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Regioselective synthesis and characterization of 6-*O*-alkanoylgluconolactones

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Abstract

6-*O*-Alkanoylgluconolactones, a novel class of carbohydrate ester-linked surfactants containing a lactone head group, have been synthesized enzymatically from the unprotected aldonolactone. The synthesis was accomplished by regioselective esterification of glucono-1,5-lactones at C-6 by porcine pancreatic lipase in the solvent pyridine. These compounds were found to exhibit a sharp increase in solubility at 90–96°C but remained soluble well below their initial dissolution temperature, precipitating at 30–37°C. To determine the cause of this unusual solubility behavior, the composition of the precipitate was characterized by ^{1}H and ^{13}C NMR, and GC–MS. Analysis of the precipitates identified the material as a hydrolysate containing alkanoylglucono-1,5-lactone, alkanoylglucono-1,4-lactone and alkanoylgluconic acid. The hydrolysis and isomerization of the lactone gave a mixture of compounds that are more soluble than the corresponding pure alkanoylglucon-δ-lactone.

Keywords: 6-*O*-Alkanoylgluconolactones; Ester-linked surfactant

1. Introduction

Fatty acid esters of carbohydrates have been used as surfactants and emulsifiers by the food, detergent, and cosmetic industry for a number of years [1]. These compounds are derived from inexpensive, renewable feedstocks and are typically nonionic, nontoxic and biodegradable [2,3]. The chemical synthesis of carbohydrate esters have been

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reported previously [4–6]. Esterification of carbohydrates can be accomplished efficiently and inexpensively using base catalyzed transesterification [7]. This procedure, however, is nonregiospecific, leading to the formation of positional isomers as well as diesters. Base-catalyzed transesterification is further complicated by the tendency of some aldonolactones to form esters through intermolecular self-condensation (to give *O*-aldonylaedonic acids) or by reaction with an alcohol [8].

In comparison, enzymatic regioselective esterification of a carbohydrate uses the intrinsic regioselectivity of the enzyme to accomplish the esterification of specific functional groups [9–11]. Selective enzymatic esterification of sugars has been developed recently [2,12–14]; the reaction has been applied to pyranosides and furanosides in pyridine with high regioselectivity using porcine pancreatic lipase (PPL) [11].

As part of an investigation of new carbohydrate-derived surfactants, we have explored the selective enzymatic esterification of aldonolactones with fatty acid derivatives. The regioselective nature of PPL has been well documented [11,15,16]. Reversal of its hydrolytic activity in low water systems such as organic solvents can be used for esterification or transesterification reactions [17]. In this study, the regioselective esterification of D-glucono-1,5-lactone was accomplished in anhydrous pyridine using PPL as the catalyst and 2,2,2-trichloroethyl alkylates [11] as the acyl donors.

Two molecules of different alkyl chain lengths were synthesized, 6-*O*-dodecanoyl-D-glucono-1,5-lactone (**1a**) and 6-*O*-decanoyl-D-glucono-1,5-lactone (**3a**). These compounds were found to have a sharp discontinuous increase in solubility at high temperatures (ca. 90–96°C) but remained soluble well below their initial dissolution temperature (precipitating at 30–37°C). To determine the cause of this unusual solubility behavior, the compositions of the precipitates were evaluated by NMR spectroscopy and gas chromatography–mass spectrometry (GC–MS). ^{1}H NMR and two-dimensional NMR permitted the establishment of bond connectivities and identification of several sugar residues. These experiments show a selective hydrolysis of the lactone functionality, resulting in a mixture of esterified 1,4- and 1,5-lactones as well as the acyclic alkanoylgluconic acid. It is clear from these results that solubilization of fatty acid esters of gluconolactone results in the hydrolysis of the lactone moiety to form a mixture of hydrolysates in aqueous solution. The formation of these hydrolysates and their corresponding solubilities partially explain the unusual solubility properties of these surfactants.

2. Results and discussion

Regioselective acylation of D-*glucono-1,5-lactone.* — The conversion of D-glucono-1,5-lactone to the monoesters, **1a** and **2a**, was accomplished using PPL. Consistent with the specificity of this enzyme for the primary hydroxyl of several carbohydrates [11], the substrate was esterified only at the C-6 hydroxyl as determined by ^{13}C NMR (Table 1). After workup (see Experimental section) **1a** and **2a** were isolated in 26 and 27% yield, respectively.

