solutions of sucrose ester with 0.1 N NaOH to phenolphthalein. Melting points (mp) were observed on a Kofler apparatus, at a heating rate of 1-2 C/min, and are uncorrected. Thin layer chromatography was carried out using silica gel coated plates (0.25 mm layer thickness), with the eluent being a mixture ($CHCl_3$:CH_3OH:CH_3COOH:H_2O, 79:11:8:2), and spots were visualized by iodine vapor.

Infrared spectra were obtained as nujol mulls between NaCl plates, using a Pye-Unicam SP3-200 spectrophotometer. For each sucrose ester sample an infrared peak height ratio HO/CO was calculated as follows: peak height OH absorption (3350 cm^{-1})/peak height C=O absorption (1730 cm^{-1}).

Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R12B spectrometer in $CHCl_3/D_2O$ solutions at 60 MHz. Chemical shifts are reported as δ (ppm) relative to tetramethylsilane. Surface tensions were recorded at ambient temperature (20±1 C) using a Du Nouy Tensiometer (Cambridge Instruments, London, England) and the glass plate method, in both distilled water and synthetic deposit water, with each sucrose ester at concentrations within the range 0.0001-2.0% w/w. The sucrose esters as supplied do not disperse easily in water, and to ensure proper dispersal the samples were first melted. Each concentration was made up separately by weighing; the prepared sample solution was heated to the melting point of the sucrose ester in a sealed flask (ca. 5 min), shaken vigorously, then cooled to ambient temperature for at least one hour prior to surface activity measurements being carried out in duplicate. Product F10 was particularly insoluble, and at the higher intended concentrations there was always visible insoluble material at the liquid surface. Consequently, for this

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*To whom correspondence should be addressed.

TABLE 1

Analytical Data for Sucrose Esters of 30:70 Palmitic/Stearic Acids

Sucrose ester product code	Acid value[a]	mp (°C)	Saponification equivalent[b]	Infrared OH/CO ratio[c]	Hydrophilic-lipophilic balance[d]
F10	0.5	57-61	481	0.38	<3
F20	2.0	65-68	526	0.65	3.0
F50	1.0	78-83	558	0.92	6.5
F70	0.9	76-80	588	0.96	7.5
F110	2.1	75-82	599	0.97	12.0
F140	1.1	64-65	606	1.18	13.0
F160	1.4	53-55	610	1.13	14.5

[a] Calculated as % w/w stearic acid.
[b] Calculated values for sucrose monoester (derived from 30:70 palmitic/stearic acids) 600.4, diester 429.2, triester 372.2.
[c] Peak height ratio [OH(3350 cm^{-1})/CO (1730 cm^{-1})].
[d] Reference 14.

product data are reported for only one concentration, thought to be close to the cmc. For the other sucrose esters, the critical micelle concentration (cmc) was measured from a plot of surface tension versus concentration, and the interfacial tension (versus n-hexadecane) was then measured at this surfactant concentration.

RESULTS AND DISCUSSION

Analytical data for the range of sucrose esters are shown in Table 1, and the results of thin layer chromatography and NMR spectroscopy are shown in Tables 2 and 3, respectively. The data suggests that the range of specifications, as indicated for example by the manufacturers, quoted hydrophile-lipophile balance (HLB) values for the different products (Table 1), corresponds to varying proportions in a mixture of predominantly sucrose mono- and diesters. Thus, in Table 1 the measured saponification values cover a range corresponding to materials approximately mostly monoesters (products F110, 140, 160) to mixtures with a high proportion of di- or triesters (product F10).

TABLE 2

Rf Values of Components of Sucrose Esters Derived from 30:70 Palmitic: Stearic Acids[a]

	Sucrose ester product code		
F10	F20-F110	F140	F160
0.96	—	—	0.96
0.84	—	—	—
0.72	0.73	0.71	0.73
—	0.64	—	—
—	0.58	0.59	0.60
—	—	0.48	0.48
0.42	0.41	0.42	0.42
—	0.31	—	—
0.20[b]	0.22	0.20	0.20
—	0.07	—	—

[a] Rf values for methyl stearate and stearic acid are 0.86 and 0.73, respectively, under these conditions.
[b] Trace only.

Sucrose esters, prepared by the Osipow procedure, have been analyzed by thin layer chromatography under the same conditions as in the present study, by previous workers (15). It was concluded that monoesters had Rf value ca. 0.2, and higher (di-, tri-, etc.) -esters had Rf values in the range 0.3-0.75. A similar interpretation of the results in Table 2 indicates that the sucrose esters of this study are mixtures, mainly of mono- and diesters, accompanied by minor amounts of materials with Rf's identical to those of methyl stearate and stearic acid, the latter being confirmed by the acid values presented in Table 1. As a reasonable approximation the SE samples range in composition from one which contains little monoester (F10, largely diester from the saponification equivalent) to ones with increasing monoester content (F20-F160). This is supported by the increasing intensity of the spot of Rf 0.20. In addition, other data presented in Table 1, such as the melting points becoming sharper and the infrared OH/CO ratios increasing, are also consistent with the composition becoming richer in monoester. That the last two members of the range are predominantly monoester is also suggested by the NMR spectroscopic data (Table 3) for which the approximation of relative number of methylene (C-CH$_2$-C) and methine (O-CH-O) protons for the two products F140 and F160 are similar to calculated values for the monoester. However, no great quantitative accuracy can be expected from the NMR data because the integrated peak ratios have to be calculated relative to the small signal produced by the unambiguously identifiable single proton in the group O-CH-O.

