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## Synthesis, characterization, and evaluation of toxicity of quaternary ammonium chlorides of glucose-based ester

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Abstract: This study presents the synthesis of glucose-based surfactants including quaternary ammonium salts. Their surface properties and influence on the soil environment were investigated. The synthesized quaternary ammonium chlorides of glucose-based ester exhibited good surface tension reduction properties and formed stable foam in contact with water. The results showed that quaternary ester ammonium salts affect the activation of metals (nickel and cadmium) from the soil matrix after their introduction into the soil environment. This phenomenon can increase the bioavailability of these metals. The introduction of glucose surfactants to the soil increased microorganism activity, which may indicate that these compounds were used as a source of carbon and energy by the microorganisms.

Key words: Quaternary ammonium compounds, glucose-based surfactants, synthesis, properties, toxicity

#### 1. Introduction

The development of industry and the high consumption of chemicals, especially surfactants, pose a threat to the environment. There is an alarming presence of synthetic surfactants in aqueous and terrestrial environments, which highlights particular risks and dangers due to their influence on such ecosystems. For example, surfactants cause the eutrophication of water, the formation of froth, the reduction of oxygen availability, the reduction of microbial growth, and increases in mobility and bioavailability of heavy metals as well as the movement of organic matter in soils. <sup>1,2</sup> Without a doubt, the presence of xenobiotics affects the functioning of the entire ecosystem. For these reasons, readily biodegradable substances obtained from available, renewable, and easy-to-handle raw materials are being sought. For years, sugars have been the object of research interest as substrates for chemical syntheses. Monosaccharides in particular, such as glucose, are of great interest as substrates for the formation of new compounds, including surfactants. <sup>3-5</sup> This mainly results from of their widespread availability and renewability. Several glucose-derived surfactants show very good properties in terms of lowering the surface tension as well as forming complexes with metals. Alkyl glucosides belonging to nonionic surfactants have been used for the purification of metal waste solutions as well as the removal of magnesium and calcium cations from water. <sup>6-8</sup> In the literature, Gan et al. <sup>9</sup> described two sugar-based ester ammonium compounds and their surface behavior and antibacterial properties.

The next popular group of compounds obtained based on renewable sources are sugar fatty acid esters, namely biocompatible nonionic surfactants. They can be enzymatically synthesized, which is a huge advantage over their chemical synthesis. Depending on the esterification degree and the nature of fatty acid and/or sugar,

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a range of sugar esters surfactants can be synthesized. Due their surface activity and emulsifying capacity, sugar esters are promising for applications in the cosmetic and food industries. These compounds also show therapeutic potential with antitumor, plant growth regulation, and antibiotic activities. <sup>10–14</sup> Perinelli et al. <sup>15</sup> described the synthesis and a comprehensive physicochemical characterization of lactose oleate, which includes a sugar-based surfactant with interesting surface and aggregation properties. Authors report that this compound displayed an acceptable cytotoxic profile and also influence on the increasing of permeability and antimicrobial activity over gram-positive and gram-negative bacteria.

Sugars are also ideal raw materials for the synthesis of new compounds, such as ionic liquids, from the viewpoints of both environmental and economic concerns. The design of environmentally benign ionic liquids has been one of the active areas of green chemistry over the past 10 years. Chemical and physical properties of ionic liquids can be tailored by modifying the structure of the cation and anion. The synthesis of the compounds from environmentally friendly and renewable raw materials (amino alcohols, hydroxyl acids, amino acids, and terpenes) is becoming more beneficial compared to the use of compounds derived from fossil fuel stocks.  $^{16-22}$ 

The purpose of the present study was to obtain surfactants based on glucose derivatives and to evaluate their basic properties such as surface tension reduction, foam formation, and stability. The influence of quaternary ammonium chlorides of glucose-based ester on the soil environmental, which included evaluation of changes in metal mobility and the changes in soil bioactivity after introduction of glucose-based surfactants, was also investigated in the framework of this study.

