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Synthesis and surface-active properties of a new class of surfactants derived from D-gluconic acid

Maryline Abert,[a] Nathalie Mora,[a] Jean-Michel Lacombe[b,*]

[a]*Laboratoire de Chimie Bioorganique et des Systèmes Moléculaires Vectoriels, Faculté des Sciences d'Avignon, 33, rue Louis Pasteur, F-84000 Avignon, France*

[b]*UMR A 408 Qualité et Sécurité des Aliments d'Origine Végétale, Faculté des Sciences d'Avignon, 33, rue Louis Pasteur, F-84000 Avignon, France*

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Abstract

Novel sugar-based surfactants were synthesized starting from D-gluconolactone. Three different functional groups were used to link the sugar moiety and the hydrophobic part. The physico-chemical properties for the use as adjuvant for pesticidal formulations of one of these compounds were evaluated and compared. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Surface active agents or surfactants are widely used as spray adjuvants in formulations of agrochemicals to improve their effectiveness following application to foliage.[1] Surfactant can be conveniently divided into two broad categories:[2] "spray modifiers" that can be added to improve physico-chemical properties of formulations, and "activators" that can be added specifically to help foliar absorption of systemic active ingredients. "Spray modifiers" are the most important category and their addition to formulations is essential for improvement of: (i) the emulsion and/or suspension stability; (ii) the increase of the contact surface on the leaves (wetting/spreading); and (iii) the physical properties of the spray deposit such as the sticking properties and persistence. Wetting agents are the most important adjuvants of the "spray modifiers" category. They avoid losses of pesticides that occur during the first stage of the application process (from atomization of spray droplets to impact on foliage). Losses may arise mainly from reflection and run off, and both factors contribute to poor overall retention and target coverage. Wetting agents are added to cause spray droplets to adhere and spread on foliage. They usually contain only non-ionic surfactants because they are generally compatible with all active ingredients. Non-ionic surfactants do not carry an electrical charge that could "short-circuit" the pesticide activity. The most common larger used non-ionic surfactants in the phytosanitary domain are *n*-alkyl polyoxyethylene glycol ethers with alkylphenols, aliphatic alcohols, or fatty acids as the hydrophobic part. Recently, attention has been paid to a different class of surfactants containing alkylsiloxane polymers as the hydrophobic moiety. Organosilicone[3] surfactants differ from conventional surfactants because of their excellent wetting and penetrating characteristics.

The main object of this paper is the synthesis of a new class of non-ionic amphiphilic molecules that possess a hydrophilic sugar portion and the study of their surface active properties. As sugars are environmentally friendly, natural substances, this class of surfactants could offer perspectives for use as attractive industrially manufactured products,[4] including use as wetting agents in agricultural spray application. Surface active agents here reported have the following general formula:

* Corresponding author. Tel.: +33-4-90144446; fax: +33-4-90144449.

E-mail address: jean-michel.lacombe@univ-avignon.fr (J.-M. Lacombe).

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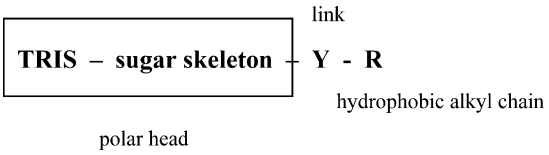
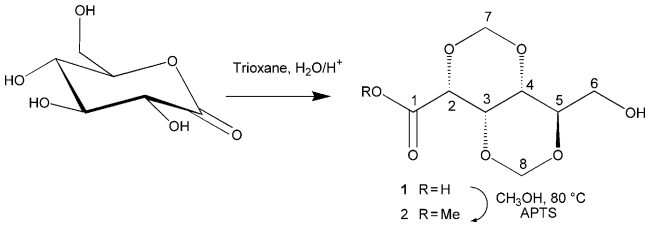


where TRIS = tris(hydroxymethyl)methylamine, sugar skeleton = a derivative of gluconic acid, and Y = (–OC(O)NH–, –NHC(O)–, or –C(O)NH–) and R = hydrophobic alkyl chain.

2. Results and discussion

Synthesis.—The key sugar skeleton **2** was obtained in two steps[5] as shown in Scheme 1. D-Gluconolactone



Scheme 1.

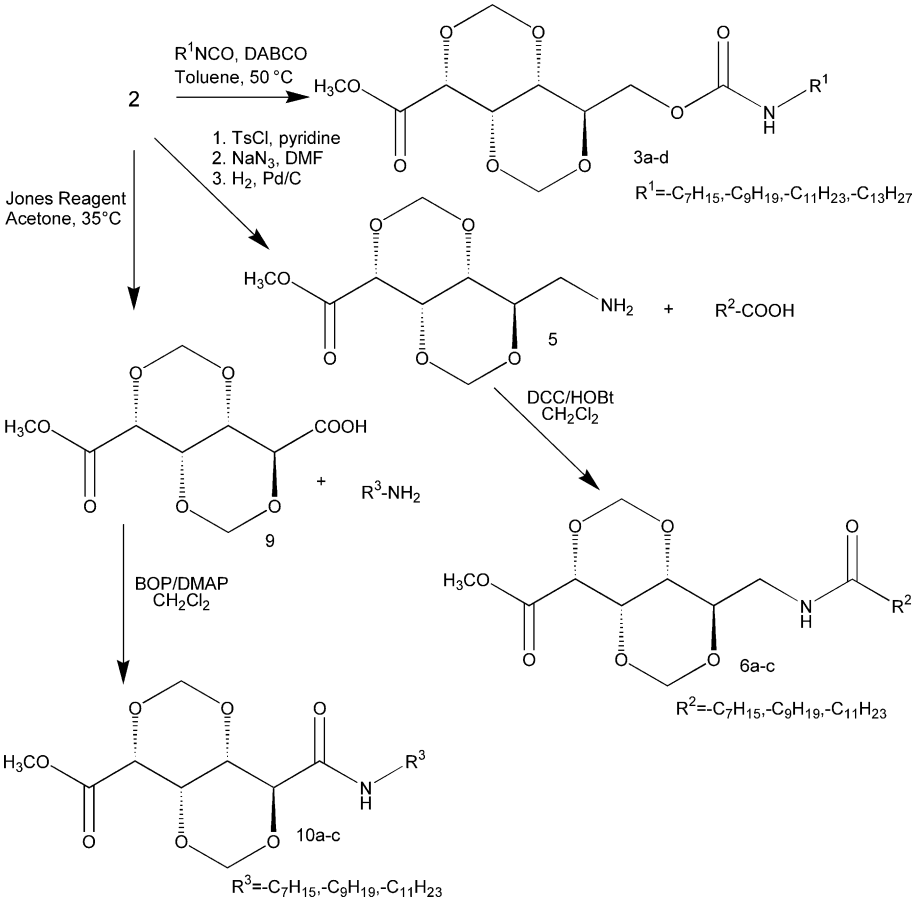
was hydrolyzed and protected in a one-step procedure[6] on its secondary hydroxyl functions. The resulting product was esterified to give methyl-2,4;3,5-di-*O*-methylene-D-gluconate which has been purified by recrystallization in methanol and characterized by NMR spectroscopy.

