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Preparation Of Novel Multihydrophilic Anionic-Nonionic Sugar-Based Surfactants: I-Study Of Surface Activity, Performance, Detergency And Antimicrobial Assessment

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Abstract

A series of novel sugar-based anionic-nonionic surfactants was prepared by carboxylation of mono-fatty acyl sugar esters. The molecular structure of these amphiphiles consists of a non-polar lipidic (octadecanoyl or hexadecanoyl) chain grafted to the primary hydroxyl group in various sugars (sucrose, maltose and glucose). An anionic hydrophilic carboxyl or methyl-carboxyl group was incorporated into a hydroxyl functionality of the sugar moiety. The configuration of this molecular structure involves a hydrophobic acyl tail and a sugar hydrophilic backbone bearing anionic polar head group.

The structure of this new molecular framework was characterized by FTIR, ^{1}HNMR and ^{13}C NMR spectroscopy. The data of this analysis agree with the suggested molecular structure. These molecules, investigated in details for their self-assembling performance, indicated their strong surface tension-lowering efficiency, distinct foamability, rapid wetting power and long-term emulsifying stability. In addition, they possess effective soil-cloth cleansing and dishwashing detergency as well as evident lime-soap dispersion efficiency. All properties analyzed were related to standard anionic surfactant (sodium dodecyl sulfate, SDS).

Besides their potent surface-active characteristics, they possess obvious sequestering tolerance to calcium and magnesium metal ions, compared with those of the commercial Ethylenediamine tetra acetic acid (EDTA). The compounds are eco-friendly and were also recognized for their distinct antimicrobial action. The current study is concerned with a comprehensive investigation and evaluation of the functionality and possible multipurpose applications of these surface-active compounds.

Keywords: Anionic- Nonionic surfactants, sugar-based emulsifier, wastewater treatment, chelation ability, detergents, antimicrobial effectiveness.

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1. Introduction

Surface-active compounds are peculiar molecular structures exhibiting unique important phenomena such as wetting, emulsification, dispersing and foaming characteristics; they are among the most representative chemical materials consumed on a world scale[1,2]. In traditional concepts, surfactants constitute one hydrophilic head group and a nonpolar or hydrophobic moiety connected together in the same molecule. This single structure provides in some cases, limitation for some practical and industrial applications which is often compensated by using mixtures of various surfactants in some particular commercial applications [3].

Sugar-derived non-ionic surfactants prepared from biodegradable renewable substrates have acquired considerable interest due to their low-toxicity, biodegradability and acceptable ecological properties. They display considerably greater solubility and better surface activity together with useful performance including personal care formulations and other technological applications, particularly, as detergents [3]. Anionic surfactants have greater use if compared with other types of surfactants (constituting 60 % of the production within the world) because of their distinguished characteristics, especially in laundry detergents, agricultural, pharmaceutical and cosmetic fields [4]. However, the utilization of this type of surfactants is limited because they suffer from irritation properties [5]. Nevertheless, to the best of our knowledge, few studies were only published on anionic-derived surfactants [6–9].

Novel anionic surfactants having tailored functionalities and exhibiting simultaneously skin nonirritant properties, have found a fundamental priority in surface tension and colloid science fields. Numerous studies of such surfactants have been reported, among them the preparation and uses of anionic glucose and galactose derivatives [10–16],which are characterized by considerable wetting efficiency in the textile and oil recovery processing. Other investigations have dealt with the physicochemical and biochemical properties having appreciable irritation of anionic carbohydrate- derived surfactants.

During the last few decades, legislation and increasing consumer trend towards the utilization of materials which are benign to the environment had a strong influence on surfactant development. Accordingly, there was a growing need to develop newly modified surfactant structures to increase sustainability for the environmental ability and therefore new sugar-based green amphiphiles were produced [17].

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Novel surfactant products possessing greater than one hydrophilic and hydrophobic groups within the same molecule have found significant interest because it was believed that they possess remarkable surface properties. For instance, Gemini surfactants containing two hydrophobic and two hydrophilic moieties have shown to display greater surface activity than do traditional products[3,18,19]. Researchers have made efforts to prepare novel structural surfactants having more efficient eco-friendly multipurpose applications. Some carbohydrate derivatives having carboxylic residues have attracted constant attention [20,21] due to their cationic sequestering properties and their potential industrial applications in detergency, cosmetic and pharmaceutical uses. One of the most useful sugar-based derivatives, gluconic acid containing a carboxylic group has found extensive application as sequestering compound in the dairy, brewing, detergent and textile industries. In the medical field, sequestering has found significant use for introducing calcium, iron and other metals as well as hydrophobic insoluble drugs and dietary supplements into persons deficient in these highly important nutritional substances.

Monoesters of long-chain fatty acyl sucrose and glucose have particularly promise characteristics as surfactants, however, with long-chain fatty acids greater than C_{14}, their water solubility becomes a problem since they are not often soluble enough in pure water to enable surface tension-lowering and other related surface-active performance.

Accordingly, it is believed that the upgrading of certain sugar esters to new products with better solubility and surface activity become a strong motive for the preparation of novel modified sugar-based fatty acid esters. Therefore, in the present work, an approach towards enhancing solubility and surface activity was performed through incorporation of a polar group such as sulfate or carboxylate within the molecular backbone of these esters. Introduction of a -COOH group was believed to be preferred over sulphate because such carboxyl derivative is suggested to be environmentally more eco-friendly. Biodegradation of carboxylate sugars leads to their primary products with no harmful adverse environmental impact causing eutrophication of lakes and rivers.

The incorporation of additional polar group within the nonionic structural framework of sugar esters transforms them into anionic- nonionic amphiphiles. It may be anticipated that this peculiar molecular configuration may enable the new molecules to acquire the properties of combined both anionic and nonionic amphiphiles, thereby enhancing surfactant characteristics and affording additional properties.

This study involves the synthesis of sugar-based surfactant bearing a lipidic fatty acyl hydrophobic chain grafted to the primary hydroxyl group of various sugars (glucose, sucrose and maltose) together with carboxyl groups incorporated into a hydroxyl functionality of the sugar moiety. Carboxylation of the prepared sugar-esters was carried out either by HNO_3 controlled oxidation or addition of monochloroacetic acid ($ClCH_2COOH$) to the sugar part to produce the corresponding carboxylated derivatives.

The main objective of this work is to evaluate novel structures consisting of anionic-nonionic molecular amphiphiles. Thus, the performance of these compounds was analyzed and compared with anionic commercial surfactants such as sodium dodecyl sulfate (SDS) whereas sequestering effectiveness was related to ethylenediamine tetra acetic acid (EDTA). The compounds were examined for their surface tension lowering effect, molecular micellization and related phenomena such as foamability, wetting power and emulsifying abilities. Detergent potentiality and tolerance capability in chelating calcium and magnesium metals were also assessed. Moreover, the biodegradability and the antimicrobial properties against some bacteria and fungi were evaluated.

2.Materials and methods:

2.1. ***Materials**:* All chemicals, sodium hydroxide, potassium carbonate, nitric acid, acetone, methyl alcohol, ethyl alcohol, ethyl acetate, chloroform, and hexane were pure analytical grade. Fatty acids (Octadecanoic and Hexadecanoic) were from Aldrich; glucose, sucrose, maltose and chloroacetic acid supplied by AL-Nasr Pharmaceutical Chemical Co, Egypt.

2.2. Methods:

***Preparation of Multi-hydrophilic Anionic- Nonionic Surfactants*:**

The anionic- nonionic Surfactants preparation was carried out via three steps as described in Scheme 1.

Anionic-nonionic sugar-based surfactants with a polar carboxylic (COOH) head and nonpolar alkyl chain bearing C_{16} (hexadecanoic) and C_{18} (octadecanoic) acids were synthesized in this study, using glucose, sucrose and maltose as renewable sugar substrates. Firstly, methyl esters of the fatty acids (hexadecanoic and octadecanoic) were respectively prepared by refluxing the fatty acid in dry methanol for about 2 hr. in the presence of CH_3ONa as catalyst. After cooling, the methyl esters were extracted by diethyl ether, washed with water and then dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure.

The second step involves the preparation of nonionic surfactants through the reaction of the methyl esters of octadecanoic and hexadecanoic acids with the sugar component glucose, sucrose and maltose through a solventless base-catalyzed procedure as described in previous work in this laboratory [22]**.** The synthesis of sucrose octadecanoate is here represented as a typical example for the preparation of various sugar esters. The sugar (0.02mol) and the corresponding fatty methyl ester (0.02mol) were stirred in a 250 ml three-necked flask, and heated slowly to 45 ◦C for ½ hr., then K_2CO_3 (0.25g) as catalyst was added and heating was continued for 3.5 hr. After cooling, the solid product was washed with three 20 ml portions of n-hexane, then filtered, the product is treated with mixture of cyclohexane and butanol and the sugar ester was crystalized from ethyl acetate, the reaction progress was monitored by T.L.C (chloroform: methanol,4:1)

Finally, in the third step, the desired anionic- nonionic surfactants where derived from the different sugar esters by introducing a COOH functionality into the structural molecular framework of the sugar esters. Carboxylation was performed by methods commonly based on two different routes: a) Oxidation of acyl sugar esters using

Conc. HNO_3 acid, b) Carboxylation by reaction with $ClCH_2COOH$.

a) Oxidation of acyl sugar esters using Conc. HNO_3 acid: *I-Preparation of octadecanoyl sucrose monocarboxylic acid:*

The desired surfactant was made by mixing sucrose octadecanoate (0.01mol) dissolved in 20 ml chloroform and 0.45ml (0.01mol) conc. HNO_3 in a three-necked round-bottomed flask, using a magnetic stirrer. The contents of the flask were heated under reflux for about 3 hr, cooled and the precipitate washed with three 10 ml portions of saturated aqueous NaCl, then twice with 10ml chloroform. The product was finally purified by crystallization from ethanol. Mono-acyl glucose and maltose carboxylic acids were also synthesized following the same procedure.

II-Preparation of octadecanoyl sucrose Di-carboxylic acid:

Di-carboxylic acid derivatives were obtained by using 0.9 ml (0.02 mol) conc. HNO_3.

b) Carboxylation of acyl sugar esters by reaction with $ClCH_2COOH$:

The synthesis of octadecanoyl sucrose methyl carboxylic acid was a typical example for preparation of the different carboxy-methyl sugar esters: Sucrose mono octadecanoate (0.01 mol) dissolved in chloroform was charged into a three-necked flask, followed by the addition of chloroacetic acid (0.95g, 0.01mol) and the mixture heated with continuous stirring for about ½ hr. using a Teflon-coated magnetic stirrer. Sodium hydroxide (0.005 mol) was then added and the contents of the flask heated slowly under reflux for about 3.5 hr until a white ppt. formed. The flask was cooled and the product purified by crystallization from ethanol.

