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Long-chain acetals derived from sucrose as a new class of surfactants

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Abstract

Classical acetalation and transacetalation of sucrose (α-D-glucopyranosyl β-D-fructofuranoside) with long-chain alkyl carbonyl derivatives lead conveniently to a new class of acetals of great interest, due to their detergent properties. © 1997 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Sugars, which have a number of hydroxy groups, are particularly interesting as they may constitute the hydrophilic part of a detergent when they are associated with a hydrophobic chain. They are generally available in large quantities (and among them, sucrose is one of the most accessible for industrial uses), are a renewable resource, and they may confer properties of biodegradability to these surfactants. Thus, several derivatives of mono- or di-saccharides that contain a long alkyl or fluoroalkyl chain are well known as tensides and surfactants. For instance, O- and C-glycosides, and mainly alkylpolyglucosides [1], S-glycosides [2], monocarbamates and *N'*-alkylurea or *N'*-alkylthiourea in the D-glucose series [2], mono- and poly-esters of sucrose [3] (obtained by action of a lipidic acid on sucrose), telomeric molecules [4], and polyols perfluoroalkylated derivatives [5] have been prepared.

The acetal function is a well-known protecting group [6] having its own unique reactivity [7], and it has been used more recently to functionalize mono- and oligo-saccharides [8]. However, the introduction of a long carbon atom chain on a glucidic derivative by means of an acetal function represents a new route that has not been explored (except for the synthesis of a derivative of 1,5-D-gluconolactone [9]). Acetal derivatives should notably provide nonionic surfactants stable in basic medium, in contrast to ester derivatives.

The mono- or poly-functionality of reaction products can be reasonably controlled using the more recent procedures for acetalation, and the preparation is convenient with disaccharides (e.g., sucrose). We report here the synthesis of a new class of acetal derivatives, namely sucrose acetals with a long carbon-atom chain that possess detergent properties.

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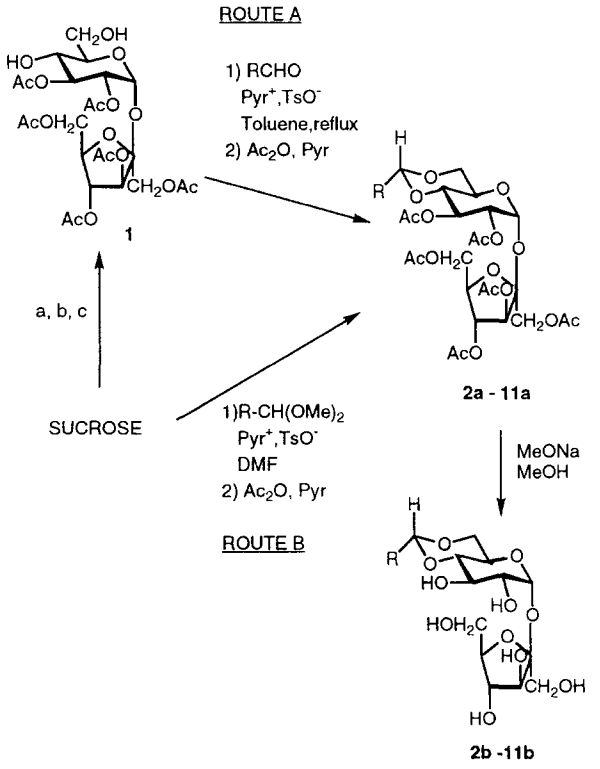
2. Results and discussion

Long-chain aldehydes or aldehyde dimethyl acetals did not react directly with sucrose (or only in a very low yield). But using 1′,2,3,3′,4′,6′-hexa-*O*-acetyl sucrose (**1**) [10] as starting material, acetalation provided sucrose acetals **2** to **8** in very good yields (Scheme 1, route A). The reaction, which was carried out in acidified refluxing toluene in an apparatus with a Dean–Stark trap, was complete within a few hours as shown by TLC. Starting from this protected sucrose derivative, the glycosidic bond was preserved. On the other hand, aryl or unsaturated aldehyde dimethyl acetals reacted directly with sucrose in DMF at room temperature. In order to purify and identify the expected acetals, the reaction mixture was acetylated before separation by column chromatography (Scheme 1, route B).