The C-6 carbon of the sugar skeleton was connected to an aliphatic alkyl chain by a carbamate, amide or "inverse" amide functionality.

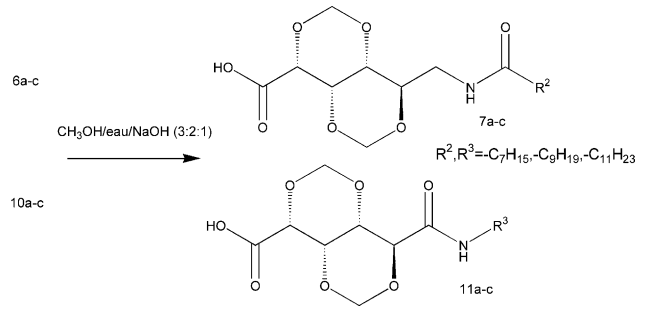
The route for the synthesis of different intermediates is shown in Scheme 2.

Compound **2** was reacted with alkyl isocyanate to give alkylaminocarbonyl 2,4;3,5-di-*O*-methylene-6-*O*-D-gluconic acid methyl ester. The reaction was carried out in toluene at 50 °C with 1,4-diazabicyclo[2.2.2]octane (DABCO)[7] and afforded **3a**–**d** in a good yields (> 70%).

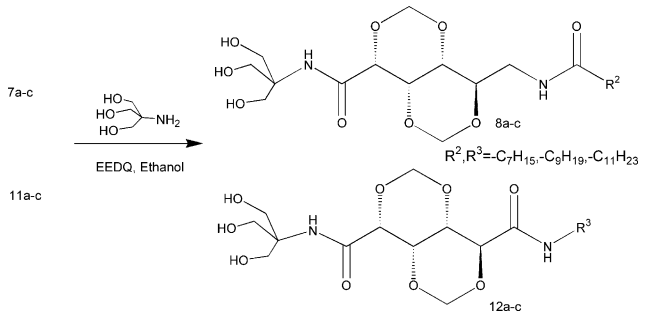
We also prepared a second series (**6a**–**c**) having an amidic linkage. Compound **2** was tosylated and subsequently substituted by an azide group that was hydrogenated using Pd–C as a catalyst to give the amine **5**. The amine intermediate was further reacted with fatty acids to generate compounds **6a**–**c**. Condensation of



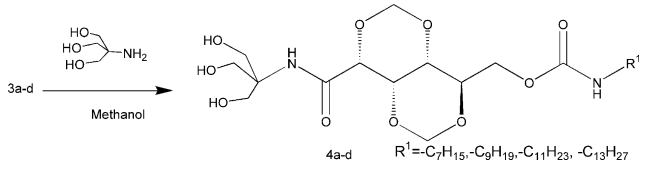
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

the hydrophobic chains with **5** was achieved in the presence of dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBT) in 52–60% yield.

A third type of linkage has been investigated by oxidation reaction[8] of compound **2** with Jones reagent[9,10] (CrO_3 in aqueous acetone) to the carboxylic acid derivative **9**. Compounds **10a**–**c** were obtained by condensation of **9** with the corresponding fatty amine. This reaction was performed in dichloromethane in the presence of benzotriazol-1-yloxy-tris(dimethylamino)-phosphonium hexafluorophosphate (BOP reagent) with a catalytic amount of dimethylaminopyridine (DMAP). Coupling yields ranged between 62 and 65%.

The water solubility of **3a**–**d**, **6a**–**c**, and **10a**–**c** was not sufficient to allow physico-chemical studies, and it was necessary to incorporate an additional polar-head group for this purpose. In this respect, the plurifunctionality of TRIS is of interest. The protecting ester group of **6a**–**c** and **10a**–**c** was first removed by alkaline hydrolysis as shown in Scheme 3. Then, they were coupled to TRIS in refluxing ethanol in the presence of 2 - ethoxy - 1 - ethoxycarbonyl - 1,2 - dihydroquinoleine (EEDQ) (Scheme 4).

Compounds **3a**–**d** were directly coupled to TRIS by refluxing in methanol. However, this reaction was possible only with a large excess of the amine reagent (TRIS) (Scheme 5).

All these compounds have been characterized by NMR spectroscopy (^1H and ^{13}C). The NMR data are collected in Tables 1 and 2.

Physico-chemical properties of the synthesized surfactants.—Several approaches can be used to study wetting properties. Initially, the tests were carried out without the pesticide in order to determine general characteristics, followed by experiments with pure pesticide and formulated product.

In the present study, we have evaluated the general characteristics of surfactants by studying the wetting efficiency and performance by measuring the reduction of static and dynamic surface tension and contact angle formed on leaf surfaces.

Static and dynamic surface tension measurements.—In a preliminary examination of surfactant properties, the surface tension (γ) and critical micellar concentration (CMC) of compounds **4a**–**d**, more easily available and with better water solubility properties than **8a**–**c** and **12a**–**c**, were measured in water at 25 °C. The tensioactive properties of the above derivatives were compared with SILWET L77 (S77) and RHODASURF 860P (R860P) as reference wetting agents. SILWET L77 (trisiloxane methyl esters) and RHODASURF 860P (polyethoxylated fatty alcohol) are usually used for their wetting properties in agricultural spray applications. Static surface tension reduction and CMC of compounds **4a**–**d**, S77 and R860P were measured by the Wilhelmy[11] plate method. Values are listed in Table 3.