Although Gutman et al. have reported that PPL catalyzes both intramolecular and intermolecular transesterification of hydroxy esters [18], their findings also show that 1,4- and substituted 1,5-hydroxy esters undergo lactonization exclusively. Consistent

Table 1
^1H and ^{13}C chemical shift assignments of sample 1 in Me_2SO-d_6 at 35°C (in ppm downfield from Me_4Si) [a]

1a	6-*O*-Dodecanoyl-D-glucono-1,5-lactone (Signal set I)					
					C-1	171.13
	H-2	3.786	OH-2	5.81	C-2	71.71
	H-3	3.510	OH-3	5.40	C-3	73.98
	H-4	3.436	OH-4	5.53	C-4	68.31
	H-5	4.231			C-5	77.52
	H-6	4.102			C-6	62.75
	H-6′	4.276				
					C(ester)	172.62
1b	6-*O*-Dodecanoyl-D-gluconic acid (Signal set II)					
					C-1	174.08
	H-2	4.032	OH-2	6.12	C-2	72.45
	H-3	3.845			C-3	70.17
	H-4	3.418			C-4	71.99
	H-5	3.623	OH-5	4.90	C-5	68.56
	H-6	3.863			C-6	65.98
	H-6′	4.154				
					C(ester)	173.00
1c	6-*O*-Dodecanoyl-D-glucono-γ-lactone (Signal set III)					
					C-1	175.25
	H-2	4.03	OH-2	5.61	C-2	72.94
	H-3	4.113			C-3	72.35
	H-4	4.336	OH-4	5.21	C-4	79.83
	H-5	3.936			C-5	66.30
	H-6	4.003			C-6	65.42
	H-6′	4.147				
					C(ester)	172.81

[a] ^{13}C chemical shifts are accurate to within ±0.02 ppm. ^1H chemical shifts are accurate to within ±0.002 ppm (except for hydroxyl protons). All ^{13}C and ^1H chemical shifts of species in sample 2 are within 0.02 ppm of their corresponding shifts in sample 1.

with the latter finding, we observed no oligomerization of D-glucono-1,5-lactone during transesterification.

Temperature solubility relationships. — Because the phase behavior of surfactants is important to many applications, an understanding of the phase behavior relative to surfactant structure is an important element in understanding surfactant structure/property relationships. The phase behavior of alkanoylglucono-1,5-lactones was initially investigated by examining temperature/solubility relationships. The solubility as a function of temperature was determined using a 0.1% (by weight) solution of either **1a** or **2a**. Both **1a** and **2a** form clear solutions upon heating to 96 and 90°C, respectively. Upon cooling, however, precipitation of the esterified aldonolactones did not occur at the original dissolution temperature. Precipitation of sample **1a** occurred at 37°C while precipitation of sample **2a** occurred at 30°C. Heating the samples for a second time resulted in a significantly lower dissolution temperature; 65°C for **1a** and 60°C for **2a**. Both samples were allowed to precipitate at 30°C for a second time and collected.

The solubility properties of **1a** and **2a** are unusual for carbohydrate-based surfactants. Typically, carbohydrate-based surfactants undergo a sharp discontinuous increase in

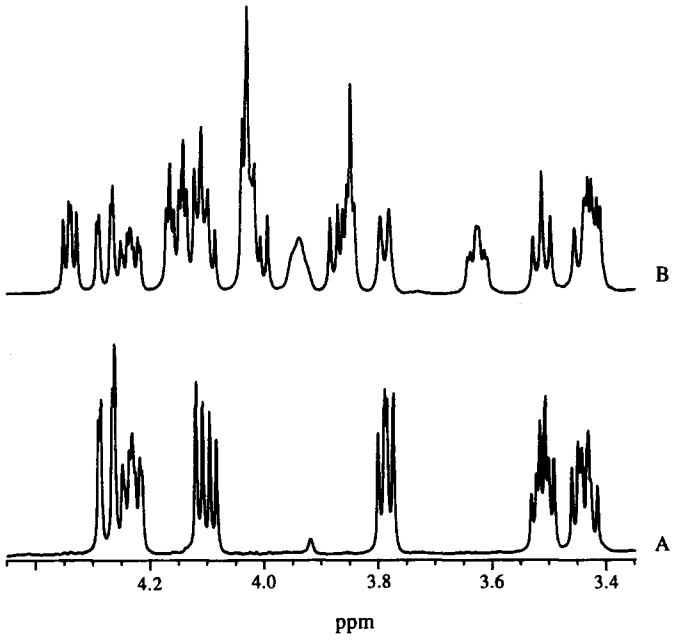


Fig. 1. Proton spectra of pure 6-*O*-dodecanoyl-D-glucono-δ-lactone in DMSO-d_6 at 35°C (spectrum A), and of sample 1 under the same conditions (spectrum B). The reduced splitting in B is due to fast exchange of the OH protons in sample **1** which eliminates scalar coupling between the hydroxyl and ring protons.