2.3. Structural analysis of the synthesized anionic-nonionic sugar- based surfactants:

The chemical structure of the synthesized anionic–nonionic surfactants was investigated by FTIR spectra (KBr, υ cm^{-1}) recorded on CARY 630 FT-IR spectrometer (Agilent, Santa Clara, CA, USA). Also, NMR spectra were estimated in (DMSO-d6) on a Bruker Avance (III) NMR spectrometer at 400 MHz; ^1H & ^{13}C-NMR at 400, and 100 MHz respectively: (Bruker, Switzerland).

The relationship between molecular structure, lipophilic- hydrophilic components, foaming, wetting ability, emulsifying properties and their surface tension reduction capabilities were determined by investigation of their surface tension-lowering, critical micelle concentration (CMC), surface tension reduction effectiveness and the HLB values.

2.4. Surface activity and critical micelle concentration (CMC): [23,24]

The concentration of critical micelle formation is defined as the value at which molecules of the surfactant start to aggregate (micelle formation).

Measurements of surface tension were carried out using Du-Nouy tensiometer. Freshly prepared surfactant solutions at concentration ranging from10^{-1} to 10^{-7} mol/l were poured into clean glass cups and then surface tension values were measured, the mean value for three readings at 25 ◦C were calculated.

The data were calculated from plots of surface tension readings against the logarithm concentration and the (CMC), γ_{CMC} were obtained from the intersection point of the two curves.

2.4.1. Efficiency (PC_{20}): [25]

The efficiency *(Pc_{20})*, refers to the concentration in (mol/L) of the surfactant solution that can reduce surface tension by 20mN/m obtained by equation:

$$Pc_{20} = -\log C_{20}$$

2.4.2. Effectiveness ($\pi_{CMC:}$) [26]

The surface tension at the critical micelle concentration used to calculate *effectiveness* (the surface pressure) was calculated as follows:

$$\pi_{CMC} = \gamma_{\square} - \gamma_{CMC}$$

Where: $\gamma_{\square}$: surface tension of pure water at 25 ◦C.

γ_{CMC}: defines surface tension of the solution at the critical concentration of micelle formation.

2.4.3. Maximum surface excess concentration (Γ_{max}): [25]

The evaluation of the surface excess concentration *(Γ_{max})* was calculated from the Gibbs adsorption equation:

$$\Gamma_{max} = -(1/2.303nRT)\ (d\gamma / d\log C)$$

Where: n defines the number of molecules at interface between air-water which change as the concentration of the surfactant was varied

R= (8.314 J/ (mol. k^{-1})

T: absolute temperature (K).

($d\gamma / d\log C$): the variation of surface tension / variation of log concentration is the slope in the surface tension isotherm

2.4.4. Area / molecule (A_{min}) at air /water interface: [27]

$$A_{min} = 1 / (N_A \Gamma_{max})$$

Where: N_A determines Avogadro's number

2.5. Kraft point: [28]

The kraft point was estimated by measuring the temperature at which 1 % aqueous sample becomes clear on slow heating. It is satisfactory measure of water solubility.

2.6. Cloud point: [29]

The cloud point was estimated by heating slowly a solution (1.0 % w/w) of the surfactant until the temperature at which the clear solutions turn cloudy. The solutions were cooled until they turn again clear which verifies repeatability of the data.

2.7. Hydrophile-lipophile balance (HLB): [25]

The HLB values of surfactants **1-9** can be calculated using Davies formula:

$$HLB = 7 + \sum (\text{hydrophilic group}) + \sum (\text{lipophilic group})$$

2.8. Foaming properties: [22,30]

The foaming power of the synthesized carboxyl sugar esters were determined at 25 ◦C ± 1 ◦C. In a typical procedure, 25ml of an aqueous solution of the relevant surfactant (1%, 0.1 % wt/v) was subjected to twenty vertical vigorous shaking into a 100 ml glass stoppered cylinder for 20 seconds and the foam height was measured immediately (0 time) and after 5 and 30 minutes respectively.

2.9. Wetting power: [22,31]

The wetting power was measured using the Draves–Clarkson skein test, the method determines the time (seconds) taken by a standard cotton skein (5 g) for sinking in a 0.1% surfactant solution at room temperature.

2.10. Drop- penetration test : [32]

The test measures the time of penetration of aqueous solution of the surfactant through soils. The method was done on commercial ground peatmoss added on a watch glass to make a thickness of 3-4 mm. The tested surfactant (2drops) was added to the peatmoss surface using a medicine dropper. The penetration time of the solution in the peatmoss layer was observed. The samples were then allowed to dry overnight and again rewetted with distilled water and time require for rewetting was recorded.

2.11. Emulsifying power: [22]

Aqueous solution of the surfactant (3ml, 0.1wt %) was mixed with sunflower oil (2ml) in a stoppered cylinder (100 ml) and shaken 20 strong shakes. The volume of the emulsion was measured at 0, 5, 15, and 30-minutes time periods until any phase separation was attained.

2.12. Biodegradability: [22]

Surface tension is used for determination of biodegradability through incubation of surfactant solution (50 ppm) in river water at 30 ºC. A sample was taken frequently for measuring surface tension values.

2.13. Detergency evaluation:

The evaluation of the potentialities of surfactant detergency includes the efficiency in cleaning and removal fatty matter from soiled textile fibers as well as in dishwashing processes.

a- Soil-cloth detergency:[33]

The detergency was determined by using a simple agitation / mixing device. The test was done under normal temperature of 25 ◦C, at rotation speed of 120 rpm. The cotton swatches, soiled by olive oil (4 %) were cut into a size of 5 cm X 5cm and each test was carried out in triplicates. The efficiency of detergency was examined using 500 ml of 0.1 % of the surfactant for15 minutes washing time followed by 2 rinsing cycles, each being 5 minutes long. The results were expressed as percent soil removal efficiency.

b- Dish washing detergency: [34,35]

The mockup soil used for the dish washing test was made by mixing beef fat (10 g), soybean oil (10 g), glycerol oleate (0.25 g) and 0.1 g Sudan II dye in chloroform (60 mL). Glass slides were soiled by dipping into the mockup soil for 1 min and air-dried at room temperature, then washed with 0.03 wt. % of the tested surfactant solution at 30°C. The 0.03 wt.% concentration was selected because it corresponds to the traditional concentration of kitchen detergents. The dish washing efficiency was determined by weighing the stained-glass slides before and after washing and drying. The detergent experiments were performed by repeating the washing with six glass slides and the mean values were determined.

2.14. Lime-soap dispersion:[36]

Lime-soap dispersion potentiality is a measure of the capability of a surfactant to inhibit or prevent the formation of visible clots of lime-soap due to the calcium ions presence in a solution containing soap and the surfactant under investigation.

The procedure involves the use of sodium oleate (5 ml) and 5 ml of the dispersing agent pipetted into a special stoppered test tube, then 10 ml of hard water and enough water added until the total volume of the mixture reached 30 ml. The tube was stoppered and shaken by inversion 20 times in 30 seconds, then it was allowed to stand for 30 seconds. If a coagulated precipitate appears, it is obvious that the dispersing agent is not enough to effect dispersion of lime soap. The amount of dispersing agent was increased and the lime-soap dispersion was measured by the surfactant amount added until the solution became translucent and no longer any large clumps present.

2.15.Chelation: calcium and magnesium tolerance: [37]

The tolerance of Ca^{++} and Mg^{++} ions was determined by the addition of different concentrations of $CaCl_2$ aqueous solution into the surfactant solution which was first heated to 60ºC and then cooled to 25ºC. Maximum surfactant tolerance to Ca^{2+} or Mg^{2+} is determined by the greatest concentration of $CaCl_2$ solution necessary to be added before the surfactant solution becomes turbid.

2.16. Antimicrobial activity:

The antimicrobial effect of carboxylated sugar derivatives against some pathogenic bacteria, together with a fungus strain was done by nutrient agar well diffusion method [38]. The inhibition zone and the minimum inhibitory concentration (MIC) in µg/ml were estimated for each compound using the broth dilution method [39,40]. The examined microorganisms *Staphylococcus aureus* (ATCC25923) and other microorganisms were tested. The procedure is described in detail in the Supplementary Materials.

3.Results & Discussion

Sugar-based nonionic surfactants became a viable biobased alternative to other amphiphiles prepared from petrochemical substrates because of their high performance, low toxicity, low irritancy towards living organisms and environmental compatibility [41–45].

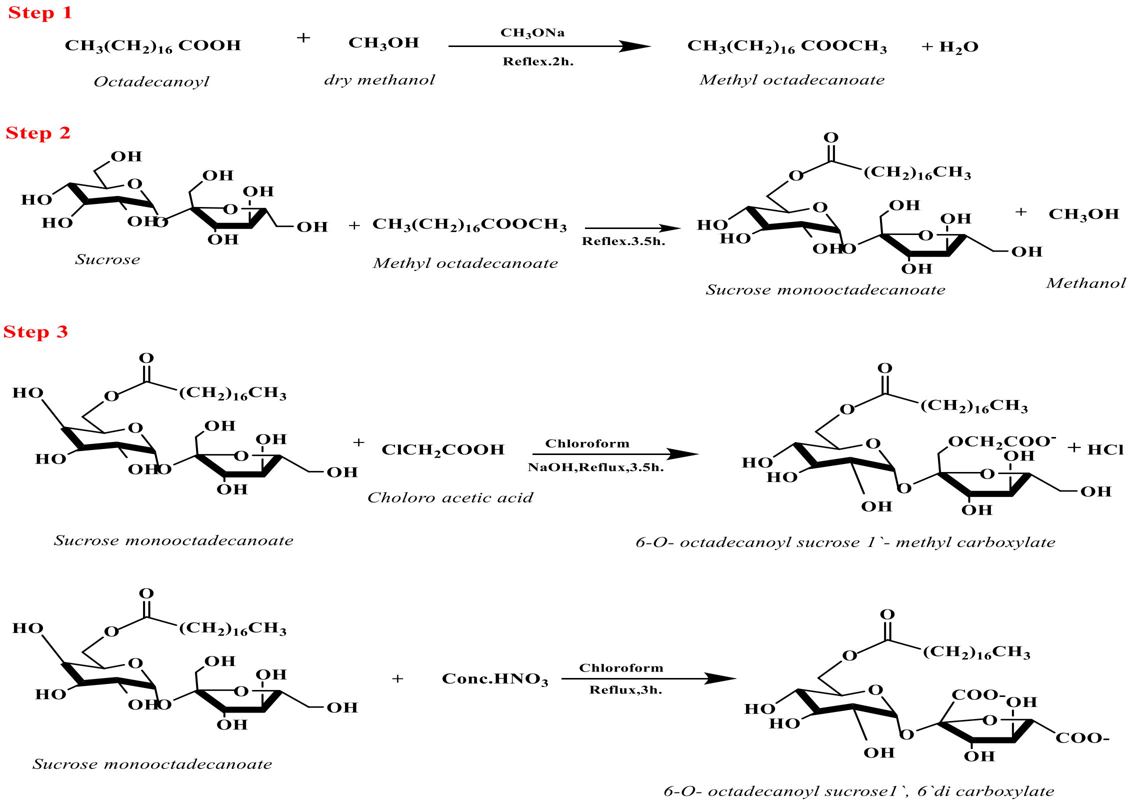
This study involves preparation and evaluation of novel modified sugar-based surfactants bearing a lipidic fatty acyl hydrophobic chain joined to the primary hydroxyl group of various selected sugars (glucose, sucrose and maltose). A carboxylate group was introduced into a hydroxyl functionality of the sugar moiety to furnish anionic-nonionic amphiphilic surfactant structures. The structure of the new anionic- nonionic surfactants was built in accordance with their predicted ability to display improved surface activity which would add new functional characteristics superior and competitive to traditional sugar esters.