We can notice that CMC decreases for each additional methylene in the alkyl chain of carbamate derivatives. The surface tension at the CMC is similar for compounds **4b**–**d**, higher for R860P and lower for S77. This latter lowers the surface tension to a value near 20 mN/m. The exceptional property of organosilicone surfactants is their ability to wet rapidly low-energy surfaces. Due to this superspreading property, they are extensively used as adjuvant in plant protection formulations.[12] The carbamate derivatives could be attractive and effective surfactants because **4b**–**d** reduce surface tension to a value lower than that of R860P and the concentration of **4c** required to reduce surface tension (i.e., CMC) is of comparable magnitude to those S77 and R860P.

Static surface-tension values of surfactants in water, however, give an incomplete indication of their capabilities as wetting agents. The effectiveness of a wetting agent depends on the ability of surfactant molecules to reduce surface tension at the droplet–leaf interface. When a new interface is created, it takes time for the surfactant molecules to diffuse to this new interface and

Table 1
^{1}H NMR chemical shifts (δ, ppm) for **2**–**12**

Compounds (solvent)	H-2	H-3	H-4	H-5	H-6	H-6′	H-7a	H-7b	H-8a	H-8b	OCH_3	CH_2OH	NH	$CH_2CH_2(CH_2)_nCH_3$			
2 (Me_2SO)	4.59	3.82	3.73–3.68	3.73–3.68	3.73–3.68	3.73–3.68	5.07	4.76	4.94	4.79	3.70						
3a ($CDCl_3$)	4.39–4.3	3.76	4.14–4.1	4.14–4.1	4.39–4.3	4.39–4.3	5.28	4.78	5.02	5.02	3.82			3.17	1.52	1.23	0.85
3b ($CDCl_3$)	4.39–4.3	3.76	4.14–4.1	4.14–4.1	4.39–4.3	4.39–4.3	5.28	4.78	5.02	5.02	3.82			3.17	1.52	1.23	0.85
3c ($CDCl_3$)	4.39–4.3	3.76	4.14–4.1	4.14–4.1	4.39–4.3	4.39–4.3	5.28	4.78	5.02	5.02	3.82			3.17	1.52	1.23	0.85
3d ($CDCl_3$)	4.39–4.3	3.76	4.14–4.1	4.14–4.1	4.39–4.3	4.39–4.3	5.28	4.78	5.02	5.02	3.82			3.17	1.52	1.23	0.85
4a ($CDCl_3$)	4.43–4.32	3.75–3.59	4.19–4.14	4.19–4.14	4.43-4.32	4.43–4.32	5.27	4.82	5.02	5.02		3.75–3.59	5.07	3.00	1.38	1.23	0.85
4b ($CDCl_3$)	4.43–4.32	3.75–3.59	4.19–4.14	4.19–4.14	4.43–4.32	4.43–4.32	5.27	4.82	5.02	5.02		3.75–3.59	5.07	3.00	1.38	1.23	0.85
4c ($CDCl_3$)	4.43–4.32	3.75–3.59	4.19–4.14	4.19–4.14	4.43–4.32	4.43–4.32	5.27	4.82	5.02	5.02		3.75–3.59	5.07	3.00	1.38	1.23	0.85
4d ($CDCl_3$)	4.43–4.32	3.75–3.59	4.19–4.14	4.19–4.14	4.43–4.32	4.43–4.32	5.27	4.82	5.02	5.02		3.75–3.59	5.07	3.00	1.38	1.23	0.85
5 ($CDCl_3$)	4.35	3.74	3.61–3.51	3.61–3.51	4.08	4.08	5.27	4.76	4.94	4.86	3.85						
6a ($CDCl_3$)	4.32	3.74	3.61–3.45	3.61–3.45	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99	3.83		5.74	2.23	1.65	1.25	0.87
6b ($CDCl_3$)	4.32	3.74	3.61–3.45	3.61–3.45	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99	3.83		5.74	2.23	1.65	1.25	0.87
6c ($CDCl_3$)	4.32	3.74	3.61–3.45	3.61–3.45	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99	3.83		5.74	2.23	1.65	1.25	0.87
7a ($CDCl_3$)	4.32	3.69–3.65	3.69–3.65	3.69–3.65	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99			5.98	2.23	1.65	1.25	0.87
7b ($CDCl_3$)	4.32	3.69–3.65	3.69–3.65	3.69–3.65	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99			5.98	2.23	1.65	1.25	0.87
7c ($CDCl_3$)	4.32	3.69–3.65	3.69–3.65	3.69–3.65	4.16–3.96	4.16–3.96	5.27	4.78	4.99	4.99			5.98	2.23	1.65	1.25	0.87
8a ($CDCl_3$)	4.21–4.00	3.87–3.63	3.87–3.63	3.87–3.63	4.21–4.00	4.21–4.00	5.3	4.82	5.04	5.04		3.87–3.63	6.04	2.23	1.65	1.25	0.87
8b ($CDCl_3$)	4.21–4.00	3.87–3.63	4.19–4.14	3.87–3.63	4.21–4.00	4.21–4.00	5.3	4.82	5.04	5.04		3.87–3.63	6.04	2.23	1.65	1.25	0.87
8c ($CDCl_3$)	4.21–4.00	3.87–3.63	3.87–3.63	3.87–3.63	4.21–4.00	4.21–4.00	5.3	4.82	5.04	5.04		3.87–3.63	6.04	2.23	1.65	1.25	0.87
9 ($CDCl_3$)	4.61	4.11	3.99	4.30			5.23	4.80	5.04	5.04	3.77						
10a ($CDCl_3$)	4.47	4.34	4.02	4.47			5.31	4.80	5.12	4.80	3.82		6.51	3.54	1.55	1.26	0.87
10b ($CDCl_3$)	4.47	4.34	4.02	4.47			5.31	4.80	5.12	4.80	3.82		6.51	3.54	1.55	1.26	0.87
10c ($CDCl_3$)	4.47	4.34	4.02	4.47			5.31	4.80	5.12	4.80	3.82		6.51	3.54	1.55	1.26	0.87
11a (CD_3OD)	4.54	4.17	4.17	4.3			5.31	4.80	5.00	5.00			6.56	3.31	1.55	1.26	0.92
11b (CD_3OD)	4.54	4.17	4.17	4.3			5.31	4.80	5.00	5.00			6.56	3.31	1.55	1.26	0.92
11c (CD_3OD)	4.54	4.17	4.17	4.3			5.31	4.80	5.00	5.00			6.56	3.31	1.55	1.26	0.92
12a (CD_3OD)	4.26	4.02	4.02	4.26			5.24	5.24	4.82	4.82	-	3.66	6.56	3.21	1.41	1.19	0.82
12b (CD_3OD)	4.26	4.02	4.02	4.26			5.24	5.24	4.82	4.82		3.66	6.56	3.21	1.41	1.19	0.82
12c (CD_3OD)	4.26	4.02	4.02	4.26			5.24	5.24	4.82	4.82		3.66	6.56	3.21	1.41	1.19	0.82