ROUTE A

R - : CH_3-$(CH_2)_n$-
(2) n = 5
(3) n = 8
(4) n = 10
(5) n = 12
(6) n = 14
(7) n = 16
R - : $(CH_3)_2C{=}CH$-$(CH_2)_2$-$C(CH_3){=}CH$- (8)

ROUTE B

R - : Ph-Ph- (9)
R - : H_3C-$(CH_2)_5$-Ph- (10)
R - : Ph-CH=C(CH3)-$(CH_2)_5$- (11)

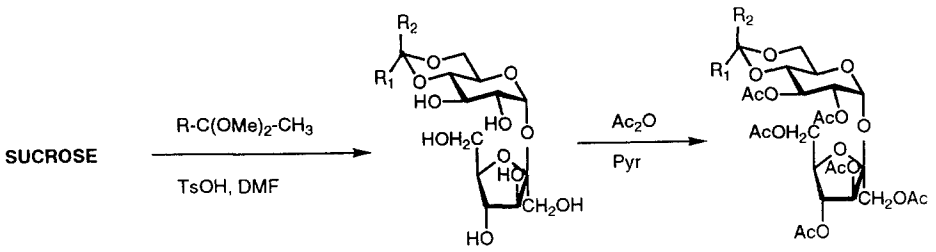
Scheme 1. Reagents and conditions: a: $H_2C{=}C(OMe)CH_3$, PyrTsOH, DMF, 0°C; b: Ac_2O, Pyr; c: 3:2 AcOH–H_2O, 1 h, 80°C.

Acetals **2** to **11** have been identified by ^1H and ^{13}C NMR spectroscopy. In general, the following signals were observed: (*i*) In the ^1H NMR spectrum, a doublet at 3.40 ppm due to H-7; (*ii*) in the ^{13}C NMR spectrum, three signals at 90.5, 104.0, and 101–102 ppm corresponding to the acetalic carbon atoms of the molecule (C-1, C-2′, and C-7, respectively) [11].

These two syntheses are regioselective and enable stoichiometric control of the introduction of a long chain, since only 4,6-*O*-*mono*acetals are obtained. In addition, only formation of one of the two possible diastereoisomers on the acetalic carbon atom is observed since the long chain is only observed in the thermodynamically favored equatorial position [12].

In addition, 2,2-dimethoxyalkanes are convenient reagents for direct transacetalation of sucrose. The reaction was achieved in DMF at room temperature, catalyzed with *p*-toluenesulfonic acid, and was complete in 90 min. In this way, acetals **12** to **14** were prepared in a 30% yield after purification by column chromatography (Scheme 2). Their identification was made on the basis of NMR spectral data and confirmed by data of their peracetylated analogues. The reaction is regioselective; but the two possible isomers on the acetalic carbon atom (alkyl chain in either an equatorial or axial position) are obtained, due to the equivalent interaction of the synaxial protons on the 1,3-dioxane ring with either the methyl group or the first methylene group of the long chain. NMR spectral data for compounds **14a,a′,b,b′** are shown in Tables 1 and 2. The structure of the two isomers can be determined from the ^{13}C NMR spectrum: (*i*) the acetalic carbon atom C-7 included in a dioxane ring in its chair conformation [11], gives two singlets at about 100 ppm; (*ii*) the methyl group α to the acetalic carbon atom gives signals (17.4 ppm for axial position and 26.2 ppm for the equatorial position), with chemical shifts corresponding to those observed for methyl groups of an isopropylidene acetal [11]; (*iii*) the first methylene group of the chain, in the α position to the acetalic carbon atom, gives a signal at 30.8 ppm when in the axial position and at 41.9 ppm when in the equatorial position.