The desired new sugar-based anionic- nonionic surfactants were synthesized (Scheme 1), first through acylation of the sugar as acyl acceptor with octadecanoyl or hexadecanoyl methyl esters, as acyl donors under controlled reaction conditions to afford regioselective acylation using the protocols previously followed in this laboratory [22,31]. These systems were prepared under conditions that reliably generated the required esters successfully in high yields, providing a substitution of the acyl chain which is rather selective giving 6-*O*- acyl esters [20,46,47]. In the second stage, a carboxylate group was introduced within a hydroxyl functionality of the sugar moiety of the prepared nonionic product to furnish the desired anionic-nonionic amphiphilic surfactant molecular structure. The carboxylation was carried out via nitric acid-controlled oxidation or by coupling with chloroacetic acid into the sugar moiety of the nonionic part to produce the desired amphiphilic type surfactant structure. Thus, in the present setting this amphiphilic molecular structure constitutes both a lipophilic alkyl chain coupled with a multi -hydroxylic sugar head moiety with an additional -

COOH functionality. Chloroacetic acid is widely used in carboxylation reactions, this carboxymethylation may be performed either neat or in aqueous solutions [48].

Characterization of acyl sugar carboxylate and methyl carboxylate ester:

Each chromatographical and purified carboxyl-containing anionic-nonionic esters was characterized by FTIR,^{1}H & ^{13}C NMR spectroscopic analyses. As for the FTIR data for 6-*O*- acyl sugar carboxylate esters shown in fig.2, the close similarity of the results to theoretical values, indicates that the synthesis of the prepared products is successful. The typical characteristic peaks of (OH) 3406.0 cm^{-1}, (C-H) vibration at 2918.03 cm^{-1}, (C=O) of the ester group at 1724.76 cm^{-1}, (C=O) of the carboxyl group at 1628.13 cm^{-1} are observed. The characteristic bands of all products are similar. The structure of the synthesized products was also confirmed by ^{1}H & ^{13}C NMR. ^{1}H-NMR results demonstrating peaks at (δ ppm) 9.38 for (O$\underline{H}$) of -COOH group, 1.23 for C$\underline{H}_2$ – chain, 0.85 for C$\underline{H}_3$. Particularly, the C$\underline{H}_2$ protons at C_6 of the sugar reacted with the C=O of fatty ester part, indicating the position of esterification as being at C_6 of the sugar moieties as reported previously [31,49]. Other key interactions for the spectral assignments present contribute to the structural characterization of these surfactants.



Scheme 1: Synthesis of Anionic –Nonionic Surfactants: acyl sugar carboxylate and methyl carboxylate esters.

FTIR and ^{1}H & ^{13}C NMR spectra:

6-O- octadecanoyl sucrose**:** white power, yield 82.60%; m.p. 76 ◦C. FT-IR (KBr, ν max cm^{-1}) (Fig. 1)[22]: ^{1}H-NMR spectrum (400 MHz, DMSO, δ ppm): (Fig. 5) demonstrated various peaks at δ 5.18 (d, 1H), 4.84 (d, 1H), 4.58 (d, 2H), 4.42 (d, 1H), 4.06 (d, 1H), 4.02 (d, 3H),3.90 (m, 1H), 3.88 (d, 2H), 3.79 (d, 3H), 3.66 (d, 1H), 3.65(dd, 3H), 3.56 (d, 1H), 3.46 (m, 1H), 2.28 (t, 2H,- C$\mathbf{H_2}$-CO-), 1.49 (m, 2H,-C$\mathbf{H_2}$-CH_2-CO-), 1.24 (m, 28H,-C$\mathbf{H_2}$ – chain), 0.83 (t, 3H, C$\mathbf{H_3}$).

6-O- octadecanoyl sucrose 1`- methyl-carboxylic acid (1): White power, yield 88.66%; m.p. 73-75 ◦C A.V = 84.15. FT-IR (KBr, ν max cm^{-1}) (Fig. 2): 3406 (OH), 2918.03 (C-H), 2850.57 (C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1313.34 and 1103.03, 1724.76 due to stretching vibration (V $_{C=O}$) of the ester group, 1628.13 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1053.95 and1228.28, 995.61 pyranose ring. ^{1}H-NMR spectrum (400 MHz, DMSO, δ ppm): (Fig. 6) demonstrated various peaks at δ 9.38 (s, 1H), 5.18 (d, 1H), 4.74 (s, 1H), 4.48 (d, 1H), 4.38 (d, 1H), 4.33 (d, 1H), 4.22 (m, 3H), 4.15 (m,1H) , 4.11 (d, 3H), 4.09(m, 1H), 3.90 (m, 1H), 3.88 (m, 2H), 3.82 (m, 2H), 3.63(m, 2H), 3.56 (m, 1H), 3.40 (m, 1H), 2.18 (t, 2H, ,- C$\mathbf{H_2}$-CO-),1.48 (m, 2H,-C$\mathbf{H_2}$-CH_2-CO-), 1.23 (m, 28H, C$\mathbf{H_2}$ – chain), 0.85 (t, 3H, **C**$\mathbf{H_3}$).

6-O- octadecanoyl maltose 6`- methyl-carboxylic acid (2): Yellowish white waxy product, yield 83.33 %; m.p. 69-71°C A.V = 85.55**.** FT-IR (KBr, ν max cm^{-1}) (Fig. 3): 3388.95 (OH), 2917.24 (C-H), 2850.04 (C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1384.30 and 1105.12, 1764.61 due to stretching vibration (V $_{C=O}$) of the ester group, 1645. 30 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-

O-C) of the pyranose moiety of maltose are observed between 1068.54 and1240.73, 941.18 pyranose ring. ^{1}H NMR (400 MHz, DMSO, δ ppm): (Fig. 7) demonstrated various peaks at δ 10.21 (s, 1H), 5.01 (d,1H), 4.98 (d, 1H), 4.91 (d, 1H), 4.50 (d, 1H), 4.34 (d,1H), 4.32 (d,1H), 4.30 (d,2H), 4.10 (d,1H), 4.07 (d,2H), 4.02 (d,1H), 3.83 (m, 2H), 3.80 (m, 1H), 3.70 (m, 1H), 3.68 (m, 1H), 3.66 (m, 1H), 3.56 (m, 1H), 3.53 (m,1H), 3.41 (m,1H), 3.40 (m,1H), 2.19 (t, 2H, $C\mathbf{H_2}$-CO-), 1.47 (m,2H,-$C\mathbf{H_2}$-CH_2-CO-), 1.23 (m, 28H,- $C\mathbf{H_2}$ – chain), 0.86 (t,3H,$C\mathbf{H_3}$).

6-O-octadecanoyl glucopyranosyl 1- methyl-carboxylic acid (3): Yellowish white power, yield 89.69 %; m.p. 75-77 ◦C, A.V = 110.79. FT-IR (KBr, ν max cm^{-1}): (Fig. 4): 3361.66 (OH), 2919.35 (C-H), 2850.09 (C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1312.15 cm^{-1} and 1186.07 cm^{-1}, 1740.17 due to stretching vibration (V $_{C=O}$) of the ester group, 1695.28 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of glucose are observed between 1077.67 and1227.43, 915.88 pyranose ring. ^{1}H NMR (400 MHz, DMSO, δ ppm): (Fig. 8) demonstrated various peaks at δ 8.26 (s, 1H), 4.91 (d, 1H), 4.90 (d, 1H), 4.33 (d, 1H), 4.27 (d,1H), 4.26 (d, 1H), 4.06 (d, 1H), 4.04 (d, 2H), 3.78 (m, 1H), 3.53 (m, 2H), 3.47 (m, 1H), 2.19 (t, 2H, $C\mathbf{H_2}$CO-), 1.49 (m, 2H, $C\mathbf{H_2}$ CH_2CO-), 1.27 (s, 28H- $C\mathbf{H_2}$ – chain), 0.83 (t, 3H, $C\mathbf{H_3}$).^{13}C-NMR (100 MHz, DMSO, δ/ppm): spectrum (Fig. 11) illustrates peaks at 14.41 attributable to carbon of ($\underline{\mathbf{C}}H_3$); 22.55($CH_3\underline{\mathbf{C}}H_2CH_2$); 24.95 ($\underline{\mathbf{C}}H_2CH_2COO$-); 29.47, 29.46, 29.42, 29.16, ($\mathbf{C}H_2)_{12}$ chain; 31.74 ($CH_3CH_2\underline{\mathbf{C}}H_2$); 34.16 ($CH_2\underline{\mathbf{C}}H_2COO$-); 61.62 ($\underline{\mathbf{C}}H_2$ –O CO CH_2); 63.40 (O-$\underline{\mathbf{C}}H_2COOH$); 71.00($\underline{\mathbf{C}}$-4); 73.52 ($\underline{\mathbf{C}}$-2); 75.26 ($\underline{\mathbf{C}}$-5); 77.17 ($\underline{\mathbf{C}}$-3); 97.34 ($\underline{\mathbf{C}}$-1); 174.84, 174.82 (O- $\underline{\mathbf{C}}$=O ester, O-$CH_2\underline{\mathbf{C}}OOH$ acid).

6-O- hexadecanoyl sucrose 1`- methyl-carboxylic acid (4): Yellowish white power, yield 87.93 %; m.p. 64- 66ºC A.V = 89.76. FT-IR (KBr, ν max cm^{-1}): (Fig. S1): 3360.98 (OH), 2917.25 (C-H), 2849.15 (C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1347.25 and 1187.63, 1737.73 due to stretching vibration (V $_{C=O}$) of the ester group, 1689.56 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1055.48 cm^{-1} and 1248.64, 923.51 pyranose ring.