Table 2
^{13}C NMR chemical shifts (δ, ppm) for **2**–**12**

Compounds (solvent)	*C*OOCH$_3$	C-2	C-3	C-4	C-5	C-6	C-7	C-8	COO*C*H$_3$	O*C*ONH	(CH$_2$)$_n$	CH$_3$	NH*C*OR	COOH	*C*ONHR	*C*ONH$_{tris}$	CH$_2$OH	C_{tris}
2 (Me$_2$SO)	167.9	76.15	75.6	70.16	68	58.68	91.3	87.3	51.8									
3a (CDCl$_3$)	167.9	77.03	74.2	70.9	67.6	61.17	92.44	88.5	52.6	155.6	41.26–22.5	14.05						
3b (CDCl$_3$)	167.9	77.03	74.2	70.9	67.6	61.17	92.44	88.5	52.6	155.6	41.26–22.5	14.05						
3c (CDCl$_3$)	168.4	77.37	74.8	71.6	68.3	61.82	93.11	89.2	53.34	156.43	41.2–23.35	14.8						
3d (CDCl$_3$)	168.4	77.37	74.8	71.6	68.3	61.82	93.11	89.2	53.34	156.43	41.2–23.35	14.8						
4a (CDCl$_3$)		77.4	74.8	71.8	68.6	62.1	92.01	88.65		155.6	41.2–23.35	14.8				168.8	63.98	62.45
4b (CDCl$_3$)		77.4	74.8	71.8	68.6	62.1	92.01	88.65		155.6	41.2–23.35	14.8				168.8	63.98	62.45
4c (CDCl$_3$)		77.4	74.8	71.8	68.6	62.1	92.01	88.65		155.6	41.2–23.35	14.8				168.8	63.98	62.45
4d (CDCl$_3$)		77.4	74.8	71.8	68.6	62.1	92.01	88.65		155.6	41.2–23.35	14.8				168.8	63.98	62.45
5 (CDCl$_3$)	167.9	76.6	73.15	70.5	67.35	66.9	92.32	88.91	52.72									-
6a (CDCl$_3$)	167.7	77.2	76.66	75.03	71.44	67.37	92.4	88.7	52.4		37.25–22.4	14.05	173.6					
6b (CDCl$_3$)	167.7	77.2	76.66	75.03	71.44	67.37	92.4	88.7	52.4		37.25–22.4	14.05	173.6					
6c (CDCl$_3$)	167.7	77.2	76.66	75.03	71.44	67.37	92.4	88.7	52.4		37.25–22.4	14.05	173.6					
7a (CDCl$_3$)		77.2	76.66	75.03	71.44	67.37	92.2	87.5			36.4–22.6	14.05	174.9	169.3				
7b (CDCl$_3$)		77.2	76.66	75.03	71.44	67.37	92.2	87.5			36.4–22.6	14.05	174.9	169.3				
7c (CDCl$_3$)		77.2	76.66	75.03	71.44	67.37	92.2	87.5			36.4–22.6	14.05	174.9	169.3				
8a (CDCl$_3$)		72.2	75.66	71.7	68.19	67.5	92.04	87.6			38.8–22.5	14.05	174.9			168.7	63.35	61.79
8b (CDCl$_3$)		72.2	75.66	71.7	68.19	67.5	92.04	87.6			38.8–22.5	14.05	174.9			168.7	63.35	61.79
8c (CDCl$_3$)		72.2	75.66	71.7	68.19	67.5	92.04	87.6			38.8–22.5	14.05	174.9			168.7	63.35	61.79
9 (CDCl$_3$)	167.59	75.21	74.42	69.96	68.7		91.3	89.18	51.8					168.1				
10a (CDCl$_3$)	168.02	77.12	76.9	70.42	69.23		93.38	90.31	52.29		40.12–23.3	14.7			168.31			
10b (CDCl$_3$)	168.02	77.12	76.9	70.42	69.23		93.38	90.31	52.29		40.12–23.3	14.7			168.31			
10c (CDCl$_3$)	168.02	77.12	76.9	70.42	69.23		93.38	90.31	52.29		40.12–23.3	14.7			168.31			
11a (CD$_3$OD)		78.4	77.3	72.3	71.6		93.38	93.1			40.12–23.3	14.7		171.1	169.7			
11b (CD$_3$OD)		78.4	77.3	72.3	71.6		93.38	93.1			40.12–23.3	14.7		171.1	169.7			
11c (CD$_3$OD)		78.4	77.3	72.3	71.6		93.38	93.1			40.12–23.3	14.7		171.1	169.7			
12a (CD$_3$OD)		77.3	77.1	71.6	71.35		93.04	92.9			39.82–23.25	14.74			167.06	169.16	64.35	62.35
12b (CD$_3$OD)		77.3	77.1	71.6	71.35		93.04	92.9			39.82–23.25	14.74			167.06	169.16	64.35	62.35
12c (CD$_3$OD)		77.3	77.1	71.6	71.35		93.04	92.9			39.82–23.25	14.74			167.06	169.16	64.35	62.35

reduce the surface tension. If surface tension is not reduced rapidly enough, the droplets may bounce from the leaf surface. This affect is thought to be related to dynamic surface tension.[13,14] In fact, when a droplet impinges on a leaf surface, it undergoes an initial flattening, causing formation of a new liquid surface, followed by recoil and bounce or retention. The change in surface tension at the new interface with time is known as dynamic surface tension. Surface tension measurements of surfactants studied are listed in Table 4.