The two protons of this last group are diastereotopic; in the ^1H NMR spectrum, they give a unique signal at 1.58 ppm when the chain is in the equatorial position, and two signals at 1.65 and 1.90 ppm when the chain is in the axial position. This confirms the presence of the severe *syn* axial interaction which limits rotation around the C-7–C-8 bond.



	R_1	R_2
12a **12b**	CH_3-$(CH_2)_4$	CH_3
13a **13b**	CH_3-$(CH_2)_7$	CH_3
14a **14b**	CH_3-$(CH_2)_{10}$	CH_3
15a **15b**	CH_3-$(CH_2)_{12}$	CH_3
16a **16b**	CH_3-$(CH_2)_5$	CH_3-$(CH_2)_5$

	R_1	R_2
12'a **12'b**	CH_3	CH_3-$(CH_2)_4$
13'a **13'b**	CH_3	CH_3-$(CH_2)_7$
14'a **14'b**	CH_3	CH_3-$(CH_2)_{10}$
15'a **15'b**	CH_3	CH_3-$(CH_2)_{12}$

Scheme 2.

On the other hand, protons of the methyl group appear as two singlets at 1.40 (axial position) and 1.25 ppm (equatorial position). According to the spectral data, the ratio of **14a**:**14a'** is estimated to be 60:40.

As a first indication of detergent properties, evolution of surface tension as a function of concentration has been evaluated in order to determine the critical micelle concentration (CMC) (Table 1). The CMC of compounds **3**–**7** and **13** and **14** is comparable with those of commercially available alkylpolyglucosides (APG). Lower CMCs are obtained for a C_{12}–C_{14} chain, which is in agreement with observations made with other derivatives [3]. The presence of a methyl group on the acetalic carbon atom has no influence on these properties (compounds **12** and **15**). Comparison of results obtained for compounds **2**, **3**, and **10** shows the influence of the phenyl group, which seems to be equivalent to a C_3 chain as far as only the CMC is concerned.

In conclusion, this new class of sucrose derivatives should receive much attention as a potentially useful application of sucrose in areas other than the classical food market. Many of these new sucrose acetals could be of interest in the detergent field, as they show promising CMC values and new structural characteristics due to the acetal group.

Table 1
CMC values for compounds **2b**–**16b**

Compounds	CMC (mg/L)	Surface tension (dyne/cm)
2b	500	30
3b	120	33
4b	60	39
5b	12	38
8b	200	40
9b	500	48
10b	200	33
11b	300	33
13b	80	31
14b	70	37
15b	18	31
16b	300	25

3. Experimental

General methods.—Melting points were determined on a Büchi apparatus. Evaporations were performed under reduced pressure. Optical rotations were measured on a Perkin–Elmer 141 polarimeter in 1-dm tubes. Column chromatography was carried out with Silica Gel 60 (E. Merck 70–230 mesh), and TLC was carried out on precoated plates (E. Merck 5724), with detection by charring with H_2SO_4. ^1H NMR spectra (60 or 400 MHz) were recorded on a Varian T-60