6-O- hexadecanoyl maltose 6`- methyl-carboxylic acid (5): Yellowish white power, yield 86.21 %; m.p. 67-69 ◦C A.V = 86.95**:** FT-IR (KBr, ν max cm^{-1}): (Fig. S2): 3355.87 (OH), -2918.13(C-H), 2850.06 (C-H) stretching for chain length of fatty acid ester. Stretching bands of O-C bond at 1307.89 and 1074.84, 1726.43 due to stretching vibration (V $_{C=O}$) of the ester group, 1623.56 duto the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of maltose are observed between 1036.85 and1208.27, 906.18 pyranose ring.

6-O-hexadecanoyl glucopyranosyl 1- methyl- carboxylic acid (6):

White power, yield 83.73 %; m.p. 54-56 ◦C A.V = 115.01**:** FT-IR (KBr, ν max cm^{-1}): (Fig. S3): 3287.16 (OH), 2918.38(C-H), 2849.69(C-H) stretching for chain length of fatty acid ester. Stretching bands of O-C bond at 1348.98 and 1187.31, 1722.26 due to stretching vibration ($V_{C=O}$) of the ester group, 1623.37 duto the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of glucose are observed between 1010.68 and1228.10, (940.08) pyranose ring.

6-O- octadecanoyl glucopyranosyl carboxylic acid (7)

Yellowish white semi solid, yield 87.44%; m.p. 59-61 ◦C A.V = 117.81**:** FT-IR (KBr, ν max cm^{-1}): (Fig. S4): 3385.33 (OH), 2917.40(C-H), 2851.64(C-H) for chain length of fatty acid ester. Stretching band of O-C bond at 1384.34 cm^{-1}, 1740.68 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, 1630.69 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of glucose are observed at 1077.94, 915.35 pyranose ring. ^{1}H-NMR (400 MHz, DMSO, δ ppm) (Fig. 9) demonstrated various peaks at 8.48 (s, 1H), 4.91 (d, 1H), 4.88 (d, 1H), 4.59 (d, 1H), 4.55 (d, 1H), 4.26 (d, 1H), 3.84 (m, 1H), 3.57 (m, 1H), 3.33 (m, 1H), 3.25 (m, 1H), 2.25 (t, 2H, $C\mathbf{H_2}$-CO-), 1.78 (s, 2H, -$C\mathbf{H_2}$-CH_2-CO-), 1.24 (m, 28H, - $C\mathbf{H_2}$ – chain), 0.84 (t, 3H, $C\mathbf{H_3}$).

6-O- octadecanoyl sucrose 1`, 6`di-carboxylic acid (8)

Yellowish white semi solid, yield 85.33 %; m.p. 62-64ºC A.V = 176.72***:*** FT-IR (KBr, ν max cm^{-1}): (Fig. S5): 3389.47 (OH), 2917.15(C-H), 2849.63(C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1382.47and 1105.28, 1729.37 due to stretching vibration (V $_{C=O}$) of the ester group, 1643.44 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed at 1049.85, 924.08 pyranose ring.

6-O- octadecanoyl maltose 1`, 6` di-carboxylic acid (9)

Yellowish white semi solid, yield 81.67 %; m.p. 65-67 ◦C A.V = 171.11***:*** IR (KBr, ν max cm^{-1}): (Fig. S6): 3601.67 (OH), 2916.45(C-H), 2850.47(C-H) for chain length of fatty acid ester. Stretching bands of O-C bond at 1375.14 cm^{-1} and 1118.94, 1722.22 due to stretching vibration (V $_{C=O}$) of the ester group, 1630.69 due to the C=O of the carboxyl group. The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of maltose are observed between 1033.36 and1226.62, 937.64 pyranose ring. ^{1}H NMR (400 MHz, DMSO, δ ppm) (Fig. 10) demonstrated various peaks at 8.39 (s, 1H), 5.18 (d,1H), 4.90 (d, 1H), 4.25 (d, 1H), 4.16 (d, 1H), 3.89 (m,1H), 3.87 (m,1H), 3.78 (d,1H), 3.64 (m, 1H), 3.55 (d, 1H), 3. 48 (m, 1H), 3.41 (m, 1H), 3.25 (d, 1H), 3.18 (m, 1H), 3.12 (m,1H), 3.04 (m,1H), 2.89 (m,1H), 2.27 (t, 2H, $C\mathbf{H_2}$-CO-), 1.46 (m,2H, -$C\mathbf{H_2}$-CH_2-CO), 1.23 (m, 28H,-$C\mathbf{H_2}$ – chain), 0.85 (t,3H,$C\mathbf{H_3}$). ^{13}C-NMR (100 MHz, DMSO, δ/ppm): spectrum (Fig.12) illustrates peaks at 14.38 attributable to carbon of ($\underline{\mathbf{C}}H_3$); 22.61($CH_3\underline{\mathbf{C}}H_2CH_2$); 26.00 ($\underline{\mathbf{C}}H_2CH_2COO$-); 29.44,29.42, 29.21, ($\mathbf{C}H_2)_{12}$ chain; 31.74 ($CH_3CH_2\underline{\mathbf{C}}H_2$); 38.42 ($CH_2\underline{\mathbf{C}}H_2COO$-); 64.62 ($\underline{\mathbf{C}}H_2$ –O CO CH_2); 70.26($\underline{\mathbf{C}}$-4); 72.75($\underline{\mathbf{C}}^{*}$-2); 73.43 ($\underline{\mathbf{C}}$-2); 74.21 ($\underline{\mathbf{C}}$-5); 74.65($\underline{\mathbf{C}}^{*}$-3); 75.62($\underline{\mathbf{C}}^{*}$-5); 76.77 ($\underline{\mathbf{C}}$-3); 77.14($\underline{\mathbf{C}}^{*}$-1); 82.16($\underline{\mathbf{C}}^{*}$-4); 104.64 ($\underline{\mathbf{C}}$-1); 166.89 (O- $\underline{\mathbf{C}}$=O ester); 173.56 ($\underline{\mathbf{C}}OOH$ acid); 176.58 ($\underline{\mathbf{C}}OOH$ acid).

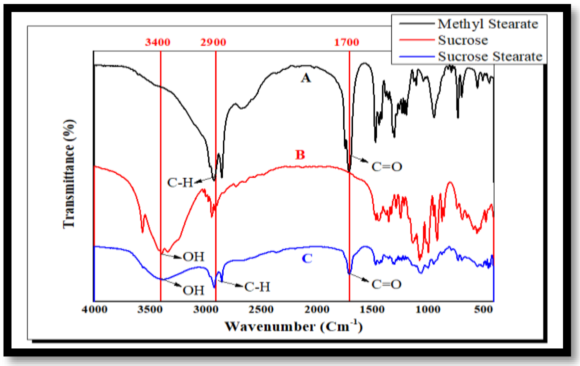


Fig.1. *FT*- IR spectrum of, (A) methyl stearate B) sucrose and (C) synthesized sucrose mono (octadecenoate)[22]

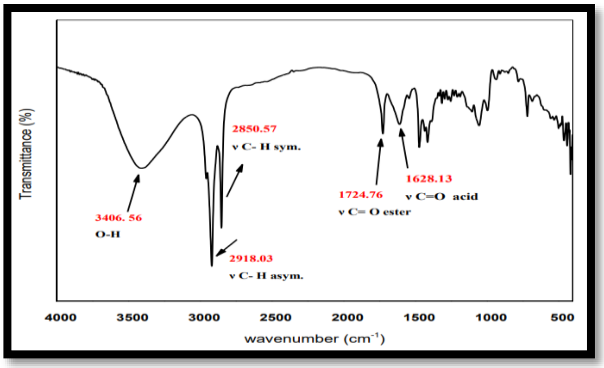


Fig.2.*FT*- IR spectrum of 6-*O*- octadecanoyl sucrose1`-methyl-carboxylic acid (**1**)

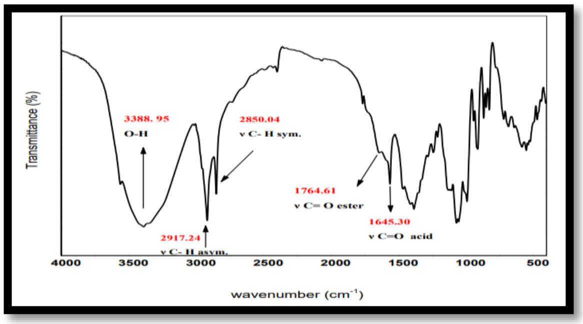


Fig.3.*FT*- IR spectrum of 6-*O*- octadecanoyl maltose 6`-methyl-carboxylic acid (**2**)

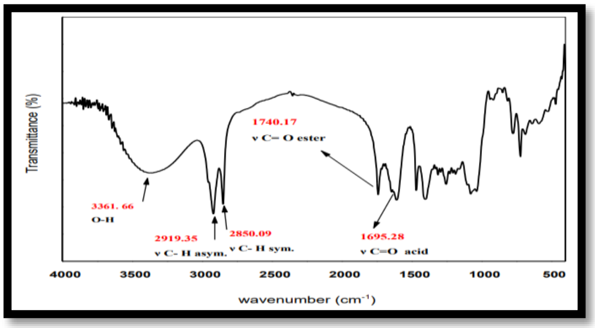


Fig.4.*FT*- IR spectrum of 6-*O*- octadecanoyl glucopyranosyl 1-methyl-carboxylic acid (**3**)

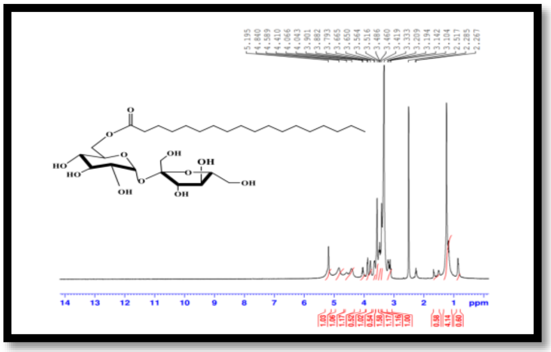


Fig.5. ^{1}H-NMR spectrum of 6-*O*- octadecanoyl sucrose

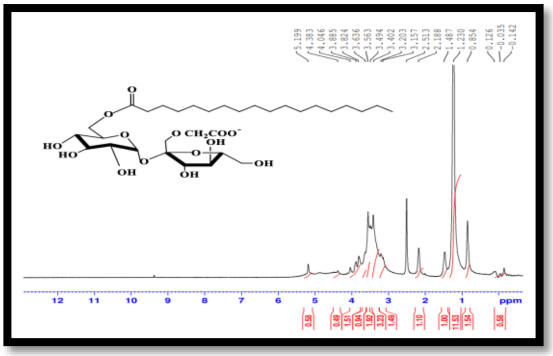


Fig.6. ^{1}H-NMR spectrum of 6-*O*- octadecanoyl sucrose 1`-methyl-carboxylic acid (**1**)