solubility at a characteristic temperature commonly know as the Krafft point (T_k). The T_k is the temperature at which the solubility of a surfactant becomes equal to the critical micelle concentration (cmc) and consequently should not depend on whether the T_k is approached from temperatures above or below T_k. As a starting point to determine the cause of this unusual solubility behavior, the precipitates collected after the second precipitation from aqueous solution were analyzed by ^{1}H NMR, ^{13}C NMR and GC–MS.

Chemical shift assignments.—The analyses and results for the precipitates of **1a** (sample 1) and **2a** (sample 2), dissolved in Me_2SO-d_6, are practically identical. Thus only the results *for* sample 1 are described here (Table 1). Fig. 1 shows the ^{1}H NMR spectra of pure (i.e., without dissolution treatment) 6-*O*-dodecanoyl-D-glucono-1,5-lactone (spectrum A) and of its precipitate from aqueous solution, sample 1 (spectrum B). GC-MS data suggested that the precipitate contains three components, **1a**, 6-*O*-dodecanoyl-D-gluconic acid (**1b**) and 6-*O*-dodecanoyl-D-glucono-1,4-lactone (**1c**). Since samples of pure **1a** and **2a** were available from enzymatic esterification, the assignments of the ^{1}H and ^{13}C NMR spectra of these two esters were made straightforwardly by 1D ^{1}H–^{1}H COSY [19], ^{13}C–^{1}H chemical shift correlation (HMQC [20] and HMBC [21]).

The only ^{13}C assignment of the parent D-glucono-1,5-lactone available in the literature [22] is ambiguous; the assignments of all four carbons of the lactone ring (C-2–C-5) were indicated as being interchangeable. To confirm our present assignment, COSY and ^{13}C–^{1}H chemical shift correlation data were obtained on a sample of

Table 2
The ^{1}H and ^{13}C chemical shift assignments of D-glucono-δ-lactone at 298 K (in ppm downfield from TMS) [a]

		C-1	174.50
H-2	3.87	C-2	73.41
H-3	4.18	C-3	71.68
H-4	3.87	C-4	67.80
H-5	4.24	C-5	82.28
H-6	3.93	C-6	60.76
H-6′	3.85		

[a] ^{1}H and ^{13}C chemical shifts are accurate to ±0.01 ppm.

D-glucono-1,5-lactone in D_2O (to reproduce the conditions of ref [22]). The resulting assignments for both ^{13}C and ^{1}H (Table 2) are unambiguous and are consistent with those of **1a** and **2a** made in this study (Table 1).

Though GC-MS had indicated the presence of three components in sample 1 (Fig. 2), the separation of ^{1}H signals corresponding to these components and their assignments were complicated by extensive spectral overlap. Information from COSY was not sufficiently conclusive, again because of spectral overlap and difficulty arising from closely-spaced cross-peaks.

1D TOCSY [23] proved to be particularly useful in generating three sub-spectra (labeled I–III in Table 1) of the various components by exciting a well-resolved signal from each component with a selective Gaussian pulse. Furthermore, by systematically increasing the mixing time for the Hartman–Hahn transfer, the propagation of the correlation and thus the *J*-coupling network can be traced [24] for each individual residue. These two features are demonstrated in Fig. 3, where the signal set III (see next section for assignment procedures) was generated by selectively exciting the signal of H-4 at 4.343 ppm.