Table 2
^{1}H NMR data for compounds **2a–15a**

^{1}H NMR	Compounds					
	2a–7a	**12a–15a**	**11a**	**10a**	**9a**	**8a**
H-1	d 5.63	d 5.63	d 5.70	d 5.66	d 5.66	d 5.66
	$J_{1,2}$ 4 Hz	$J_{1,2}$ 4 Hz	$J_{1,2}$ 4 Hz	$J_{1,2}$ 4 Hz	$J_{1,2}$ 4 Hz	$J_{1,2}$ 4 Hz
H-3,3',4'	m 5.40	m 5.40	m 5.46	m 5.43	m 5.43	m 5.43
H-2	dd 4.76	dd 4.76	dd 4.86	dd 4.86	dd 4.86	dd 4.86
	$J_{2,3}$ 10 Hz	$J_{2,3}$ 10 Hz	$J_{2,3}$ 10 Hz	$J_{2,3}$ 10 Hz	$J_{2,3}$ 10 Hz	$J_{2,3}$ 10 Hz
H-5'	d 3.56	m 3.66	d 3.60			
H (acetal)	t 3.40		t 3.30			
	J 3.5 Hz					
$-CH_2-$OAc	m 4.27	m 4.00	m 4.23	m 4.23	m 4.23	m 4.23
OAc	m 2.10	m 2.10	m 2.10	m 2.10	m 2.10	m 2.10
CH_3 (acetal)		2 s 1.40				
		1.30				
$-(CH_2)_n-$	m 1.34	m 1.95–1.15	m 1.30	m 1.30		
$-(CH_2)_n-CH_3$	m 0.93	m 0.90	m 0.90	m 0.95		
			(Ph) s 7.26	(Ph) m 7.40	(Ph) m 7.4	(chain)
			(HC=) s 6.7			m 5.15
			(H_2C–C=) m 2.10			m 3.50
						m 2.10
						m 1.70

[a] In $CDCl_3$.

spectrometer or on a Bruker AC 400 spectrometer. Chemical shift data are given in ppm measured downfield from internal Me_4Si, and spin–spin coupling data are in Hz. ^{13}C NMR spectra were recorded on a JEOL FX 60 or on a Bruker AC 400 spectrometer. Surface tensions were measured with a Prolabo TD 2000 tensiometer. Elemental analyses were carried out by the Service Central d'Analyses du CNRS in Lyon, France; compounds **1** to **14** gave C, H analysis ±0.5%.

*Reaction of aldehydes with 1,'2,3,3',4',6'-hexa-*O*-acetyl sucrose* (**1**)*: General method for the synthesis of acetals* **2–8**.—Three mol equiv of aldehyde and a catalytic amount of *p*-toluenesulfonic acid were added to a solution of the diol **1** in anhydrous toluene, and the solution was refluxed with water removal via a Dean–Stark trap. After 3 to 4 h, all starting material had disappeared as indicated by TLC (1:1 AcOEt–hexane). The solution was then neutralized with Na_2CO_3 and filtered, and the solvent was evaporated under reduced pressure. The crude syrup was purified on a silica gel column (2:1 hexane–AcOEt:). Sucrose acetals **2a–8a** were obtained in 60–80% yield. Deacetylation was then achieved with sodium methanolate, according to the classical Zemplén procedure (catalytic amount of sodium methoxide–methanol, room temperature) to give **2b–8b**.

Reaction of aldehyde dimethyl acetals with sucrose: General method for the preparation of acetals **9–11**.—The reagent (2 mol equiv) was added to a suspension of sucrose in anhydrous DMF at room temperature. A catalytic amount of pyridinium *p*-toluenesulfonate was added, and the mixture was stirred for 20 h at room temperature. Progress of the reaction was monitored by TLC (12:5:3 acetone–AcOEt–H_2O). The mixture was then neutralized with Na_2CO_3 and filtered, and the solvent was removed under reduced pressure. The resulting viscous residue was acetylated in pyridine at 0°C with acetic anhydride. After the usual treatment (neutralization with an ice–Na_2CO_3 mixture, extraction with dichloromethane, washing with a saturated $NaHCO_3$ solution, and drying), the resulting syrup was chromatographed, and the sucrose acetals were obtained in ~ 30% yield.