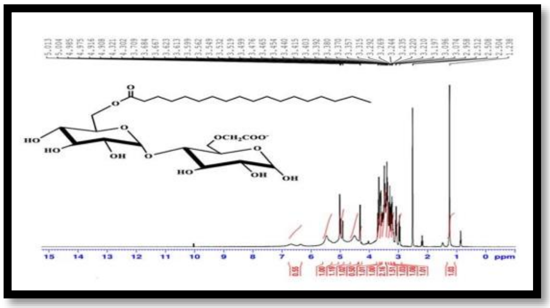


Fig.7.^{1}H-NMR spectrum of 6-*O*- octadecanoyl maltose 6`-methyl-carboxylic acid (**2**)

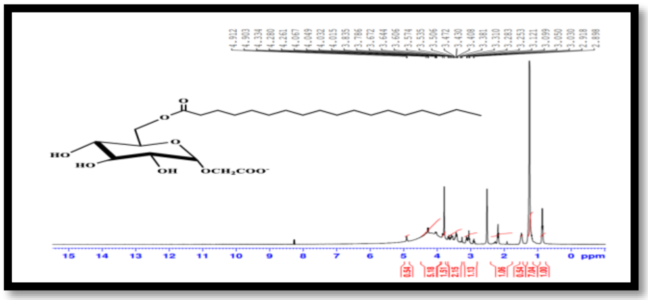


Fig.8. ^{1}H-NMR spectrum of 6-*O*- octadecanoyl glucopyranosyl 1- methyl-carboxylic acid (**3**)

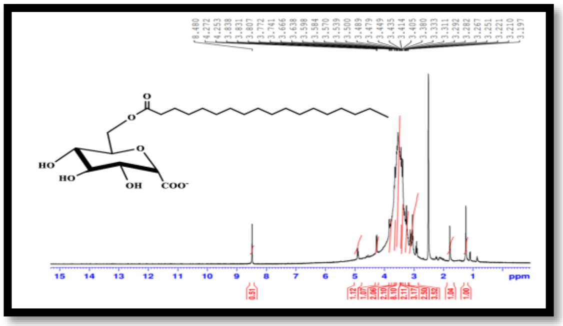


Fig.9. ^{1}H-NMR spectrum of 6-*O*- octadecanoyl glucopyranosyl carboxylic acid (**7**)

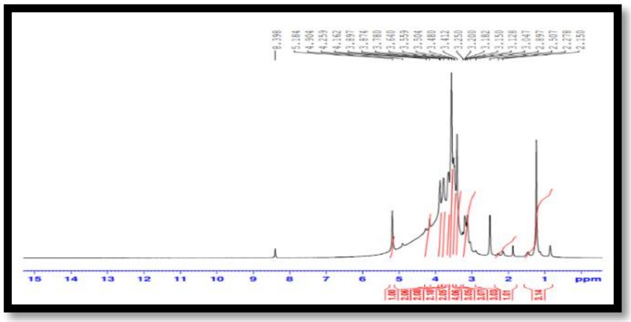


Fig.10. ^{1}H-NMR spectrum of 6-*O*- octadecanoyl maltose 1`, 6` di-carboxylic acid (**9**)

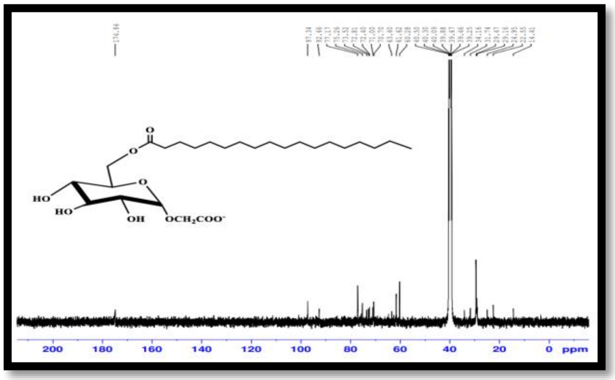


Fig.11. ^{13}C-NMR spectrum of 6-*O*- octadecanoyl glucopyranosyl1- methyl-carboxylic acid (**3**)

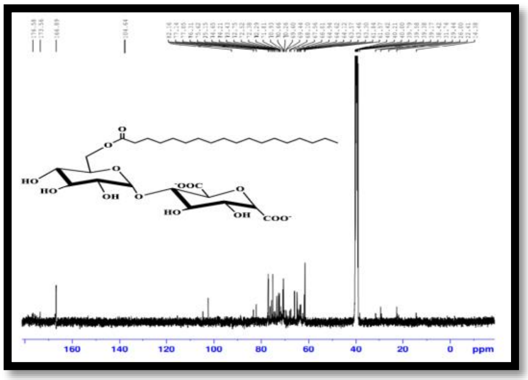


Fig.12. ^{13}C-NMR spectrum of 6-*O*- octadecanoyl maltose 1`, 6` di-carboxylic acid (**9**)

Physicochemical and surface- active performance:

In particular, the advantages of the synthesized esters are manifested by excellent water solubility, low viscosity and good amphipathic properties that make this molecular structures considered as good candidates in multifunctional purposes, probably in surfactant-promoted remediation of contaminated soils [37,50]. Thus, the resulting carboxylation enhanced solubility and consequently is suggested to improve surfactant performance having exceptionally low CMCs. These setting which has a terminal anionic carboxylic head together with a hydrophobic acyl chain coupled with the sugar part produce a unique molecular structure enables them to possess characteristics combining those of both anionic and nonionic surfactants which would improve surfactant properties and other practical functionalities.

Table 1. Physicochemical characteristics of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters.

Methyl ester	surfactants	Sugar	Surfactants	Formula	M. Wt.	M.P ◦C	Yield %	Cloud point ◦C	Kraft point ◦C
Octadecanoyl	Monomethyl carboxy-	Sucrose	**1**	$C_{32}H_{57}O_{14}$	666	73-75	88.66	12	25
		Maltose	**2**	$C_{32}H_{57}O_{14}$	666	69-71	83.33	20	25
		Glucose	**3**	$C_{26}H_{47}O_{9}$	504	75-77	89.69	19	24
Hexadecanoyl		Sucrose	**4**	$C_{30}H_{53}O_{14}$	638	64-66	87.93	13	24
		Maltose	**5**	$C_{30}H_{53}O_{14}$	638	67-69	86.21	11	24
		Glucose	**6**	$C_{24}H_{43}O_{9}$	476	54-56	83.73	12	23
Octadecanoyl	Mono- carboxy	Glucose	**7**	$C_{25}H_{46}O_{8}$	474	65-67	81.67	20	25
	Di-carboxy	Sucrose	**8**	$C_{32}H_{56}O_{14}$	636	62-64	85.33	24	30
		Maltose	**9**	$C_{32}H_{56}O_{14}$	650	59-61	87.44	22	35

***Surface- Active Properties*:**

Surface tension, CMC and migration to the interface which are essential important phenomena of liquid interfacial properties that explain theoretical mechanism of surfactant process, can be estimated from surface tension data. Accordingly, surface tension and other related properties are traditionally examined firstly when a new surfactant was synthesized. To act as surfactant, compounds must possess good surface activity, being able to produce low surface and interfacial tensions in the system in which they are used and have the tendency to migrate to the interface.

Therefore, the mean air-water surface tension reduction of aqueous solutions obtained from the prepared anionic-nonionic surfactants was analyzed to examine their potential efficiencies. As a primary indication of the surface-active properties, experimental determination of their surface tension versus concentration proved that they were able to reduce surface tension of water (72.8 mN/m) and undergo micellization in aqueous media, which are typical phenomena of surfactant molecular structure. In this context, the results of the surface tension at CMC (Υ_{CMC}) which is an important measure of the effectiveness of a surfactant to lower surface tension of the solvent and the lowest value that a surfactant solvent system is reached, is represented in **table 2**. All nine amphiphilic compounds of this study showed values of Υ_{CMC} of about the same magnitude with slight variations. Compound **6** (6-*O*-hexadecanoyl glucose-1- methyl carboxylate) is the most effective surfactant (Υ_{CMC} = 35.0 mN/m) whereas compound **1** has the highest Υ_{CMC} value (40.0 mN/m) being the less effective candidate of this carboxylated sugar fatty acid esters compared with the commercial anionic surfactant (SDS) which has lower magnitude of Υ_{CMC} (33mN/m). Therefore, in this respect, it can be concluded that the most efficient and interesting surfactants bearing carboxylic groups are compounds **4,5** and **6.** Further, the surface-active performance, as judged by hydrophilic-lipophilic balance (HLB) data, indicates that all nine tested compounds of this study are considered hydrophilic amphiphiles since their estimated HLB values ranged between 8.65 to 15.65 and their apparent water solubilities match their HLB prophiles. Hydrophile- lipophile balance (HLB) is considered as a traditional expression for hydrophilicity of a surfactant, in which the higher HLB (above 11) being the more soluble the surfactant and the lower one being below 9.It determines the relation between the surfactants hydrophilic and lipophilic characteristics [51].

For instance, glucose-derived compounds have lower values (9.48,10.43 and 8.65) for compounds (**3,6** and **7**), respectively compared with those of sucrose and maltose congeners (**1,2,4,5,8,9**) with greater estimated HLB (12.80 - 15.65). The greater HLB values corresponding to higher hydrophilicity of these surfactants may be due to their higher free multi- hydroxyl groups present in this disaccharide head groups moiety. Consequently, carboxyl sugar ester surfactants with different HLB values would be suggested to have different emulsifying properties [52]. As shown in **table 4** since all the tested esters have HLB values ranging from (8.65-15.65) they all represent efficient emulsifiers of oil-water mixtures [53,54] and cleansing agents or detergents[55]. Unsurprisingly, the hydrophobic acyl side-chains incorporated into sugar mono-esters has a great effect on their water solubility. The minimum surfactant concentration required for molecules to form micelles, (critical micelle concentration, CMC) was determined graphically from the inflection appearing in the plots of surface tension vs logarithm concentration (fig.13,14). All synthesized compounds in this study, follow the typical graphics showing an abrupt change in slope at the intersection of the curves corresponding to the critical micelle concentration. This parameter has a useful practical importance because it indicates the concentration at which the surfactant affects solubilization of hydrophobic molecular substances in water [56], thus it is an important impact in drug delivery, pharmaceutical and cosmetic applications.