Table 3
Surfactants properties of **4a**–**d**, S77 and R860P

Product	CMC [a] (mM)	$\gamma_{stat.}$ (mN/m)
4a	n.d. [b]	n.d. [b]
4b	0.8	29.5
4c	0.33	28.5
4d	0.011	27.7
S77	0.12	20
R860P	0.19	33.2

[a] Measured at 25 °C in water
[b] Not determined.

Table 4
Surface tension data for the surfactants

Surfactant	concentration (%)	$\gamma_{stat.}$ (mN/m)	$\gamma_{dyn.}$ (mN/m)
4b	0.01	38	69
	0.05	29.5	65
4c	0.01	34	70
	0.05	28.5	69
4d	0.01	27.7	70
	0.05 [a]		
R860P	0.01	46	67
	0.05	33.2	45
S77	0.01	26.1	70
	0.05	20	62

[a] Insoluble at this concentration.

Table 5
Contact angle measurements on wheat (average of ten measurements)

Surfactant	concentration (%)	Contact angle θ (°) on wheat [b]
Water		123(2.5)
4b	0.01	109.5(3.4)
	0.05	83.0(4.1)
4c	0.01	82.9(5)
	0.05	72.4(4.5)
4d	0.01	61.8(4.6)
	0.05 [a]	
R860P	0.01	100.4(3.6)
	0.05	60.8(5.1)
S77	0.01	47.8(6.5)

[a] Insoluble at this concentration.
[b] The contact angle standard deviations are given in parentheses.

Under equilibrium and near static conditions, among hydrocarbon-based surfactants, **4b**–**d** have sufficient time to achieve optimum interfacial packing to produce low static surface tension whereas R860P does not pack at the interface as well. The dynamic surface tension lowering is faster for R860P than for **4b**–**d**. These results suggest that R860P molecules can migrate in the expanding droplet–leaf interface more effectively than the carbamate derivatives. Compounds **4b**–**d** provide dynamic surface tension values comparable to S77 at the same concentration. Compound S77 reduces static surface tension of spray solutions to levels lower than those that can be achieved by conventional hydrocarbon-based surfactants. Dynamic surface tension of S77 and general silicone surfactants, however, is not consistently lower than that of conventional surfactants.

Contact angle measurements.—The angle contact[15] between a liquid and a solid is a measure of the tendency for the liquid to spread over or wet the solid surface. The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs at an angle of zero degree.

Contact angles were determined using ten replicate droplets (1 μL) on ten different leaves of wheat. Measurements are reported in Table 5.

Wheat was used as the target surface in the present study because the dense coating of crystalline epicuticular wax on its leaves provides an extremely hydrophobic, reflective surface. Plant species with less waxy cuticles retain spray more readily, and therefore the effects of surfactants on adhesion are less marked.[16] It can be seen (Table 5) that, in all cases, the addition of surfactant reduced the contact angle compared with no surfactant (123° for water). The increase in surfactant concentration sharply decreased the contact angle. Contact angle is predominantly a function of surface tension. Higher values of the contact angle were recorded from solutions having higher surface tension, and vice-versa. Reduction in surface tension lowers the pulling force of the surface of the drop; the drop tends to flatten, reducing the contact angle and providing greater plant surface wetting by a given drop of liquid.

Maximum reductions in contact angle were obtained at 0.01% of **4d** and S77 and at 0.05% of R860P. At 0.01%, **4d** reduced contact angle to a value distinctly lower than the one of R860P. This phenomenon corroborates the results obtained for static surface tension data of these two surfactants.

The low contact angle of spray droplets of S77 on leaf surfaces is related to the low static surface tension of the spray solutions of S77. But, the risk of using solutions containing organosilicone surfactants is that extensive spreading droplets may lead to run-off of spray solution from foliage.

In conclusion, the physico-chemical data presented in this paper indicate that carbamate derivatives of gluconic acid may be attractive as wetting agents. They enhance droplet spreading and, thus, improve target coverage, though they have little activity upon the increase of retention. The main interest of these compounds is that they can be quickly synthesized and so could be useful in adjuvant blends commonly used in the phytosanitary domain. Further study of the scope and limitations concerning the optimization and application of these surfactants is presently in progress.

3. Experimental

General methods.—Melting points were determined on an electrothermal 9100 apparatus and are uncorrected. TLC analysis was performed on aluminium sheets coated with Silica Gel 60 F 254 (E. Merck). Compounds detection was achieved by iodine absorption, exposure to UV light (254 nm) or by charring after a 10% H_2SO_4 ethanolic solution or ninhydrin ethanolic spray (to detect the amine-containing compounds). Purifications were performed by column chromatography (Silica Gel Si 60). Optical rotations were recorded on a Perkin–Elmer 241 polarimeter in a 1 dm cell. ^1H and ^{13}C NMR spectra were recorded on a Brüker AC 250 spectrometer working at 250 and 80 MHz, respectively, with Me_4Si as internal reference. Elemental analysis were performed by the ''Service Central de Microanalyse de Vernaison''. All reagents were of commercial quality and were purchased from Aldrich.

The critical micellar concentration (CMC) was determined by measuring the surface tension in aqueous solutions at 25 °C by the plate method with a tensiometer Krüss K-12. The CMC was measured at the break of the slope in the γ versus log C plots as usual. The contact angles were determined with a microscope by measuring the height and diameter of the spray droplet, and assuming it spherical.[17] The dynamic surface tension measurements were determined using the maximum bubble pressure method using the Krüss dynamic surface tensiometer BP-2.

Methyl 2,4;3,5-di-O-*methylene*-D-*gluconate* (**2**).—1,5-D-Gluconolactone (4.5 g, 25.3 mmol) was dissolved by shaking in concd HCl (20 mL). Trioxane (2.3 g, 25.3 mmol) was then added and the mixture was stirred at rt for 24 h. The precipitate reaction product was collected, washed with toluene, and filtered off to afford **1** as a white powder (4.67 g, 85%). Compound **1** (3 g, 13.6 mmol) was then dissolved in dry MeOH in the presence of drierite and a catalytic amount of *p*-toluenesulfonic acid. The solution was stirred under reflux for 12 h. The precipitate was filtered off and the solvent removed under diminished pressure. The syrupy residue was purified by recrystallization (MeOH–ether) to afford pure compound **2** as a white powder (2.87 g, 90%): mp 154 °C; $[\alpha]_D$ +22.2° (*c* 1.0, DMF); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_9H_{14}O_7$: C, 46.15; H, 6.03. Found C, 46.19; H, 6.10.