#### 2. Results and discussion

#### 2.1. Synthesis of glucose-based esters quaternary ammonium salts

Quaternary ammonium chlorides of glucose-based esters were obtained using a synthesis pathway presented in the Scheme, which is based on the modified method proposed by Gan et al.  $^9$  In the first stage, chloroacetyl chloride was added to glucose and the product 6-O-(2-chloroacetyl)-D-glucose was obtained with 92% yield. In the next stage, 6-O-(2-chloroacetyl)-D-glucose was dissolved in propan-2-ol, then appropriate tertiary amines were added in a dropwise manner, and the solution was heated at a temperature not exceeding 55  $^{\circ}$ C. Three compounds with different lengths from the alkyl chain in the amino group were obtained with a yield of 68% to 76% (Table 1). The purity and structure of the obtained products were confirmed by spectroscopic methods (IR,  $^{1}$ H NMR,  $^{13}$ C NMR). The changes in the second stage of the synthesis brought a beneficial effect. Namely, the reaction was carried out in propan-2-ol without water in the system and eliminating the problem of foaming of the mixture during evaporation of the solvent. The synthesis, conducted at a temperature not exceeding 55  $^{\circ}$ C, prevented the products of reaction, and the color of the reaction mixture did not change. During the purification of the products, it was not necessary to add to  ${\rm H_2\,O_2}$ , which could lead to the oxidation or destruction of the obtained compounds.

#### 2.2. Analysis of glucose-based compounds properties

#### 2.2.1. Surface tension

The main interfacial properties of the synthesized compounds were analyzed in order to determine their potential efficiency. The relation between the surface tension and concentration (log c) of the quaternary ammonium chlorides of glucose-based esters are presented in Figure 1. The studied concentrations were selected to cover a large range (from  $2.0 \times 10^{-5}$  to 0.02 mmol/L) in order to describe all the expected changes in the surface tension

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**Scheme.** The synthesis of quaternary ammonium chlorides of glucose-based esters (where  $R = C_{12}H_{25}$ ,  $R = C_{14}H_{29}$ ,  $R = C_{16}H_{33}$ ).

Table 1. The abbreviation of quaternary ammonium chlorides of glucose-based esters.

Glucose-based ester quaternary ammonium	Abbreviation	Yield [%]
D-Glucosyl 2- $(N, N$ -dimethyl- $N$ -dodecyl ammonium)-acetate chloride	QSGC12	68.0
D-Glucosyl 2- $(N, N$ -dimethyl- $N$ -tetradecyl ammonium)-acetate chloride	QSGC14	72.0
D-Glucosyl 2- $(N, N$ -dimethyl- $N$ -hexadecyl ammonium)-acetate chloride	QSGC16	76.0

behavior of the synthesized compounds in the aqueous solutions. The surface tension versus concentration relations were characterized by two regions, one at a lower concentration range characterized by a fast decrease in the surface tension values, and the other at higher concentration range at which the surface tension values remained almost constant (Figure 1). The concentration at the intercept of these two regions indicates the critical micelle concentration (CMC) by extrapolation. The results are presented in Table 2. The  $\gamma$ CMC parameter is a useful measurement of the effectiveness of the surfactant in terms of surface tension reduction. It gives an idea about its foaming behaviors, as the reduction of the surface tension improves foam formation. The presence of the hydrophobic tails (long alkyl chain (contained from C12 to C16)) with respect to the hydrophilic heads in the molecule of quaternary ammonium chloride of glucose-based ester resulted in the reduction of CMC and  $\gamma$ CMC from 33.11 mN/m to 21.14 mN/m. Gan et al. 9 also synthesized quaternary ammonium surfactants of glucose-based ester with an alky chain containing 12 and 16 carbon atoms and obtained similar values of CMC equal to 0.955 and 0.0794 mmol/L for QSGC12 and QSGC16, respectively.

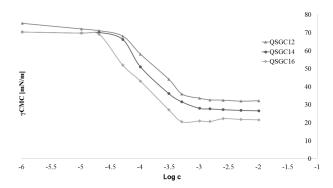


Figure 1. Surface tension  $\gamma$  versus logarithm of the concentration of the quaternary ammonium salts of quaternary ammonium chlorides of glucose-based esters (concentration range  $2.0 \times 10^{-5}$ –20 [mmol/L]).

Table 2. Interfacial properties of quaternary ammonium chlorides of glucose-based esters.