Reaction of ketone dimethyl acetals with sucrose: General method for transacetalation for the synthesis of acetals **12–16**.—Sucrose was suspended in dry DMF, and 2 mol equiv of the chosen dimethyl acetal were added with a catalytic amount of *p*-toluenesulfonic acid. Stirring was continued along 120 min. Progress of the reaction was monitored by TLC (1:1 acetone–AcOEt, or 12:5:3 AcOEt–EtOH–H_2O). The solution was then neutralized with Na_2CO_3 and fil-

Table 3
^{1}H NMR data for compounds **4a**, **14a,a′,b,b′**, and **16a**

^{1}H NMR (400 MHz)	Compound						
	4a	**14a,a′**	**16a**	**14b**		**14b′**	
	$CDCl_3$	$CDCl_3$	$CDCl_3$	Me_2SO-d_6	$+D_2O$	Me_2SO-d_6	$+D_2O$
H-1	m 5.60	m 5.61	m 5.54	d 5.20	d 5.19 $J_{1,2}$ 3.9 Hz	d 5.20	d 5.17 $J_{1,2}$ 4.5 Hz
H-2	m 4.77	m 4.80	dd 4.82				
H-3,3′,4′	m 5.45–5.30	m 5.43–5.30	m 5.45–5.30	m 3.95–3.25	m 3.90–3.20	m 3.95–3.25	m 3.95–3.25
H-1′,4,5,6,6′	m 4.30–3.30	m 4.30–3.55	m 4.30–3.55				
CH_3 (OAc)	2.20–1.95	2.20–2.05	2.20–2.00	–	–	–	–
H (acetal)	t 4.42	–		–	–	–	–
$-CH_2-$C (acetal)	m 1.55	m 1.65–1.57	m 1.90; 1.65; 1.55	m 1.52	2m 1.92; 1.67	2m 1.87; 1.68	J_{gem} 12 Hz
H_3C-C (acetal)	–	s 1.40 (ax) s 1.20 (eq)		s 1.40	s 1.36	s 1.25	s 1.25
$-(CH_2)_n-$	m 1.35–1.15	m 1.45–1.15	m 1.35–1.20	m 1.40–1.20	m 1.30–1.15	m 1.35–1.20	m 1.30–1.15
$-(CH_2)_n-CH_3$	t 0.84	t 0.86	2t 0.90; 0.87	t 0.88	t 0.84	t 0.87	t 0.85
OH		–		5.28; 5.20; 4.97; 4.85; 4.27	–	5.28; 5.20; 5.05; 4.85; 4.27	–

Table 4
^{13}C NMR data for compounds **2a–15a**

^{13}C NMR [a]	Compounds					
	2a–7a	**12a, 13a, 14a, 15a**	**11a**	**10a**	**9a**	**8a**
CH_3–$(CH)_n$–	13.9, 14.1	14.0	13.8	14.1		alkyl chain
–CH_2–C (acetal)		30.8; 41.8	C=C 136.7; 137.6	Ph 126.8; 128.2; 134.4; 143.9	Ph 126.8–142.0	
			Ph 126.7; 128.0; 128.6			
–$(CH_2)_n$–	21.2–34.1	22.6–31.9	22.4–31.3	22.5–35.7		120–143.4
CH_3–CO–	20.5	20.7	20.4	20.6	20.7	20.7
CH_3–C (acetal)		17.5; 24.0				
C-1	90.4–90.6	90.6	90.2	90.5	90.6	90.5
C-7	102.8–102.9	101.0; 101.7	103.4	101.8	101.5	99.6
C-2′	104.0–104.1	104.0; 104.2	103.8	104.1	104.2	104.0
–CO–	169.0–171.0	169.0–171.0	169.0–171.0	169.0–171.0	169.0–171.0	169.0–171.0

[a] In $CDCl_3$.