Surfactant behavior, in both distilled water and synthetic deposit water, of the range of sucrose esters is summarized in Table 4. In each case a distinct minimum in the measured properties is observed for sucrose ester mixtures of saponification equivalent ca. 580-600, for example as represented by the product F70. Whether this minimum represents optimal practical characteristics will of course depend on the particular surfactant application.

TABLE 3

NMR Spectroscopic Data for Sucrose Esters Derived from 30:70 Mixtures of Palmitic/Stearic Acids

Chemical Shift δ (ppm)	Assigned group[a]	Measured number of protons		Calculated number of protons for pure sucrose esters[b]	
		F140[c]	F160[c]	monoester	diester
0.85	CH_3-C	4	6	3	6
1.28	C-CH_2-C	26	38	29	58
2.25	C-CH_2-CO-O-	2	4	2	4
3.6	O-CH-C/O-CH_2-C	7	9	11	9
4.05	C-CH_2-O-CO	3	3	2	4
5.3	O-CH-O	1	1	1	1

[a] All groups shown for each sucrose ester.
[b] Corrected for presence of palmitic and stearic side chains.
[c] Sucrose ester product code.

TABLE 4

Surfactant Properties of Sucrose Esters Derived from 30:70 Mixtures of Palmitic/Stearic Acids

Product code	Distilled water			Synthetic deposit water		
	ST[a]	IFT[b]	cmc[c]	ST[a]	IFT[b]	cmc[c]
F10*	(59.5	17.9		33.2	15.8	.[d]*
F20	25.2	16.8	0.14	20.0	14.0	0.2
F50	21.1	12.1	0.11	19.9	9.9	0.2
F70	23.7	10.2	0.01	19.7	9.5	0.01
F110	20.8	10.3	0.015	21.0	9.2	0.02
F140	37.2	10.7	0.08	22.9	13.5	0.03
F160	37.7	14.0	0.04	29.1	13.7	0.05

[a] Surface Tension (ST) dynes/cm, at cmc.
[b] Interfacial Tension (IFT) dynes/cm, at cmc.
[c] Critical micelle concentration, % w/w.
[d] This sample measured only at one concentration, 0.5% w/w.

Comparison of these data with literature values for similar sucrose ester products is surprisingly difficult, one reason why the present study was undertaken. Often the products have been incompletely characterized; in other cases, data are provided simply for (supposed) mono- or diesters and not for mixtures. Other reported measurements have been carried out at different temperatures from the present study (20).

Data for pure sucrose monostearate, a near equivalent to some of the materials in this study, are, however, available. Osipow and co-workers (21) report a surface tension of ca. 33-34 dynes/cm and interfacial tension of ca. 6-8 dynes/cm at concentrations in the range 1.0-0.05%; Wachs and Hoyano give the cmc for this same product as 0.003% at 20 C (22).

These figures are broadly similar to those for the monoesters in this study (products F160 and F140), while the product comprising mostly diester (F10), for which an accurate measurement of cmc was not possible, shows the expected very poor properties related to the low bulk solubility of sucrose diesters (23). An interesting point about the surfactant data of Table 4 is the relatively low values of surface tension shown by products in the middle of the range (F50, F70, F110 comprising mixtures of mono and higher esters), which are comparable to those reported for fluorinated polyoxyethylene compounds [ca. 20 dynes/cm: (20)] and citric acid esters (ca. 27 dynes/cm) (24).

A possible interpretation of this observation is that as the mixture range of sucrose esters is traversed from predominantly monoester to increasing amounts of higher esters, a number of structural features change:

- The chain length of the hydrophobic portion of the molecules remains constant, but the total concentration per molecule increases.
- The hydrophilic portion shifts from a terminal to an essentially central position in the molecule.

However, these concepts are insufficient to explain the surface activity in terms of the effect of structural changes on either the efficiency or effectiveness of the surfactant system (16). Consideration of the system as a mixture of mono- and diester allows a qualitative application of the well known Gibbs adsorption equation for a two-component system (17). Thus, the predominantly monoester F-160 will have its own characteristic surfactant properties. Addition of a second surfactant (diester) will cause a further reduction in surface tension and interfacial tension. Similar arguments would apply to the reduction in surfactant properties by the addition of monoester to the predominantly diester F10.

The absolute effects on surfactant properties of replacing distilled water with synthetic deposit water are not dramatic, a result which is characteristic of non-ionic surfactants.

Enhanced oil recovery requires a brine/oil/surfactant system such that optimal three-phase behavior is obtained. In this state equal volumes of oil and water are solubilized in the surfactant-rich middle phase which is in equilibrium with both a water phase and an oil phase (18). It is therefore interesting to note that the sucrose ester mixture with optimum surfactant behavior has an HLB value of ca. 7.5 (product code F-70, saponification equivalent 588), intermediate between that required for a w/o emulsion (HLB ca. 4) and an o/w emulsion (HLB 10-10.5) (19). Hence, other factors being equal, surfactants with HLB's of about 7.5 could be expected to yield emulsions with similar water and oil contents.

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