Compounds	CMC [mmol/L]	$\gamma \text{CMC [mN/m]}$
QSGC12	1.036	33.11
QSGC14	0.787	27.68
QSGC16	0.588	21.14

The obtained values were compared with the values for glucose and lactose surfactants. <sup>15,20-23</sup> The CMC of obtained quaternary ammonium chlorides of glucose-based ester were lower than the octyl- $\alpha$ -D-glucopyranoside (CMC: 10 mmol/L,  $\gamma$ CMC: 36.4) and than the N<sup>1</sup>-hydroxy-N<sup>2</sup>-(octyl- $\alpha$ -D-glucopyranosiduronyl)glycinamide (CMC: 13.8 mmol/L,  $\gamma$ CMC: 37.0 mN/m), and N<sup>1</sup>-hydroxy-N<sup>2</sup>-(octyl- $\beta$ -D-glucopyranosiduronyl)-glycinamide (CMC: 29.3 mmol/L,  $\gamma$ CMC: 34.1 mN/m). However, the values of CMC of quaternary ammonium chlorides of glucose-based ester were higher than for lactose oleate surfactant (0.244 mmol/L).

#### 2.2.2. Formation of foam

The quaternary ammonium chlorides of glucose-based esters quickly formed foam and its stability was good, as it lasted for approximately 20 min (Table 3). Comparison of these properties with, for example, the foamability of CATB (commonly used cationic surfactant)<sup>9</sup> and the alkyl polyglycoside (APG)<sup>9</sup>, showed that the foaming properties of QSGC12 and QSGC14 were slightly lower compared to those of CATB, whereas the foam of QSGC16 was quite low. Despite their small initial foam height, the obtained compounds formed a stable and persistent foam.

Table 3. Foaming properties of quaternary ammonium chlorides of sugar-based esters.

Compounds	Foam height [mm]		
Compounds	1 [min]	5 [min]	20 [min]
QSGC12	26.5	25.0	18.0
QSGC14	27.0	24.0	15.5
QSGC16	24.0	20.0	12.0
CTAB	28.0	25.0	_
APG (alkyl polyglycoside)	32.0	25.5	_

#### 2.3. Influence on the soil environment

#### 2.3.1. The changes in metal mobility in soil

The soil samples collected from an industrial area and used for this study were polluted by Ni (41 mg/kg), Cd (120 mg/kg), and Pb (1382.10 mg/kg). Introduction of the glucose-based surfactants increased the amount of nickel as well as cadmium in the fraction eluted by water (Table 4). This demonstrates that the quaternary ammonium chlorides of glucose-based ester can increase the mobility of nickel and cadmium in the soil. However, the surfactants did not affect the mobility of lead in the soil profile.

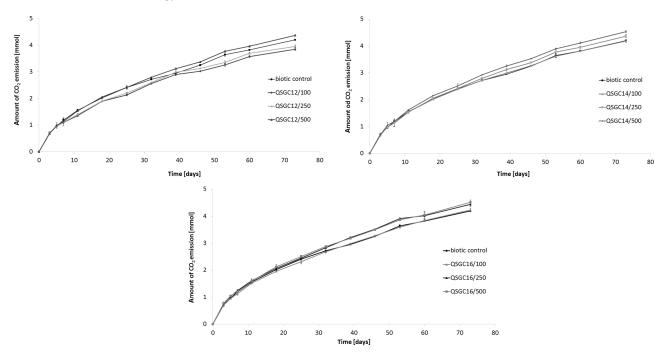
		BCR			
Metal	Concentration of	I (0.1 mol/L	II (0.5 mol/L	III (30% $H_2O_2 + 0.5$	IV (residual
	QSGC14	$CH_3COOH)$	NH <sub>2</sub> OH*HCl)	mol/L CH <sub>3</sub> COONH <sub>4</sub> )	fraction)
	[mg/kg d.w.s]	[%]	[%]	[%]	[%]
Ni	0	60.49	11.71	3.66	24.49
	100	84.88	3.90	3.66	7.89
	250	84.88	2.93	7.32	4.96
	500	83.00	4.88	6.10	4.70
Cd	0	5.67	13.0	18.75	63.33
	100	24.66	14.67	18.33	45.42
	250	24.56	14.33	17.35	42.92
	500	24.67	14.30	18.54	43.17
Pb	0	0	2.87	0	98.13
	100	0	3.15	0	95.90
	250	0	3.21	0	96.79
	500	0	2.98	0	97.12