In general, the longer the acyl-chain of the surfactant, the lower will be the corresponding CMC [57–59]. Compound **1** has lower CMC value (7.51 x10^{-7} M/l) than the hexadecanoyl (C_{16}) candidate (3.93x10^{-6} M/l).

Further, the effectiveness of the surfactant to lower the surface tension (π_{CMC}) dictates that compounds with higher value indicates greater ability to adsorb at the interface than smaller π_{CMC}. In this regard, the calculated results (**table 2)**, clearly show that the tittle molecular structure has great ability to be adsorbed at air-water interface which may be arranged in the following sequence: **6**> **5** > **4** > **2** > **3**, **7** > **8** > **9** > **1.** Once again, **table 2** also presents the results of Pc_{20} which is an indication of the efficiency of adsorption at the interface. The greater the Pc_{20}, the more potent the surfactant molecular structure. The Pc_{20} values indicated that these anionic- nonionic type amphiphiles possess almost equivalent efficiencies (about 5.0) which is comparable with (5.1) for the anionic commercial surfactant (SDS) used as control, in this study. It is noteworthy that, introducing a carboxyl functionality into these sugar esters enhanced surface activity characteristics and furnished anionic-nonionic surfactants with greater hydrophilicity and lower CMC making these carboxylated amphiphiles especially attractive for varying industrial applications.

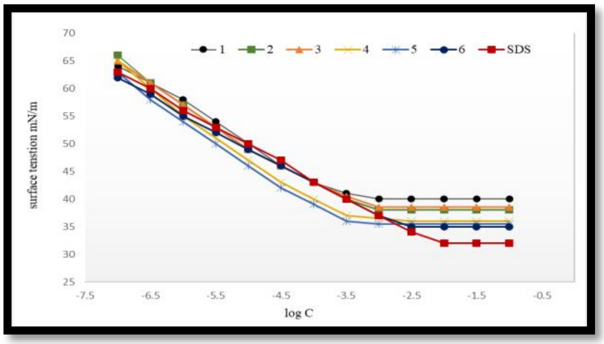


Fig.13. Surface tension (ϒ) Vs log c of 6-*O*- acyl sugar monomethyl carboxylic acid (**1-6).**

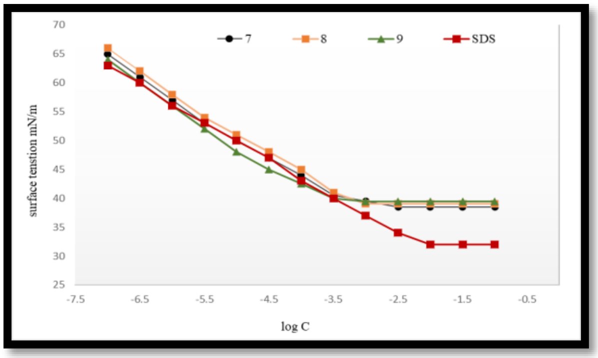


Fig.14. Surface tension (ϒ) Vs log c of 6-*O*- acyl sugar mono- (**7**) and di-carboxylic acid (**8,9).**

Table 2. Surface active parameters of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters aqueous solutions at 25 °C.

Surfactant		**CMC (M/l)**	**ϒCMC** (mN/m)	**π CMC** (m.N/m)	**Pc20**	**Γ max** (µ mol/m ^{2})	**Amin** (nm^2)
Monomethyl carboxy-	**1**	7.51x10^{-7}	40	32	5.2	1.61	0.103
	2	4.23x10^{-6}	38	34	5.25	1.79	0.93
	3	6.27x10^{-6}	38.5	33.5	5.3	1.75	0.95
	4	3.93x10^{-6}	36	36	4.95	1.43	1.16
	5	4.42x10^{-6}	35.5	36.5	4.8	1.61	1.03
	6	7.46 x10^{-6}	35	37	4.9	1.7	0.98
Mono- carboxy	**7**	6.37x10^{-6}	38.5	33.5	5.35	1.75	0.95
Di- carboxy	**8**	7.03x10^{-6}	39	33	5.15	1.7	0.98
	9	4.86x10^{-6}	39.5	32.5	5.30	1.66	1.10
	SDS	4.67 x10^{-3}	33	39	5.1	2.02	0.82

S.D.S: Sodium dodecyl sulfate

Foaming properties:

Next to wetting and emulsification, foaming is another important function of an aqueous surfactant solutions. Figures 15,16 show plots of the foam heights at zero (initial), 5 min. and 30 min. The results suggest that the tittle carboxyl sugar ester derivatives have significantly considerable foaming ability which could be due to the influence of the hydroxyl groups of the sugar moieties and the carboxylate head group. It is also noteworthy that the foam heights did not change much on standing from 0 to 30 minutes which indicate the distinct stability of foam created by this molecular structure.

Aerated texture of food products is present in bread, cakes as well as varying food products, enable these materials to acquire special features which make food products readily acceptable. The introduction of air bubbles in food makes generation and stabilization of foam a useful way in some commercial food manufacture.

From the analysis of the CMC and the surface tension at CMC (ϒ$_{CMC}$), it may be expected that these new anionic- nonionic carboxyl sugar esters are able to produce foam, since a low surface tension at cmc would be capable to favor foam formation [60].

Foaming of these newly synthesized esters produce moderate to high foam, although with heights slightly less than that of sodium dodecyl sulphate (SDS). The figures revealed that a modest positive correlation between foamability as measured by foam formation and surfactant concentration. Foam creation and foam stability, as indicated by the time of persistence of foam height are conceivable that they arise through a variety of factors such as adsorption ability of the surfactant at air/ water interface and the rate of diffusion of gas captured in the foam [61].The lowest value of surface tension (ϒcm) that the surfactant system can reach is an important indication of the effectiveness of the compound to lower the surface tension and gives a measure of its foaming capability (**table** auxiliaries in modern textile scouring and technological **2**), since reduction of surface tension facilitates foam formation [62,63]. The estimated values of the ϒ$_{cmc}$ of these novel esters were quite homogenous (between 35 and 40.0 mN/m) in pure water. Furthermore, Pc$_{20}$ is another way to predict foaming ability, for instance, the more efficient surfactant and the better foamability correlate with greater Pc$_{20}$. All candidates synthesized in this study had Pc$_{20}$ values amounting to approximately 5.0 which are nearly equivalent to that of the anionic control surfactant (SDS: 5.1). The comparatively lower foaming property in some candidates relative to SDS may be due to the occurrence of multi- hydrophilic groups (multiple OH of the sugar head and the -COOH) which cause considerable increase in the area occupied per molecule, thus, producing less cohesive forces at the surface[64,65].

Generally, the foam produced by this type of carboxyl sugar esters are considerably stable as there is only a slight decrease in height over 30 minutes of standing. Foamability of this anionic-nonionic sugar esters may be arranged as: **1> 8 > 4 > 9 > 5 > 2 > 7 > 3 > 6** showing 165mm > 164 > 148 > 138 > 126 > 115 > 78 > 77 > 72 mm height, respectively, compared with 180 mm for SDS.

Generally, the data support the suggestion that these carboxyl-sugar esters may function as efficient foaming products, which may present a great interest in various industrial applications including food, pharmaceutical, cosmetics, mineral flotation, oil exploitation and detergency [66–69]. It is noteworthy that, light-duty dishwashing and detergency consider foaming is an important characteristic, because consumers relate foaming to cleaning performance efficiency [70]. On the other hand, such relatively moderate foaming tendency of some candidates of this molecular structure may be an advantageous property required in some other applications such as dyeing

processes of the textile industry.

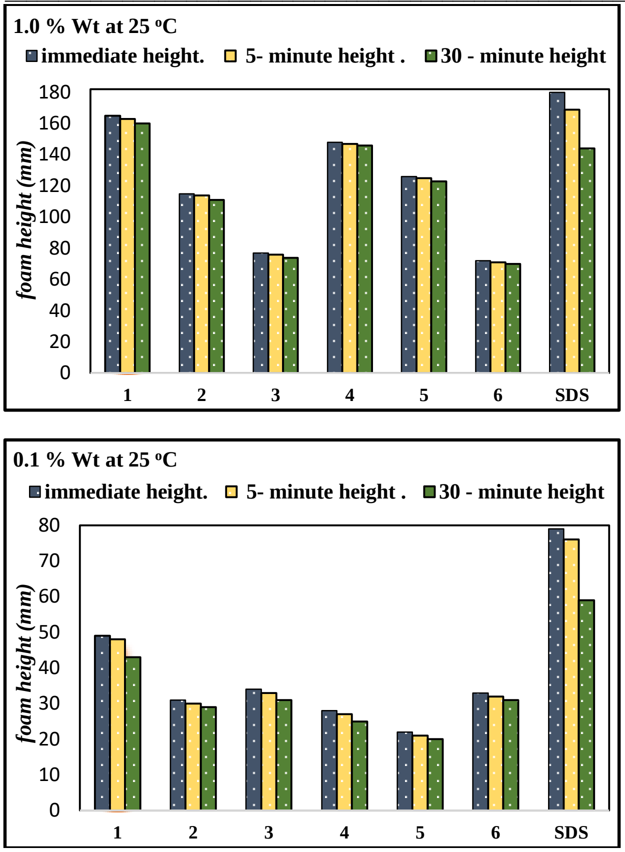


Fig.15. Foam properties of 6-*O*- acyl sugar monomethyl carboxylic acid (**1-6**) at concentrations (1.0 ,0.1 wt. %) at 25°C.

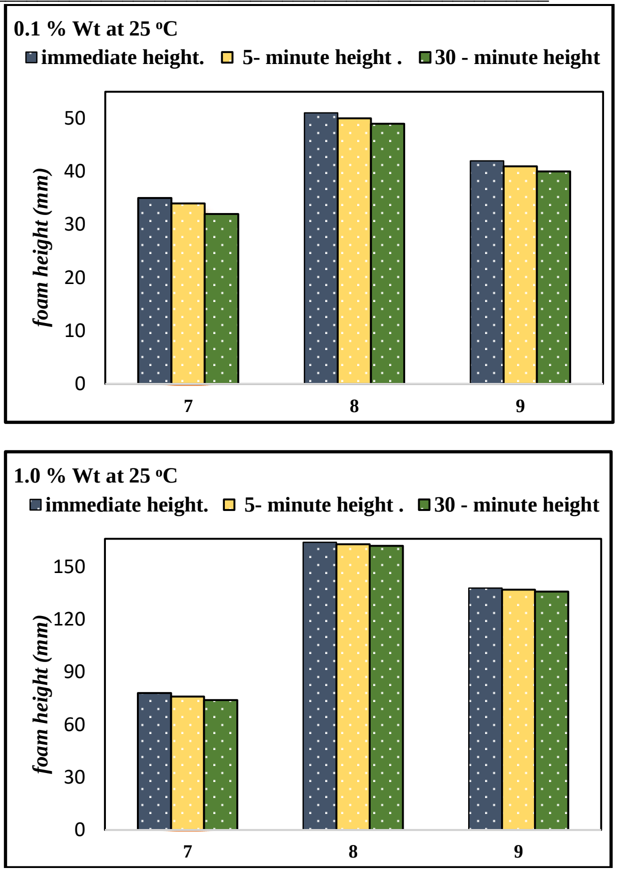


Fig.16. Foam properties of 6-*O*- acyl sugar mono- (**7**) and di-carboxylic acid (**8,9**) at concentrations (1.0 ,0.1 wt. %) at 25°C

Wetting Properties:

Wetting, together with foaming and emulsifying properties are the most important characteristics exhibited by most surfactants which are necessary functional phenomena in many operations and industrial processes. The greatest single applications for wetting function are manifested in the textile processing acting as assistants, in mercerization facilitating dyeing materials to be absorbed easily and evenly by the textile fabrics. Furthermore, they accelerate the uniform absorption action in other commercial textile finishing applications.[71,72].