General procedure for the synthesis of methyl 6-O-*alkylaminocarbonyl-2,4;3,5-di*-O-*methylene*-D-*gluconate* (**3a**–**d**).—A mixture of **2** (1.5 g, 6.4 mmol), alkyl isocyanate (7.7 mmol) and a catalytic amount of DABCO in toluene (50 mL) was stirred under reflux for 6 h. After evaporation to dryness, the mixture was purified by column chromatography on silica gel with 3:2 EtOAc–hexane as eluent. The product was crystallized from ether–hexane.

Methyl 6-O-*heptylaminocarbonyl-2,4;3,5-di*-O-*methylene*-D-*gluconate* (**3a**). From **2** and heptyl isocyanate (1.08 g); white powder (1.73 g, 73%); mp 81.1 °C; $[\alpha]_D$ +9.1° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{17}H_{29}NO_8$: C, 54.39; H, 7.79; N, 3.73. Found C, 54.42; H, 7.83; N, 3.69.

Methyl 2,4;3,5-di-O-*methylene-6*-O-*nonylaminocarbonyl*-D-*gluconate* (**3b**). From **2** and nonyl isocyanate (1.3 g); white powder (1.8 g, 70%); mp 84.6 °C; $[\alpha]_D$ +8.6° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{19}H_{33}NO_8$: C, 56.56; H, 8.24; N, 3.47. Found C, 56.79; H, 8.28; N, 3.57.

Methyl 2,4;3,5-di-O-*methylene-6*-O-*undecylaminocarbonyl*-D-*gluconate* (**3c**). From **2** and undecyl isocyanate (1.51 g); white powder (2.2 g, 80%); mp 74.5 °C; $[\alpha]_D$ +8.1° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{21}H_{37}NO_8$: C, 58.45; H, 8.64; N, 3.25. Found C, 58.76; H, 8.69; N, 3.35.

Methyl 2,4;3,5-di-O-*methylene-6*-O-*tridecylaminocarbonyl*-D-*gluconate* (**3d**). From **2** and tridecyl isocyanate (1.73 g); white powder (2.35 g, 80%); mp 87 °C; $[\alpha]_D$ +8.6° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{23}H_{41}NO_8$: C, 60.11; H, 8.99; N, 3.05. Found C, 60.28; H, 9.07; N, 3.17.

General procedure for the synthesis of 6-O-*alkylaminocarbonyl-2,4;3,5-di*-O-*methylene*-N-*tris(hydroxymethyl)methyl*-D-*gluconamide* (**4a**–**d**).—A mixture of compound **3a**–**d** (1 mmol) and tris(hydroxymethyl)methylamine (0.69 g, 5 mmol) in dry MeOH was refluxed for 36 h. After evaporation to dryness, the mixture was purified by column chromatography on silica gel with 24:1 EtOAc–MeOH as eluent.

6-O-*Heptylaminocarbonyl-2,4;3,5-di*-O-*methylene*-N-*tris(hydroxymethyl)methyl*-D-*gluconamide* (**4a**). From **3a** (0.37 g) and TRIS; amorphous hygroscopic solid (0.28 g, 60%); $[\alpha]_D$ +21.7° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C

NMR, Tables 1 and 2. Anal. Calcd for $C_{20}H_{36}N_2O_{10}$: C, 51.71; H, 7.81; N, 6.03. Found C, 51.65; H, 7.89; N, 6.07.

2,4;3,5-Di-O-methylene-6-O-nonylaminocarbonyl-N-tris(hydroxymethyl)methyl-D-gluconamide (**4b**). From **3b** (0.4 g) and TRIS; amorphous hygroscopic solid (0.44 g, 90%); $[\alpha]_D$ +19.6° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{22}H_{40}N_2O_{10}$: C, 53.65; H, 8.19; N, 5.69. Found C, 53.1; H, 8.14; N, 5.58.

2,4;3,5-Di-O-methylene-N-tris(hydroxymethyl)methyl-6-O-undecylaminocarbonyl-D-gluconamide (**4c**). From **3c** (0.43 g) and TRIS; amorphous hygroscopic solid (0.35 g, 67%); $[\alpha]_D$ +18.8° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{24}H_{44}N_2O_{10}$: C, 55.37; H, 8.52; N, 5.38. Found C, 55.39; H, 8.56; N, 5.34.

2,4;3,5-Di-O-methylene6-O-tridecylaminocarbonyl-N-tris(hydroxymethyl)methyl-D-gluconamide (**4d**). From **3d** (0.46 g) and TRIS; amorphous hygroscopic solid (0.33 g, 61%); $[\alpha]_D$ +17.4° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{26}H_{48}N_2O_{10}$: C, 56.92; H, 8.82; N, 5.11. Found C, 56.99; H, 8.87; N, 5.14.

Methyl 6-amino-6-deoxy-2,4;3,5-di-O-methylene-D-gluconate (**5**).—Compound **2** (3 g, 12.8 mmol) was dissolved in dry pyridine and tosyl chloride (3.65 g, 19.2 mmol) was added dropwise within 10 min. After stirring for 24 h at rt, the solution was poured into cold water and the aqueous layer was extracted twice with EtOAc. The organic layer was washed with 1 N HCl, satd $NaHCO_3$, dried over sodium sulfate, and concentrated under diminished pressure. The resulting syrup was purified by recrystallization in ether–hexane and the ''tosylated'' compound was obtained as white crystals (5.6 g, 93%). It (1.65 g, 3.5 mmol) was then dissolved and sodium azide (0.7 g, 20.4 mmol) was added in DMF (20 mL). The mixture was sonicated for 30 min at rt. The solvent was removed and the syrupy residue was dissolved in EtOAc, concentrated to dryness and purified by recrystallization in MeOH–ether. The ''azido'' derivative was obtained as white crystals (0.75 g, 83%). This latter compound (1.4 g, 5.4 mmol) was dissolved in MeOH. After cooling the solution, Pd–C (325 mg) was added. The mixture was hydrogenated for 12 h. After filtration on Celite, the solvent was removed under diminished pressure. Compound **5** was obtained as a clear oil (1.17 g, 93%); $[\alpha]_D$ +10.5° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_9H_{15}NO_6$: C, 46.35; H, 6.48; N, 6.01. Found C, 46.39; H, 6.55; N, 6.10.