Figs. 3A–D shows that, by increasing the mixing period from 20 to 120 ms, the transfer of magnetization from H-4 to other protons through *J*-correlation propagates

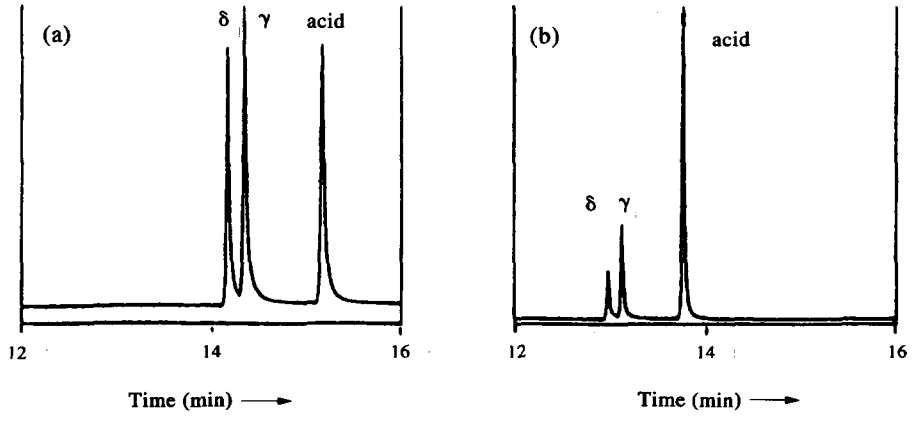


Fig. 2. GC–MS total ion chromatograms of TMS derivatives of (a) sample 1 and (b) sample 2.

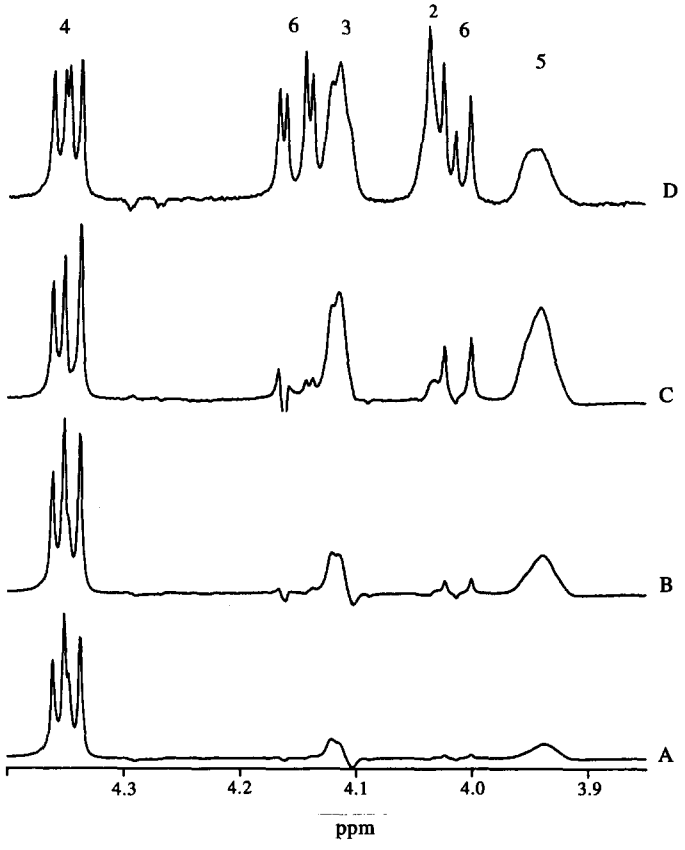
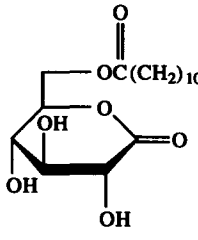


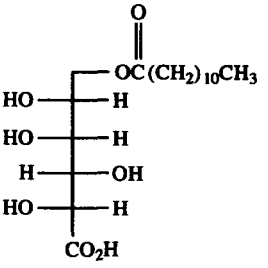
Fig. 3. Proton ID TOCSY spectra of 6-*O*-dodecanoyl-D-glucono-γ-lactone (**1c**) in sample 1 in Me_2SO-d_6 at 35°C. H-4 of **1c** at 4.343 ppm was selectively excited by a 105 ms Gaussian pulse. The MLEV-17 mixing times were 20, 40, 80 and 120 ms, respectively, in A–D. The signals of H-3 and H-5 emerge at short mixing times, followed by those of H-2 and H-6 at longer mixing times.

initially to H-3 and H-5 (Figs. 3A–B) and eventually to H-6 and H-2 (Figs. 3C–D). This propagation revealed by 1D TOCSY provides a powerful way to assign the proton resonances of the ring protons in saccharides.