**Table 4.** The metals content in particular soil fractions.

#### 2.3.2. Evaluation of changes in biological activity of soil

Introduction of xenobiotics to the soil undoubtedly influenced the development and activity of the microflora. The presence of xenobiotics can affect the development of soil microflora activity, but can also cause an inhibition of microbial growth. Both microorganisms and their metabolites (enzymes) are actively involved in the decomposition of organic matter and detoxification of xenobiotics (herbicides, heavy metals, surfactants, or drugs). It is therefore very important to investigate the effects of xenobiotics and their influence on the biological activity of soils, and to evaluate the development of plants in the presence of these substrates. These parameters significantly reflect the amount of environmental pollution. Due to this, appropriate measures can be taken to remove these pollutants from the environment. For these reasons, identification of changes in soil biological activity under the influence of synthesized compounds was also undertaken in the presented work. The biological activity was analyzed at selected intervals, based on the amount of secreted  $\mathrm{CO}_2$ . Warder's respirator method was used to determine the emitted amount of  $\mathrm{CO}_2$ . This method accurately determines the amount of carbon dioxide released as a result of processes in the soil, including the biological processes carried out by microorganisms.

For the first 30 days of measurements, a gradual increase in secretion of CO<sub>2</sub> was observed, which indicated the intensive development of microorganisms, but after that time an increase in the amount of carbon dioxide secreted in samples containing glucose-based surfactants was observed (Figure 2). This trend may indicate that glucose-based surfactants increased the activity of soil microorganisms and thus were used as a source of carbon and energy.



**Figure 2**. Amount of emitted CO<sub>2</sub> plotted against total duration of incubation (days) for soil samples with quaternary ammonium chlorides of glucose-based esters (a: soil samples with QSGC12, b: soil samples with QSGC14, c: soil samples with QSGC16).

#### 2.4. Conclusions

The quaternary ammonium chlorides of glucose-based ester were obtained based on modified methods from Gan et al. Introduction of changes in the second stage of synthesis of quaternary ammonium chlorides of glucose-based ester caused compounds obtained in good yields. Quaternary ammonium chlorides of glucose-based ester were characterized by good surface tension reduction properties and formed stable foam in contact with water, which were often better compared to the commercial cationic surfactants. The results showed that quaternary ammonium chlorides of glucose-based ester affect the activation of metals (nickel and cadmium) from the soil matrix and increase their concentration in the fraction extracted with water after their introduction into the soil environment. This phenomenon can increase the bioavailability of these metals, which may be used for the removal of such pollutants from soil using methods such as phytoremediation or metal leaching with surfactant solutions. The results regarding the changes in biological activity of the soil under the influence of quaternary ammonium chlorides of glucose-based ester seem promising, since the activity of microorganisms was increased, which may indicate the use of these compounds as a source of carbon and energy by the microorganisms.

The quaternary ammonium chlorides of glucose-based ester can be proposed as new environmentally friendly surfactants, which could be used in different industrial application such as the remediation of soil and water.

#### 3. Synthesis of sugar-based surfactants

#### 3.1. Materials and methods

D-Glucose (1 g, 0.0056 M) and potassium carbonate (1 g, 0.007 M) were dissolved in dried chloroform (20 mL) in a 100-mL flask equipped with a dry tube and then a solution of chloroacetyl chloride (0.8 g, 0.007 M) in dry chloroform (5 mL) was added dropwise in small portions, with constant stirring of the reaction system. The reaction was carried out for 3 h at ambient temperature. The product, 6-O-(2-chloroacetyl)-D-glucose, was obtained as a white solid with 92% yield. After the solvent was separated by filtration, the crude product was used in the second stage of the synthesis, where 6-O-(2-chloroacetyl)-D-glucose was dissolved in propanol (20 mL) and the corresponding tertiary amine (N, N-dimethyldodecylamine, N, N-dimethyltetradecylamine or N, N-dimethylhexadecylamine) was added dropwise in small portions. The whole system was heated at a temperature not exceeding 55 °C with simultaneous stirring for 5 h. Stepwise control of the reactions was readily achieved by analytical TLC performed using silica gel plates with 3:1 chloroform–methanol followed by adsorption with iodine. After this time, the reaction was terminated and the reaction mixture was concentrated to approximately three-quarters volume and placed in a refrigerator. After a few days, glucose surfactants were precipitated as a white precipitate. The resulting product was filtered and the product recrystallized from ethanol.