General procedure for the synthesis of methyl 6-alcanecarboxamido-6-deoxy-2,4;3,5-di-O-methylene-D-gluconate (**6a**–**c**).—To a solution of **5** (0.93 g, 4 mmol) and the corresponding carboxylic acid (4.8 mmol) in CH_2Cl_2 (50 mL) were added dicyclohexylcarbodiimide (DCC) (0.99 g, 4.8 mmol) and a catalytic amount of hydroxybenzotriazole (HOBT). The mixture was stirred for 12 h at rt. After filtration of the formed dicyclohexylurea (DCU), the solvent was removed under diminished pressure and the syrupy residue was purified by column chromatography on silica gel with 19:1 EtOAc–MeOH as eluent. The product was crystallized from EtOAc–hexane.

Methyl 6-deoxy-6-heptanecarboxamido-2,4;3,5-di-O-methylene-D-gluconate (**6a**). From **5** and octanoic acid (0.69 g); white crystals (0.74 g, 52%); mp 120 °C; $[\alpha]_D$ +16° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{17}H_{29}NO_7$: C, 56.81; H, 8.13; N, 3.90. Found C, 56.83; H, 8.07; N, 3.93.

Methyl 6-deoxy-2,4;3,5-di-O-methylene-6-nonanecarboxamido-D-gluconate (**6b**). From **5** and decanoic acid (0.82 g); white crystals (0.82 g, 53%); mp 119.8 °C; $[\alpha]_D$ +18.5° (*c* 0.76, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{19}H_{33}NO_7$: C, 58.90; H, 8.58; N, 3.61. Found C, 58.93; H, 8.61; N, 3.57.

Methyl 6-deoxy-2,4;3,5-di-O-methylene-6-undecanecarboxamido-D-gluconate (**6c**). From **5** and dodecanoic acid (0.96 g); white crystals (1.01 g, 61%); mp 124 °C; $[\alpha]_D$ +16° (*c* 0.65, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{21}H_{37}NO_7$: C, 60.70; H, 8.98; N, 3.37. Found C, 60.73; H, 9.01; N, 3.39.

General procedure for the synthesis of 6-alcanecarboxamido-6-deoxy-2,4;3,5-di-O-methylene-D-gluconic acid (**7a**–**c**).—Compound **6a**–**c** (1 mmol) was added to 3:2:1 MeOH–water–NaOH 1 N (50 mL) and stirred for 12 h at rt. MeOH was removed under diminished pressure. The pH was adjusted to 2–3 adding 1 N HCl. The product was extracted twice by EtOAc. The solvent was evaporated to dryness.

6-Deoxy-6-heptanecarboxamido-2,4;3,5-di-O-methylene-D-gluconic acid (**7a**). From **6a** (0.36 g); amorphous hygroscopic solid (0.32 g, 95%); $[\alpha]_D$ +17.2° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{16}H_{27}NO_7$: C, 55.64; H, 7.88; N, 4.06. Found C, 55.72; H, 7.93; N, 4.11.

6-Deoxy-2,4;3,5-di-O-methylene-6-nonanecarboxamido-D-gluconic acid (**7b**). From **6b** (0.38 g); amorphous hygroscopic solid (0.35 g, 94%); $[\alpha]_D$ +20.2° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Table 1 Table 2. Anal. Calcd for $C_{18}H_{31}NO_7$: C, 57.89; H, 8.37; N, 3.75. Found C, 57.93; H, 8.41; N, 3.80.

6-Deoxy-2,4;3,5-di-O-methylene-6-undecanecarboxamido-D-gluconic acid (**7c**). From **6c** (0.41 g); amorphous hygroscopic solid (0.37 g, 94%); $[\alpha]_D$ +31.4° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{20}H_{35}NO_7$: C, 59.83; H, 8.79; N, 3.49. Found C, 59.90; H, 8.77; N, 3.51.

General procedure for the synthesis of 6-alcanecarboxamido-6-deoxy-2,4;3,5-di-O-methylene-N-tris(hydroxymethyl)methyl-D-gluconamide (**8a**–**c**).—Compound **7a**–**c** (1.1 mmol) and tris(hydroxymethyl)methylamine (0.2 g, 1.66 mmol) were dissolved in abs EtOH (50 mL).

After adding EEDQ (1.07 g, 4.66 mmol), the mixture was refluxed for 24 h. Ethanol was evaporated under diminished pressure and the resulting oil was purified by column chromatography on silica gel with 47:3 EtOAc–MeOH as eluent.

6-Deoxy-6-heptanecarboxamido-2,4;3,5-di-O-*methylene*-N-*tris(hydroxymethyl)methyl-*D*-gluconamide* (**8a**). From **7a** (0.36 g) and TRIS; amorphous hygroscopic solid (0.25 g, 52%); $[\alpha]_D$ +30° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{20}H_{36}N_2O_9$: C, 53.56; H, 8.09; N, 6.25. Found C, 53.51; H, 8.02; N, 6.29.

6-Deoxy-2,4;3,5-di-O-*methylene6-nonanecarboxamido*-N-*tris(hydroxymethyl)methyl-*D*-gluconamide* (**8b**). From **7b** (0.41 g) and TRIS; amorphous hygroscopic solid (0.30 g, 58%); $[\alpha]_D$ +34.7° (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{22}H_{40}N_2O_9$: C, 55.45; H, 8.46; N, 5.88. Found C, 55.40; H, 8.49; N, 5.92.

6-Deoxy-2,4;3,5-di-O-*methylene*-N-*tris(hydroxymethyl)methyl-6-undecanecarboxamido-*D*-gluconamide* (**8c**). From **7c** (0.44 g) and TRIS; amorphous hygroscopic solid (0.33 g, 60%); $[\alpha]_D$ +28.6 (*c* 1.0, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{24}H_{44}N_2O_9$: C, 57.12; H, 8.79; N, 5.55. Found C, 57.18; H, 8.71; N, 5.59.