Herein, wetting power is evaluated by the Draves- wetting test [73] of cotton skein for the tittle novel surfactants of the present study (**Table 3)**. The results indicated that all compounds display strongly efficient wetting capabilities even at dilute concentrations (0.1% and 0.01% w/w). This great ability is pointed by considerable efficiency to reduce the time necessary for wetting cotton skein in about 29-19 seconds at 0.1 % concentration and 25 ◦C compared with that of water (194 seconds) depending upon the molecular structure of these compounds, generally, wetting ability is enhanced parallel to the increase in concentration.

As expected, rewet time is attained in significantly shorter periods (12 seconds- 6 seconds) at 0.1%w/w solutions compared with rewetting of water (96 seconds). Wetting and rewetting properties follow the same trend and serve to confirm the results of the wetting tests. Obviously, because of the combination of structure influence wetting ability, introducing a - COOH group in the backbone molecular framework of the sugar acyl esters had a significant positive effect on enhancing wetting efficiency. For instance, wetting power increases with shorter chain length of the hydrophobic acyl substituent.

The results are consistent with the ability of this molecular structure to reduce the surface and interfacial tensions to a greater extent by members with shorter hydrophobic chain. The results of wetting properties of the tittle compounds are in agreement with the findings reported by Bistline et. al. [74] showing that wetting properties are mainly attributed to the hydrophobic part of the surfactant and not greatly improved by the structure of the head group.

It is noteworthy that wetting agents are useful in cleaners, cosmetics [75] and in hydrophobic soils which are needed to be treated with surfactants as conditioners to promote water infiltration with the purpose of stimulating growth. This treatment is done for overall improving performance of soils by increasing water absorption, with the net result of enhancing availability of fertilizer to growing plants and corresponding fertility.

Accordingly, Savage at al [32] developed a method depending upon drop penetration. The method is applied to offer additional information enabling the exploration of the capability in using these newly synthesized sugar esters in soil treatment and remediation. Besides, they found many applications in cleaning, cosmetic, textile and dyeing processes. In general, wetting ability, surface and interfacial tensions together with HLB are all closely related to molecular configuration of this particular structure.

Emulsifying capability:

An emulsion may be formed by mixing two or more liquids that are normally immiscible. Emulsion creation and stabilization of the resulting emulsion are usually achieved with the aid of amphiphilic molecules that act to reduce the surface tension and the electrostatic repulsion of the formed emulsion droplet [76].The period in which the emulsion state remains stable is an index of stability and an indicator for evaluation of a new surfactant as emulsifier in food, cosmetic and pharmaceutical formulae where there is a need to avoid phase separation of the emulsions and a key issue associated with the development of new industrial emulsifiers [77]. As it is clear from the data presented in **Table 4** that all anionic-nonionic carboxyl-bearing sugar esters prepared during the course of this study possess distinct emulsifying properties with great stability as indicated by long persisting time of the generated emulsions.

In general, the anionic-nonionic surfactants bearing an octadecanoyl group possess relatively higher lipophilicity than those of hexadecanoyl derivatives which result in their greater solubility in oil and fats. For instance, candidates with longer hydrophobic chain length (**1,2,3**) embodying C_{18} hydrophobic acyl chain produce emulsions that remain stable for periods reaching about 11-14 weeks compared with compounds (**4,5,6**) which formed emulsions stable to only 7-8 weeks, and those of SDS 50 days [78]**.** Again, introducing an additional carboxyl group enhanced the shelf-life stability period of the emulsions. The carboxylate moiety at the head of the molecular structure of these surfactants serve as a hydrophilic functionality and together with OH groups constituting the sugar part, they contribute to molecular structure having strong emulsifying properties.

Thus, the present data offer an aid for proper application of the synthesized surfactants as emulsifiers of desirable stability for the particular purpose requiring emulsions possessing long shelf-life stability and avoiding phase separation. Accordingly, the new surfactants of the present study are believed to offer potential applications in cosmetics, pharmaceuticals and food industries due to their effective stable emulsion stability.

Table 3. Wetting power (sec.) of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters.

surfactants	0.1 %		0.01 %		Peatmoss 0.1 %	
	Wetting (sec.)	Rewetting (sec).	Wetting (sec.)	Rewetting (sec.)	Wetting (sec.)	Rewetting (sec.)
Dis. H_2O	194	96			24 sec	
SDS	13	7	15	8	6	4
1	27	8	30	16	12	4
2	29	12	35	16	6	4
3	25	9	32	14	7	4
4	21	8	28	12	7	4
5	23	10	27	13	5	3
6	22	10	26	12	6	3
7	19	6	29	13	8	2
8	25	9	31	15	7	3
9	28	10	37	17	8	3

S.D.S: Sodium dodecyl sulfate.

Table 4. Emulsifying properties of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters.

Surfactants		Emulsifying properties																		HLB value
		Volume of remaining emulsion (ml) at different periods																		
		Minutes				Hour			Days						weeks					
		0	5	15	30	1	2	5	1	3	10	22	28	45	7	8	11	12	14	
Monomethyl carboxy-	**1**	5.5	5.5	5.5	5.5	5	5	5	5	5	4	4	3	3.5	3	2	2	Dis.		12.80
	2	6	6	6	6	6	6	6	6	5	4.5	4	3.5	2	2	2	Dis.			14.70
	3	6	6	6	6	5.5	5.5	5.5	5.5	5	4.5	4.5	4	4	3.5	3.5	3	2	Dis.	9.48
	4	6	6	6	6	6	6	6	5	4.5	3.5	2.5	2.5	1.5	Dis.					13.75
	5	5.5	5.5	5.5	5.5	5.5	5	5	4.5	3.5	3.5	3	2.5	2.5	Dis.					15.65
	6	5.5	5.5	5.5	5.5	5.5	5.5	5	5	4	3.5	2	2	1.5	1.5	Dis.				10.43
Mono-carboxy	**7**	6	6	5.5	5.5	5.5	5.5	5	5	4.5	4.5	4.5	4.5	4	3	2.5	Dis.			8.65
Di-carboxy	**8**	6	6	6	6	5.5	5.5	5.5	5.5	5	5	5	5	4	3.5	3	2.5	2	Dis.	14.55
	9	6	6	6	6	5.5	5.5	5.5	5.5	5.5	4.5	4	4	3.5	3	2.5	2.5	1.5	Dis.	14.55

S.D.S: Sodium dodecyl sulfate. **Dis.: disappearance**

Biodegradation:

Biodegradability determines the decomposition of organic compounds into environmentally friendly molecular structures through the action of naturally occurring bacteria and fungi thereby reinducing the produced degradation molecules into the environment as a means of ecological protection. In this article, the progress of biodegradation of the newly synthesized carboxylated sugar ester was followed by examination of surface tension versus time [79]. The results in **table 5** showed complete loss in surface activity attained within 5-6 days. The rate of biodegradation took similar periods for various members of these novel anionic-nonionic surfactants. The simplest pathway of this degradation is suggested to be an attack of microorganisms at the hydrophobic part causing shortening its length until the hydrocarbon chain is completely decomposed. In this respect, the extent of biodegradation agrees with the international suggestion of biodegradable materials in drain water [80].

Table 5. Biodegradability of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based ester.

Acyl radical	**Surfactants**		**Days**							
			1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
R. W			71	71	71	71	71	71	71	71
S.D. S			41	48	57	62	69	71	71	71
Octadecanoyl	Monomethyl carboxy-	**1**	46	51	55	59	63	70	70	70
		2	48	52	56	60	64	70.5	70.5	70.5
		3	46	50	55	63	69	70	70	70
Hexadecanoyl		**4**	43	50	57	62	69	69	69	69
		5	45	49	53	56	66	71	71	71
		6	47	51	55	59	65	70	70	70
Octadecanoyl	Mono carboxy-	**7**	46	51	55	62	67	70	70	70
	Di-carboxy	**8**	47	51	56	58	63	70.5	70.5	70.5
		9	48	52	57	64	70	70	70	70

S.D.S: Sodium dodecyl sulfate R.W: River water

Detergency evaluation:

Although the surface-activity of sugar esters have received great attention since their preparation on a practical scale [11,12,81], little work on anionic sugar-ester surfactants and their potentialities have appeared in the literature[8,9,82] .

An interesting goal of this study was to explore the detersive capabilities of novel anionic-nonionic carboxyl-bearing-derived sugar esters, when they can be made up to be involved into typical heavy household laundry detergents or as dish-washing cleaning. Accordingly, the following investigations were determined: detergency of soiled cloth, dishwashing detergency and the lime-soap dispersing power was also evaluated.

In this context, detergency, which is the largest application of surfactants involves varying phenomena that enable a detergent to exhibit cleaning properties. The process constitutes removal of liquid or solid soil from a surface of a substrate through desorption and solubilization of soils by means of surfactant allowing cleaning process to take place. This mechanism starts by adsorption of the surfactant at interfaces; therefore, the lowering of interfacial tension is an important parameter that favors removal of soil from the substrate.

In particular, removal of soil from textile fabrics is a complex interaction between surfactants, the particular soil and the textile surface. The soil present on fabric may vary widely, therefore different mechanisms will be responsible for removal of different types of soil components. Thus, particulate solid soil clay is removed by wetting and dispersion processes in which the surfactant is assisted by ionic functionality. On the other hand, oily soils are removed through emulsification between the oil and the surfactant solution, a process requiring a low interfacial tension which is finally solubilized or dispersed into the detergent solution [83]. Accordingly, wetting, emulsification and foaming are co-operating in cleansing functionality. Consequently, based on the data obtained in **tables 3, 4** for the surface- active performance, the anionic and nonionic functionalities in the present amphiphilic surfactants are suggested to have a great impact to display efficient detergent capabilities.