All the chemical shifts are reported in the supplementary information section.

D-Glucosyl 2-(N,N-dimethyl-N-dodecyl ammonium)-acetate chloride (QSGC12):

IR (KBr,  $cm^{-1}$ ): 3600-3100, 2934, 2865, 1645, 1438, 1422, 1389, 1089, 1020, 706.

<sup>1</sup> H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 0.89 (t, 3H, -CH<sub>3</sub>), 1.18 (m, 20H, -CH<sub>2</sub>-), 1.25–1.42, (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>-), 1.52–1.71 (t, 2H, NCH<sub>2</sub>-), 2.38 (s, 6H, -NCH<sub>3</sub>), 2.84 (br. s, 2H, -OCOCH<sub>2</sub>N-), 3.25–3.34 (d, 4H, H-2, H-3, H-4, H-5), 3.53 (br. d, 2H, -CH<sub>2</sub>OCOCH<sub>2</sub>N-), 3.86 (br s, OH), 4.0–4.10 (m, 1H, H-1 $\beta$ , J = 7.8 Hz), 4.96 (m, 1H, H-1 $\alpha$ ).

 $^{13}\,\mathrm{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta\colon$  12.51, 21.52, 27.67–30.25, 36.91, 37.95, 40.54, 61.59, 63.67, 69.47, 71.57, 72.53, 73.74, 96.49, 160.52.

D-Glucosyl 2-N, N-dimethyl-N-tetradecyl ammonium)-acetate chloride (QSGC14):

IR (KBr,  $cm^{-1}$ ): 3600-3050, 2943, 2862, 1650, 1472, 1423, 1390, 1088, 1059, 710.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 0.91 (t, 3H, -CH<sub>3</sub>), 1.08 (m, 20H, -CH<sub>2</sub>-), 1.15–1.35, (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>-), 1.62–1.81 (t, 2H, NCH<sub>2</sub>-), 2.99 (s, 6H, -NCH<sub>3</sub>), 3.24 (br. s, 2H, -OCOCH<sub>2</sub>N-), 3.29–3.30 (d, 4H, H-2, H-3, H-4, H-5), 3.53 (br. d, 2H, -CH<sub>2</sub>OCOCH<sub>2</sub>N-), 3.86 (br s, OH), 3.85–4.13 (m, 1H, H-1 $\beta$ , J = 7.8 Hz), 4.66 (m, 1H, H-1 $\alpha$ ).

 $^{13}\,\mathrm{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta\colon$  13.83, 22.05, 28.63–31.2, 36.99, 39.83, 40.04, 62.05, 63.35, 69.93, 71.93, 72.69, 73.78, 96.09, 160.81.

 $\hbox{D-Glucosyl 2-($N$,$N$-dimethyl-$N$-hexadecyl ammonium)-acetate chloride (QSGC16):}$ 

IR (KBr,  $cm^{-1}$ ): 3600-3100, 2956, 2876, 1635, 1433, 1403, 1387, 1076, 1055, 716.

 $^{1}$  H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta\colon$  0.90 (t, 3H, -CH<sub>3</sub>), 1.07–1.28 (m, 22H, -CH<sub>2</sub>–), 1.52 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>–), 1.62–1.71 (t, 2H, NCH<sub>2</sub>–), 3.01(s, 6H, -NCH<sub>3</sub>), 3.28 (s, 2H, -OCOCH<sub>2</sub>N–), 3.30–3.38 (d, 4H, H-2, H-3, H-4, H-5), 3.54 (br. d, 2H, -CH<sub>2</sub>OCOCH<sub>2</sub>N–), 3.86 (br s, OH), 4.05–4.10 (m, 1H, H-1 $\beta$ , J=7.8 Hz), 4.64–4.70 (m, 1H, H-1 $\alpha$ ).

 $^{13}\,\mathrm{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta\colon$  14.13, 23.15, 29.86–31.3, 37.89, 38.51, 41.4, 63.5, 64.83, 70.79, 72.95, 73.64, 74.38, 97.09, 161.28.