1-Methyl hydrogen 2,4;3,5-di-O-*methylene*-D-*glucarate* (**9**).—Compound **2** (1 g, 4.27 mmol) was dissolved in acetone (30 mL) and treated with Jones reagent (11 mL, 11.82 mmol; prepared from 2.1 g of CrO_3, 1.8 mL of H_2SO_4 and 15 mL of water). The reaction mixture was refluxed for 4 h and then quenched with isopropanol (5 mL) and the clear supernatants were decanted and evaporated to give the crude product. The resulting product was purified by column chromatography on silica gel with 23:2 CH_2Cl_2–MeOH as eluent to afford pure **9** as a white powder (0.7 g, 60%): mp 110.8 °C; $[\alpha]_D$ +32.3° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_9H_{12}O_8$: C, 43.55; H, 4.87. Found C, 43.50; H, 4.93.

General procedure for the synthesis of methyl N-*alkyl-2,4;3,5-di*-O-*methylene*-D-*glucar-6-amate* (**10a**–**c**).—Compound **9** (1.14 g, 4.6 mmol) was dissolved in CH_2Cl_2 (50 mL). Alkylamine (5.5 mmol) and BOP reagent (1.87 g, 5.5 mmol) were added and the mixture stirred for 24 h at rt. After evaporation of solvent under reduced pressure, the resulting oil was dissolved in CH_2Cl_2 (50 mL) and washed successively with 1 N HCl and satd $NaHCO_3$. After drying over sodium sulfate, the solution was concentrated under diminished pressure and the resulting syrupy was purified by column chromatography on silica gel with 3:2 EtOAc–hexane as eluent.

Methyl N-*heptyl-2,4;3,5-di*-O-*methylene*-D-*glucar-6-amate* (**10a**). From **9** and heptylamine (0.63 g); clear oil (1 g, 63%); $[\alpha]_D$ +26° (*c* 0.75, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{16}H_{27}NO_7$: C, 55.64; H, 7.88; N, 4.06. Found C, 55.69; H, 7.80; N, 4.15.

Methyl 2,4;3,5-di-O-*methylene*-N-*nonyl*-D-*glucar-6-amate* (**10b**). From **9** and nonylamine (0.78 g); clear oil (1.06 g, 62%); $[\alpha]_D$ +20.3° (*c* 0.7, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{18}H_{31}NO_7$: C, 57.89; H, 8.37; N, 3.75. Found C, 57.81; H, 8.41; N, 3.69.

Methyl 2,4;3,5-di-O-*methylene*-N-*undecyl*-D-*glucar-6-amate* (**10c**). From **9** and undecylamine (0.94 g); clear oil (1.2 g, 65%); $[\alpha]_D$ +20° (*c* 0.65, CH_2Cl_2); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{20}H_{35}NO_7$: C, 59.83; H, 8.79; N, 3.49. Found C, 59.91; H, 8.70; N, 3.41.

General procedure for the synthesis of N-*alkyl-2,4;3,5-di*-O-*methylene*-D-*glucar-6-amic acid* (**11a**–**c**).—Compound **10a**–**c** (1 mmol) was added to a mixture of 3:2:1 MeOH–water–NaOH 1 N (50 mL) and stirred for 12 h at rt. MeOH was removed under diminished pressure. The pH was adjusted to 2–3 adding 1 N HCl. The product was extracted twice by EtOAc. The solvent was evaporated to dryness.

N-Heptyl-2,4;3,5-di-O-*methylene*-D-*glucar-6-amic acid* (**11a**). From **10a** (0.34 g); white powder (0.31 g, 95%); mp 168 °C; $[\alpha]_D$ +64.7° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{15}H_{25}NO_7$: C, 54.37; H, 7.60; N, 4.23. Found C, 54.39; H, 7.65; N, 4.26.

2,4;3,5-Di-O-*methylene*-N-*nonyl*-D-*glucar-6-amic acid* (**11b**). From **10b** (0.37 g); white powder (0.33 g, 94%); mp 172.3 °C; $[\alpha]_D$ +65.1° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{17}H_{29}NO_7$: C, 56.81; H, 8.13; N, 3.90. Found C, 56.85; H, 8.17; N, 3.92.

2,4;3,5-Di-O-*methylene*-N-*undecyl*-D-*glucar-6-amic acid* (**11c**). From **10c** (0.4 g); white powder (0.36 g, 93%); mp 171.2 °C; $[\alpha]_D$ +72° (c 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{19}H_{33}NO_7$: C, 58.90; H, 8.58; N, 3.61. Found C, 58.92; H, 8.60; N, 3.63.

General procedure for the synthesis of 6-N-*alkyl-2,4;3,5-di*-O-*methylene-1*-N-*tris(hydroxymethyl)methyl-*D*-glucarodiamide* (**12a**–**c**).—Compound **11a**–**c** (1.45 mmol) and tris(hydroxymethyl)methylamine (0.26 g, 2.17 mmol) were dissolved in abs EtOH (50 mL). After adding EEDQ (0.5 g, 2.17 mmol), the mixture was refluxed for 24 h. Ethanol was evaporated under diminished pressure and the resulting oil was purified by column chromatography on silica gel with 47:3 EtOAc–MeOH as eluent.

6-N-*Heptyl-2,4;3,5-di*-O-*methylene-1*-N-*tris(hydroxymethyl)methyl-*D*-glucarodiamide* (**12a**). From **11a** (0.48 g) and TRIS; amorphous hygroscopic solid (0.36 g, 57%); $[\alpha]_D$ +98.8° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{19}H_{34}N_2O_9$: C, 52.52; H, 7.89; N, 6.45. Found C, 52.45; H, 7.80; N, 6.49.

2,4;3,5-Di-O-methylene-6-N-nonyl-1-N-tris(hydroxymethyl)methyl-D-glucarodiamide (**12b**). From **11b** (0.52 g) and TRIS; amorphous hygroscopic solid (0.43 g, 65%); $[\alpha]_D$ +7.48° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{21}H_{38}N_2O_9$: C, 54.53; H, 8.28; N, 6.06. Found C, 54.45; H, 8.21; N, 6.16.

2,4;3,5-Di-O-methylene-1-N-tris(hydroxymethyl)methyl-6-N-undecyl-D-glucarodiamide (**12c**). From **11c** (0.56 g) and TRIS; amorphous hygroscopic solid (0.42 g, 60%); $[\alpha]_D$ +80.2° (*c* 1.0, MeOH); ^1H and ^{13}C NMR, Tables 1 and 2. Anal. Calcd for $C_{23}H_{42}N_2O_9$: C, 56.31; H, 8.63; N, 5.71. Found C, 56.39; H, 8.69; N, 5.78.

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