Table 5
^{13}C NMR data for compounds **4a**, **14a,a',b,b'** and **16a**

^{13}C NMR	Compound **4a** $CDCl_3$	**16a** $CDCl_3$	**14a,a'** $CDCl_3$	**14b** Me_2SO-d_6	**14b'** Me_2SO-d_6
C-1	90.35	90.32	90.51; 90.42	92.32	92.32
C-2'	104.11	103.90	104.05; 103.94	104.10	104.10
C-2–C-5		79.1–64.5	79.35–64.30	82.49–63.80	82.49–63.26
C-3'–C-5'	79.53–61.76				
C-1',6,6'		64.5–61.5	64.67; 61.62	62.06; 61.82; 61.60	62.06; 61.78; 61.39
C (acetal)	103.60	102.6	101.64; 101.00	99.90	100.53
H_3C–C (acetal)	–		26.19; 17.42	17.48	26.35
$-H_2C$–C (acetal)	33.92–22.60	38.3; 28.9	41.90; 30.82	41.92	30.47
$-(CH_2)_n-$		31.0–20.6	31.92–22.69	31.40–22.13	31.40–22.20
$-(CH_2)_n-CH_3$	14.04	14.1	14.13	14.00	14.00
CO (OAc)	170.50–169.70	170.64–169.86	170.65–169.81	–	–
CH_3 (OAc)	20.67–20.52	20.7	21.22–20.59		

Table 6
Optical rotations for compounds **2a,b–16a,b** [a]

Compounds	$[\alpha]_D^{20}$	Compounds	$[\alpha]_D^{20}$
2b	+17°	**2a**	+51°
		3a	+43°
4b	+25°	**4a**	+46°
5b		**5a**	+44°
	+27°	**6a**	+48°
7b	+27°	**7a**	+48°
8b	+65°	**8a**	+59°
		9a	+35°
10b	+44°	**10a**	+37°
11b	+46°	**11a**	+50°
12b	+33°	**12a**	+52°
13b	+31°	**13a**	+46°
14b	+16°	**14a**	+45°
		16a	+37°

[a] *c* 0.1, $CHCl_3$.

tered, and the solvent was evaporated under reduced pressure. Further purification of the syrupy residue on a silica gel column gave acetals **12b–16b** in ~30% yield. These compounds were quantitatively acetylated by the usual method (see preceding section). Physical constants and spectral data for acetals **1–16** are given in Tables 2–7.

Acknowledgements

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Table 7
Elemental analyses

Compound	Formula	Calcd:			Found:		
		% C	% H	% O	% C	% H	% O [a]
2a	$C_{31}H_{46}O_{17}$	53.91	6.71	39.38	54.05	6.98	39.06
3a	$C_{34}H_{52}O_{17}$	55.73	7.15	–	56.12	7.15	–
4a	$C_{36}H_{56}O_{17}$	56.83	7.42	35.75	56.99	7.46	35.93
5a	$C_{38}H_{60}O_{17}$	57.86	7.67	–	58.25	8.06	–
6a	$C_{40}H_{64}O_{17}$	58.81	7.90	33.29	58.57	7.90	33.03
7a	$C_{42}H_{66}O_{17}$	59.84	7.89	32.27	59.67	8.31	32.18
8a	$C_{34}H_{48}O_{17}$	56.04	6.64	37.32	56.31	6.55	37.60
9a	$C_{37}H_{42}O_{17}$	58.67	5.58	–	58.99	5.66	–
10a	$C_{37}H_{50}O_{17}$	57.96	6.57	35.47	58.12	6.54	35.82
11a	$C_{39}H_{52}O_{17}$	59.08	6.61	34.31	59.01	6.76	34.09
12a	$C_{31}H_{46}O_{17}$	53.91	6.71	–	54.42	6.78	–
13a	$C_{34}H_{52}O_{17}$	55.73	7.15	37.12	55.64	7.18	37.42
14a	$C_{37}H_{58}O_{17}$	57.35	7.34	35.10	57.22	7.67	34.35
16a	$C_{37}H_{58}O_{17}$	57.35	7.54	35.10	57.78	7.37	35.01

[a] Measured by pyrolysis.

and (*E*) of compound **8** has been carried out (G. Descotes et al., UMR 143 Béghin-Say CNRS, to be published). We thank C. Lamazzi for a study of compound **16**.

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