#### 3.2. Evaluation of glucose-based surfactants properties

#### 3.2.1. Surface tension

Air–water surface tension ( $\gamma$ ) was measured at 20 °C by using an Attension Theta Optical Tensiometer (Biolin Scientific, Gothenburg, Sweden). The surface tension was measured using freshly prepared aqueous solutions of the quaternary ammonium chloride of sugar-based esters in a concentration range of 2 × 10<sup>-5</sup>–0.02 mmol/L at 20 °C. The surface tension was determined using the pendant drop method. <sup>24</sup> This method consists of fitting the Young–Laplace equation to the digitized shape of a drop suspended from the end of a capillary tube. The image of the drop (6  $\mu$ L) was taken from a charge couple device camera. The critical micellar concentration (CMC) was determined by extrapolation of the two straight trends in low and high concentration regions in surface tension curves (the  $\gamma$  versus log C plot). Apparent surface tensions were measured three times for each sample.

#### 3.2.2. Foaming formation

The foaming ability, formation, and stability of the synthesized quaternary ammonium chlorides of glucose-based esters were investigated by oscillation methods at a concentration of 0.01 mol/L, which was performed at room temperature  $(20 \, {}^{\circ}\text{C})^{23}$ . An aqueous sugar-based ester quaternary ammonium compounds solution (10 mL, in pure water, which was obtained by purification at reverse osmosis systems) was loaded into a stopped cylinder of 50 mL, and then shaken rigorously 10 times at a speed of twice per second. The height of the foam produced after shaking was measured at 1, 5, and 20 min. The product was repeated five times and averaged.

#### 3.3. Influence of the soil environment

#### 3.3.1. The changes in metal mobility in soil

One of the steps of the study was focused on the determination of changes of metal mobility (Ni, Cd, Pb) in historically contaminated soil due to the presence of quaternary ammonium chlorides of glucose-based esters. Soil samples from these sites were collected in triplicate and dried at 105  $^{\circ}$ C to constant weight. Total metal concentrations were determined by digestion with acidic (73% HF, 65% HNO<sub>3</sub>, and 30% H<sub>2</sub>O<sub>2</sub>) solutions, according to the technical protocol developed by Lukaszewski et al. <sup>25</sup> Digests were filtered through filter paper into 25-mL flasks. The digested samples were analyzed for the metals by atomic absorption spectrophotometer using flame atomization.

First, the quaternary ammonium chlorides of glucose-based esters were added to the soil. The compound with an alkyl chain containing 14 carbon atoms was selected for this study. The QSGC14 (range of concentrations from 100 to 500 mg/kg d.w.s.) was added to the soil and dried to constant weight at  $60 \,^{\circ}\text{C}$ . Next, the soil samples containing quaternary ammonium chlorides of sugar-based esters were analyzed by the BCR sequential extraction procedure described by Rauret et al.  $^{26}$  and Jakubowska et al.  $^{27}$ 

In the first step, metals dissolved in the water were extracted. Approximately 1 g of each soil sample was placed in a plastic container, then 40 mL of 0.11 mol/L acetic acid solution was added and it was mechanically shaken at 280 rpm for 16 h. The extracts were separated from the solid residue by centrifugation at 10,000 rpm for 10 min and collected in polyethylene containers. In the second step, the reducible fraction was extracted.

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A 40-mL aliquot of 0.5 mol/L hydroxyl ammonium chloride solution was added to the residue soils, and resuspended mixtures were mechanically shaken for 16 h. The acidity level of this reagent was adjusted to pH 1.5 with HNO<sub>3</sub>. In the third step, the oxidizable fraction was extracted. The samples were treated with 10 mL of 30%  $\rm H_2O_2$  solution and the mixture was digested for 1 h at 85  $\pm$  2 °C. The mixtures were evaporated to a volume of less than 3 mL. A second aliquot of 10 mL of 30%  $\rm H_2O_2$  was added to the samples, which were shaken for 1 h at 85  $\pm$  2 °C, and the mixture evaporated to 2 mL. The residues were treated with 50 mL of 1.0 mol/L ammonium acetate solution, adjusted to pH 2 with HNO<sub>3</sub>, and shaken for 16 h. The extracts were separated. In the fourth step, the residual solids were digested using an acidic (73% HF, 65% HNO<sub>3</sub>, 30%  $\rm H_2O_2$ ) solution. Two independent replicates were performed in parallel for each sample, and blanks were measured for each set of analyses using acid extraction and BCR procedures, respectively.