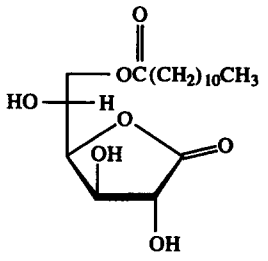
After separating the proton signals into three sets and assigning them in each set, the assignment of the three sets of ^{13}C chemical shifts for the protonated carbons 2–6 was made via ^{13}C–^{1}H chemical shift correlation. The carbonyl carbons (lactone and ester) were further differentiated and assigned via long-range (usually two- or three-bond) correlations between ^{1}H and ^{13}C obtained from the HMBC experiment. Thus the carbonyl carbons on the acyl chain are recognized by their three-bond correlations with H-6 of the respective species, and the lactone carbonyl carbons by their correlation with H-2, H-3 or even H-4 of the respective species. In signal set III, the C-1–H-3 correlation was not observed while the C-1–H-4 correlation was present. It has been shown that, in



6-*O*-dodecanoyl-D-glucono-δ-lactone (**1a**)



6-*O*-dodecanoyl-D-gluconic acid (**1b**)



6-*O*-dodecanoyl-D-glucono-γ-lactone (**1c**)

Scheme 1.

several similar 1,4-lactones, $^3J_{C1,H3}$ is close to zero, while $^3J_{C1,H4}$ is relatively large (3–4 Hz) [25].

Assignment of the structures and quantification in samples 1 and 2. — The three species in the samples 1 and 2, the six-membered ring **1a**, the open-ring **1b** and the five-membered ring **1c**, have similar NMR characteristics including similar *J*-coupling patterns. Thus, there is no a priori criterion for assigning the three sets of NMR signals to these three species. However, 6-*O*-dodecanoyl-D-glucono-1,5-lactone exists in pure form and its structure has been confirmed by the fragmentation pattern produced by electron-ionization MS to be a six-membered ring 1,5-lactone. Thus, the assignment of the NMR signals (signal set I) to this species (and similarly for 6-*O*-decanoyl-D-glucono-1,5-lactone in sample 2) was straightforward.

Differentiation of the signals for **1b** and **1c** was more difficult. The ^{13}C chemical shifts for C-2–C-6 of D-gluconic acid occur generally at higher field than those for the corresponding glucono-1,4-lactone [22,26]. Typically, the difference between corresponding carbons is no more than 2.5 ppm except for C-4, where that of gluconic acid (ca. 73 ppm) is at a significantly higher field (ca. 8 ppm) than that of glucono-1,4-lactone (ca. 80.5 ppm). Comparing the present results with those reported for the parent gluconic acid and glucono-1,4-lactone in the literature [22], the presence of the C_{10} or C_{12} acyl chain at C-6 in general has little effect on the chemical shifts of C-1–C-4. The largest change, as expected, occurs in the C-6 of both the acylated gluconic acid and acylated glucono-1,4-lactone, where a large (ca. 3 ppm) downfield shift is observed. Since $C\text{-}4_s$ of both acylated species are not much affected by the acylation at C-6, the C-4 of signal set II (71.99 ppm) is found to be at a significantly higher field ($\sim$ 8 ppm) than that of signal set III (79.83 ppm). Signal set II was therefore assigned to **1b** and signal set III to **1c**. It can also be noted that C-4 of **1c** is bonded to the ester oxygen in the sugar ring, and thus should have similar chemical shift as C-5 of **1a**. Indeed, C-5 of signal set I (77.52 ppm) is close to C-4 of signal set III (79.83 ppm) (**1c**) and not to C-4 of signal set II (71.99 ppm) (**1b**).

This assignment based on NMR was correlated with the corresponding GC–MS data (Fig. 2). The intensities for the three sets of signals in sample 1, based on the integration of respective ^1H signals is about 0.85(I):1.00(II):0.89(III), whereas the GC–MS data

gave an intensity ratio of 0.73(**1a**):1.00(**1b**):0.98(**1c**). Because of the similar relative intensities, the comparison between the NMR and GC-MS intensity data does not provide an unambiguous confirmation of the NMR assignment. The relative GC-MS intensities for sample 2, on the other hand, are different (0.17, **2a**); 1.00, 6-O-decanoyl-D-gluconic acid **2b**; 0.33, 6-O-decanoyl-D-glucono-1,4-lactone, **2c**. By NMR, the ratio is 0.42(I):1.00(II):0.40(III). Thus, the intensity ratios from NMR and GC-MS data both show that the major component in the mixture is the acylated gluconic acid (signal set II). Signal set III is therefore that of the acylated glucono-1,4-lactone.