All solutions were prepared in water by reverse osmosis in a Watek-Demiwa 5 Rosa system (Ledeč nad Sázavou, Czech Republic), followed by triple distillation from a quartz apparatus. Only freshly distilled water was used.

#### 3.3.2. Evaluation of changes in biological activity of soil

Observation of changes in biological activity in soil was carried out with soil samples, which were collected from the same industrial areas as for experiments regarding the influence of glucose-based surfactants on mobility of metal. The control samples were soil samples without glucose compounds. The experiment was conducted in sterile Simax bottles (Kavalier, Sázava, Czech Republic) containing 100 g of soil and a suitable quaternary esters ammonium salts concentration of 100, 250, or 500 mg/kg of soil and a vial with 10 mL of 0.75 M NaOH. The alkali traps were changed and titrated with 1 M HCl to determine  $\rm CO_2$ . During the experiment, the moisture content of the soil samples was maintained at a constant level of 50% of the total water capacity. Each attempt was made in 3 repetitions. At periods of time (75 days of incubation), the biological activity of the soil was determined on the basis of the amount of  $\rm CO_2$  excreted. The amount of emitted  $\rm CO_2$  was determined using Warder's method with potentiometric titration. <sup>28</sup>

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#### **Supplementary Matirial**

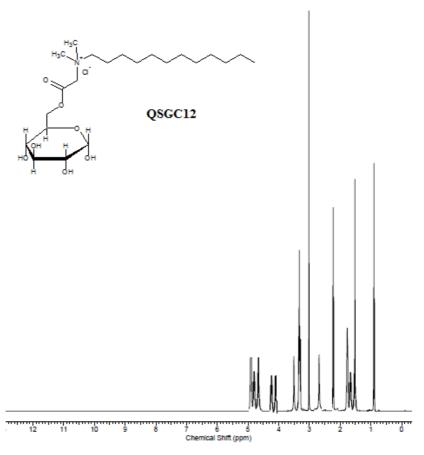
# Synthesis, characterization, and evaluation of toxicity of quaternary ammonium chlorides of glucose-based ester

### Anna PARUS<sup>1,\*</sup>, Grzegorz FRAMSKI<sup>2</sup>

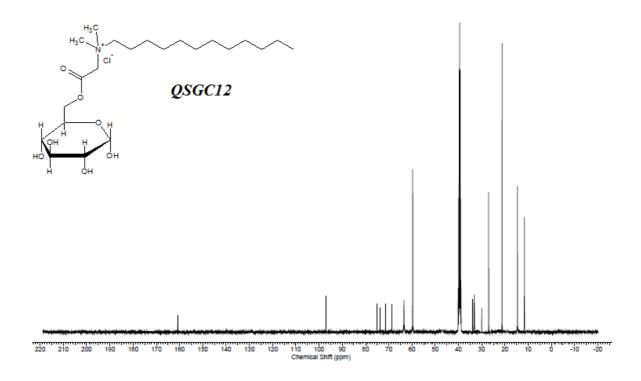
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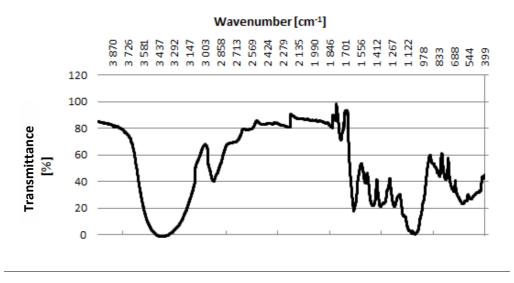
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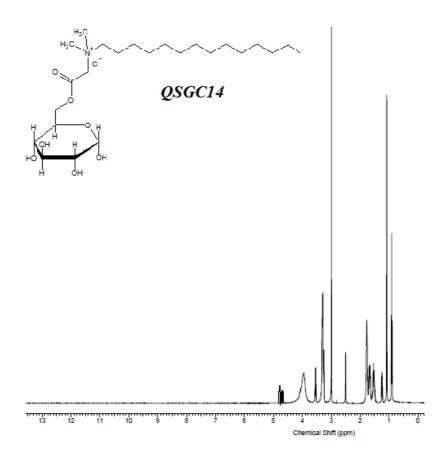
**Figure S1.** <sup>1</sup>H NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-dodecyl ammonium)-acetate chloride (QSGC12).



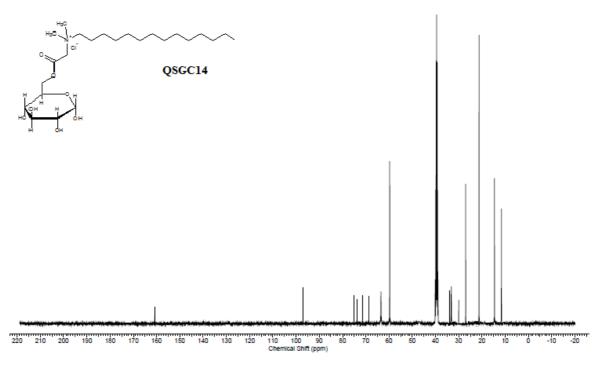
**Figure S2.** <sup>13</sup>C NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-dodecyl ammonium)-acetate chloride (QSGC12).



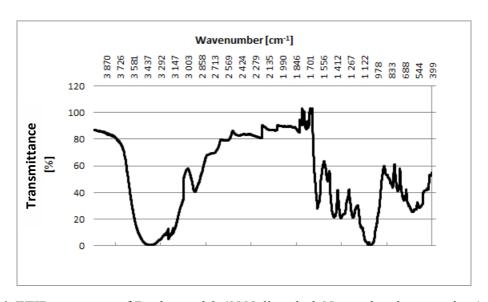
**Figure S3.** FTIR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-dodecyl ammonium)-acetate chloride (QSGC12).



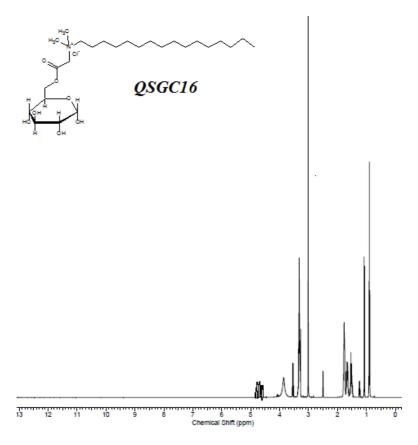
**Figure S4.** <sup>1</sup>H NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-tetradecyl ammonium)-acetate chloride (QSGC14).



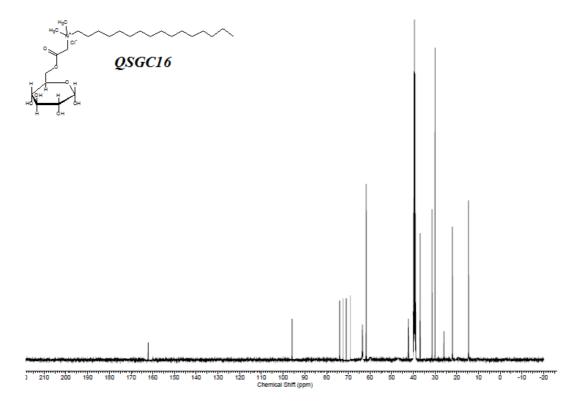
**Figure S5.** <sup>13</sup>C NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-tetradecyl ammonium)-acetate chloride (QSGC14).



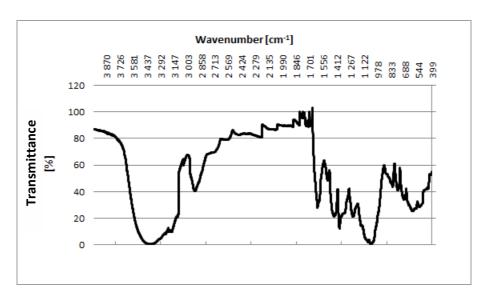
**Figure S6.** FTIR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-tetradecyl ammonium)-acetate chloride (QSGC14).



**Figure S7.** <sup>1</sup>H NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-hexadecyl ammonium)-acetate chloride (QSGC16).



**Figure S8.** <sup>13</sup>C NMR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-hexadecyl ammonium)-acetate chloride (QSGC16).



**Figure S9.** FTIR spectrum of D-glucosyl 2-(*N*,*N*-dimethyl-*N*-hexadecyl ammonium)-acetate chloride (QSGC16).