^{13}C 2D exchange spectroscopy [27] of sample 1 performed at 35 and 90°C showed no exchange cross-peaks between corresponding signals of the three species with mixing times up to 0.5 s. Thus, it can be concluded that the exchange between these species is substantially slower than the ring-chain isomerization observed in aldoses [28].

In summary, it can be concluded from the present data that the dissolution of 6-*O*-alkanoylglucono-1,5-lactones in aqueous solution results in the hydrolysis of the lactone, yielding a mixture of 1,5-lactone, 1,4-lactone and open-chain forms, the latter being the dominant species in the hydrolysates. The composition of the hydrolysates also partially explain the unusual solubility behavior of these compounds. Mixtures of isomeric materials generally have considerably lower T_k values than those of individual compounds [29]. The hydrolysis and isomerization of the lactone forms a mixture of compounds that is more soluble than the corresponding pure alkanoylglucono-1,5-lactone. The hydrolysates, consequently, precipitate at a temperature 60°C lower than the initial dissolution temperature of their parent 1,5-lactones.

Reduction of the T_k values has practical consequences since a high T_k limits the applications of a surfactant. Forming hydrolysates of alkanoylgluconolactones produces materials with solubilities closer to those needed for detergent applications. The selective hydrolysis of the lactone also allows for the preparation of mixtures of nonionic and anionic surfactants by forming salts of the alkanoylgluconic acid [30]. Mixtures of nonionic and anionic surfactants frequently exhibit properties significantly better than those obtained with either component alone [31].

The formation of hydrolysates upon dissolution may not, however, fully explain the solubility behavior of these compounds. It is not clear, for example, why the dissolution temperature for the precipitate is 30°C higher than the temperature at which the precipitate originally formed. Further work needs to be done to determine the effect of factors such as temperature on the distribution of isomers in solution and the subsequent effect on the surfactant phase behavior. The NMR procedure developed and assignments obtained in this work provide the basis for future analysis of carbohydrate surfactants based on gluconolactones and other aldonolactones.

3. Experimental

General procedures.—Melting points were obtained using a Thermogravimetric Analyzer (DuPont TEA2950). Diffuse Reflectance Infrared Fourier Transform spectra (DRIFTS) (Bio-Rad FTS-60A) were obtained neat using KBr powder as a matrix. Reactions were monitored by gas chromatography using a Hewlett–Packard 5890 Series II gas chromatograph (Hewlett–Packard, Palo Alto, CA) equipped with an HP1

crosslinked 5% phenyl methylsilicone capillary column (25 m × 0.32 mm × 0.52 mm, Hewlett–Packard, Palo Alto, CA), a split injector (using a 100:1 split ratio), and a flame ionization detector. Helium was used as the carrier gas, and the detector and injection ports were set at 250°C. Oven temperature was set at 140°C for 2 min, then ramped at 8°C/min to 250°C and a end time of 10 min. Reaction samples were subjected to precolumn derivatization with SilPrep (Alltech, Inc., Deer Park, IL) at room temperature for a minimum of 30 min. Pyridine (Aldrich, anhydrous 99 + %) containing glucono-δ-lactone (Aldrich) was stored over 4 Å molecular sieve prior to use. Porcine pancreatic lipase Type II (Sigma) contained less than 1% water by Karl Fischer analysis and was used as supplied. The 2,2,2-trichloroethyldecanoate and 2,2,2-trichloroethyldodecanoate were prepared following a general methodology [32].

6-O-Dodecanoyl-D-glucono-1,5-lactone (**1a**).—To a solution of D-glucono-1,5-lactone (2.23 g, 12.52 mmol) and 2,2,2-trichloroethyl dodecanoate (12.01 g, 36.22 mmol) in dry pyridine (50 mL), PPL (12 g) was added and the mixture stirred for three days at 40°C. The reaction was stopped by filtration to remove the enzyme. The solvent was evaporated under reduced pressure and the residual material washed with chloroform (25 mL) and filtered. The filtrate was then evaporated under reduced pressure and the product (**1a**) was washed with 95% ethanol to recover a white crystalline powder (1.22 g, 26%): mp 120°C; DRIFTS (KBr powder) 3476.09 cm^{-1}, 3389.31, 2956.22, 2920.74, 2852.00, 1748.92, 1716.06, 1469.70, 1174.5, 1166.85, 1061.92, 1007.96, 722.31.

6-O-Decanoyl-D-glucono-1,5-lactone (**2a**).—To a solution of D-glucono-1,5-lactone (8.30 g, 46.60 mmol) and 2,2,2-trichloroethyl decanoate (50.00 g, 164.66 mmol) in dry pyridine (200 mL), PPL (48 g) was added and the mixture stirred for five days at 40°C. The reaction was stopped by filtration to remove the enzyme. The solvent was evaporated under reduced pressure and the residual material washed with chloroform (100 mL) and filtered. The filtrate was then evaporated under reduced pressure and the product (**2a**) was washed with 95% ethanol to recover a white crystalline powder (4.30 g, 27%): mp 127°C; DRIFTS (KBr powder), 3473.64 cm^{-1}, 3390.84, 2956.34, 2922.15, 2853.08, 1749.20, 1715.48, 1469.05, 1167.28, 1061.96, 1011.7, 723.06.

Temperature–solubility measurements.—Solubility as a function of temperature for **1a** and **2a** was determined using a 0.1% aqueous solution of either compound. The temperature of the solution was increased at 1°C/min and the temperature at which the solution cleared was recorded. The solution was then cooled at 1°C/min. and the temperature at which the first precipitate occurred was noted. This cycle was repeated twice, the precipitate collected and analyzed by ^{1}H NMR, ^{13}C NMR and GC–MS.

NMR spectroscopy.—NMR experiments were performed on a Bruker AMX-500 spectrometer (University of Missouri) operating at 500.1 MHz for ^{1}H and 125.4 MHz for ^{13}C. For ^{1}H, the 90° pulse was 9.2 μs. Typical conditions were: block size 32K and 32 scans. The spectral width was 4000 Hz. A "reverse detection" 5 mm probe was used. For ^{13}C, the 90° pulse was 7.9 μs, block size 32K and 256 scans. The spectral width was 22,500 Hz. Composite pulse decoupling (GARP [33]) was used to decouple protons on a 5 mm broadband probe.

^{1}H–^{1}H COSY spectra (magnitude mode) were recorded with 2K and 512 data points in the t2 and t1 dimensions, respectively, using a reverse detection probe. Data sets were processed with zero-filling in t1 to give a 1K × 1K contour map.

One-bond $^{13}C-^{1}H$ chemical shift correlation was obtained via the HMQC technique [20]. The experiment was run in phase-sensitive mode using the TPPI method [34]. Bilinear rotation (BIRD) [35] pulses were used at the beginning of the HMQC pulses to remove the signals arising from protons attached to ^{12}C [20]. Long-range $^{13}C-^{1}H$ chemical shift correlation was obtained via the HMBC technique without ^{13}C-decoupling [21]. Long-range $^{13}C-^{1}H$ coupling was optimized at 7 Hz. In both of experiments, data were accumulated with $2K \times 512$ points in the t2 and t1 dimensions, respectively. Zero-filling in the t1 dimension during processing gives a $1K \times 1K$ contour map.

^{13}C 2D exchange spectra [27] were obtained in the TPPI mode with a $512 \times 2K$ data matrix and zero-filling in the t1 dimension to give a $1K \times 1K$ contour map. Mixing times ranged from 0.3 to 0.5 s.

The pulse sequence of Kessler et al. [23] was used to generate 1D-TOCSY spectra. A selective Gaussian pulse of 105 ms (270° pulse) was generated from the Bruker waveform memory unit. A Z-filter [36] was used in this experiment to produce absorption line-shape.

Gas chromatography-mass spectrometry.—Lactone esters were analyzed as their trimethylsilyl (TMS) ethers. A 5–10 mg sample was dissolved in 1.0 mL SilPrep (Alltech, Inc., Deer Park, IL) and allowed to react at room temperature for a minimum of 30 min. A 1.0 L aliquot was analyzed by GC–MS using a Finnigan SSQ-710 mass spectrometer equipped with a Hewlett–Packard 5890 Series II gas chromatograph and Finnigan A200S autosampler.

GC analysis employed a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm, J & W Scientific, Folsom, CA); column pressure, 12.0 psi; injector temperature, 250°C; oven temperature, 150°C for 2 min, ramped at 15°C/min to 300°C; transfer line temperature, 275°C. The mass spectrometer was scanned from 20–800 Da at 0.8 s/scan. Electron ionization was employed at 70 eV. Source temperature was 150°C; collision dynode potential, −5 kV.

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