According to Davies method [25] the HLB values (8.65-15.65) of these amphiphiles indicate that they possess good solubility in aqueous solutions as well as sustainable detergent and cleansing functionalities. Detergency results of the various surfactants are in parallel to those of surface and interfacial tension reduction and in general, the relation between detergency and interfacial reduction is well known [84] and is compatible with this study.

Soil cloth detergency:

As shown in **table 6**, the soil cloth removal efficiency of the nine (**1-9**) amphiphilic compounds showed obviously excellent detersive power (about 82.36%) as judged by comparing soil removing data with those of the favored well known commercial anionic surfactants; sodium dodecyl sulfate, SDS (94.12%).

It is clear that within these compounds, those of C_{18} -monomethyl carboxyl candidates **(1,2,3)** gave generally better (80%) soil-removal than those of the shorter hexadecanoyl (C_{16}) derivatives **(4,5,6)**. The distinct cloth removal detersive power of this molecular structure is suggested to be due to the combination effect of both the anionic carboxyl head group together with the multi-hydroxylic functionality of the sugar moieties. The negative charge of the carboxylate anion is responsible to their active characteristics since it enables the solubilization of oil and grease in aqueous solution especially in detergency [85–87] .

The data are compatible with the surface-tension lowering effect (7.51x10^{-7}), foamability about (150-160 mm height), excellent rapid wetting (29-19 seconds) as well as emulsifying capability, which all form co-operative parameters in the detersive process.

Dish washing detergency properties:

In evaluation of detergency, foamability and foam volume are important characteristics of detergency, especially dishwashing, because greater foam heights being more favored for consumptions that treat foaming and cleaning efficiency as closely related properties [88,89].

Additionally, the data demonstrate that the synthesized surfactive compounds may act as superior dishwashing agents since the exploratory dishwashing experiments for soil removal attained values reaching 95.14% to 96.35%, compared with those of the anionic (SDS) surfactant 97.39%. The data also showed that there is no significant difference among the nine surfactants under study with regard to soil removal efficiencies.

These results may be summarized by consideration that the anionic-nonionic carboxyl sugar ester derivatives may provide outstanding soil-removal performance mostly equal to some conventional anionic surfactants such as sodium dodecyl sulfate (SDS).

Lime-soap Dispersing power:

The lime-soap dispersing efficiency can be determined by the ability of surfactants to prevent formation of visible clots of lime-soap in a solution containing calcium ions. This is estimated by the lowest percentage of surfactant which prevents clotting or precipitation of lime-soap. Thus, the lower the value of this experiment, the greater will be the lime-soap dispersion power of the given surfactant. In this respect, the data in **table 7** showed values ranging from 60-70% which are much superior relative to the anionic SDS surfactant (89.5%). The relative rating of mono-carboxyl and di-carboxyl sugar ester derivatives of this study (**7,8,9**) suggest that these surfactants have a significant priority to be easier involved into solid detergent formulations.

The tests which were used for lime-soap dispersion may be developed to be translated directly into practical performance under particular conditions. It is noteworthy that, the actual proportion of these modified carboxyl sugar ester surfactants that is required to be added in the formula of a soap- bar or soap powder to prevent hard water coagulation is probably greater than the amounts indicated in the test above. The relative ratings of this series of surfactants, however is reliable, nonirritant and more ecofriendly to be incorporated into detergent applications.

Table 6. Detergency evaluation (Soil cloth detergency % and Dish washing%) of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters.

Surfactants		*Soil cloth detergency %*	*Dish washing %*
Monomethyl carboxy-	**1**	82.36	96.28
	2	79.41	95.92
	3	81.18	95.21
	4	76.47	94.99
	5	75.29	95.74
	6	70.00	95.07
Mono-carboxy	**7**	70.59	95.14
Di-carboxy	**8**	76.47	96.35
	9	81.76	95.57
	SDS	94.12	97.39

S.D. S: sodium dodecyl sulfate

Table 7. lime soap dispersion of 6-*O*- acyl sugar monomethyl carboxylic acid (1-6), 6-*O*- acyl sugar mono- (7) and di-carboxylic acid (8,9) sugar-based esters.

Acyl radical	**Sugar**	**Surfactants**		*lime soap dispersion %*
Octadecenoyl	**Sucrose**	Monomethyl carboxy-	**1**	68.00
	Maltose		**2**	70.00
	Glucose		**3**	75.00
Hexadecanoyl	**Sucrose**		**4**	69.00
	Maltose		**5**	71.00
	Glucose		**6**	76.00
Octadecenoyl	**Glucose**	Mono-carboxy	**7**	67.00
	Sucrose	Di-carboxy	**8**	60.00
	Maltose		**9**	63.00
			SDS	89.50

S.D. S: sodium dodecyl sulfate

Chelation: Calcium and magnesium tolerance:

Some carbohydrate derivatives having carboxylic residues obtained by oxidation of sugar substrates have extracted constant attention [21,90], and are among the numerous possible chemical transformation of sugars due to their cationic sequestering properties and their potential industrial applications in detergency, cosmetics and medicinal uses.

One of the most useful sugar-based derivatives, gluconic acid containing a carboxylic group has found extensive application as sequestering compound in the dairy, brewing detergent and textile industries. In the medical field it has found significant use for introducing calcium, iron and other metals as well as hydrophobic insoluble drugs and dietary supplements to persons deficient in these highly important nutritional materials.

In particular, the surface activity of the surfactants is significantly inhibited due to interference of the metal ions present in hard water. Consequently, some compounds must be used to prevent this address in industrial applications of surfactants. The detergent substances in house- hold cleansing agents are usually anionic due to their sensitivity to Ca^{+2} and Mg^{+2} species [91]. On the other hand, a nonionic surfactant, may increase the hardness tolerance of anionic amphiphiles thereby enhancing their water solubility [92,93]. Consequently, house- hold detergency generally uses formulations of mixed anionic and nonionic surfactant species.

Therefore, new surfactants, namely self-sequestering compounds were developed recently for this purpose[3,94]. Some carbohydrate derivatives are able to form chelate compounds with metal cations by their hydroxylate groups [95]. However, because fatty acyl sugar esters have not enough efficiency in chelating cation, in this study, additional complexing carboxyl functionality was added after the oxidation of C_6 of the sugar moiety or coupling of mono chloroacetate within the structure of traditional sugar esters to furnish anionic- nonionic amphiphiles. These novel development in chemical composition of substance may have utility in sequestering metal ions, particularly calcium and magnesium in addition to surface-active performance.

Accordingly, the self-sequestering properties of the anionic -nonionic amphiphilic compounds were evaluated via the determination of calcium and magnesium tolerance potency as if they were to be used in hard water detergency. The choice of chelating agent depends to a great extent upon the conditions under which it is applied, for example, the EDTA family is effective in acid, neutral or alkaline media [96]. Batch chelation experiments were performed and three factors were explored for their influence on the chelation of Ca^{+2} and Mg^{+2}, the chelating agent, the effect of pH, the contact reaction time and the temperature.

The effect of pH of the solution has a significant impact on the uptake of the metal ions. The results showed that the maximum tolerance of the surfactants was observed at alkaline pH values (12.5-13.5). Further, the contact time had a significant positive influence on the chelation of the metals. The data in **table 9** represent the effect of contact time on tolerance capabilities which showed that the tolerance of chelating Ca^{+2} and Mg^{+2} ions increase with time of contact until a maximum of 40 minutes.

The data showed that all members of these novel surface-active materials obviously possess autonomous sequestering capability in addition to their unique surfactant performance and detergency characteristics.

As expected, the chelation ability is attributed to the multi-hydroxylic groups present in the sugar moiety in combination with the carboxyl functionality. The carbohydrate head bears multiple hydroxyl groups having defined orientation allowing formation of cooperative hydrogen bonds between the surfactant molecules as well as with other functionality of varying substances including dyes, organic compounds, as well as metals.

Preliminary examination of chelation tolerance showed that the highest concentrations of $CaCl_2$ that can be tolerated by the test surfactants before their solution becomes turbid were 10.0,12.5 and 8.0 ml for the monomethyl carboxyl derivatives **(1,4,5),** respectively and 9.0 ,8.0 ml for di-carboxyl compounds (**8,9),** compared with those of EDTA (7ml). On the other hand, these surfactants showed greater tolerance to Mg^{+2} ions as shown by compounds **1,2,3,4, 5** and **6 (**16.5, 17, 18, 17.5, 16 and 16ml) respectively, compared with those of EDTA (12 ml) (**table 8**).

Furthermore, increasing the contact time increases the Ca^{+2} tolerance of the surfactants. Also, the temperature was found to enhance Ca^{+2} and Mg^{+2} tolerance up to 40 ◦C (**table 9**).

Consequently, the addition of a carboxyl function in the traditional sugar ester may be an advantage in improving surface-active characteristics and probably creating sequestering functionality. However, the presence of an additional second carboxyl group afforded no significant benefits over the mono carboxylated derivatives with respect to their metal tolerance potentiality. The mechanism of sequestering suggests that the lipophilic tail of the surfactant dictates the transfer from the solution to the interface between solid and liquid; however, the polar head groups bearing substituents rich with electrons interact with active centers especially cations enabling chelation resulting in their solubilization or precipitation. It is noteworthy that, when the chelating ability is paired with surface activity, a chelating surfactant is created, surfactants should result in good detergency even in hard water, i.e. they should be able to chelate metals avoiding precipitation, and there for more ecologically accepted.

Accordingly, all these new anionic-nonionic surfactants are made from renewable materials and biodegradable which suggest that they can found considerable potential commercial value [97].

Antimicrobial effectiveness:

Several investigations have studied the antibacterial action of carbohydrate ester derivatives, a phenomenon that can be utilized to maintain nutritional substances [98]. The present study assessed the correlation between the structure and antimicrobial effectiveness. The inhibitory effect of sugar esters is dependent on the esterification level (e.g., the length of aliphatic chain) and the nature of the carbohydrate [99]. Accordingly, the inhibition zone diameter was measured following the agar well diffusion procedure (**Table 11**), and the minimum inhibitory concentrations (MIC) were examined through the broth dilution procedure (**Table 12**) for various carboxyl- sugar esters. These tests were conducted using pathogenic Gram-positive and negative bacteria, in addition to two fungi compared against *Penicillin G* and *Ciprofloxacin* as standard organisms, respectively, and *ketoconazole* as antifungal compound. The data obtained (**Table 11**) indicate that all tested organisms are susceptible to all compound examined in this study to different extent. The tested carboxylated sugar esters inhibited microorganism by inhibition zone attaining from 10.00 ± 0.00 to 23.67 ± 1.53 mm and 6.67 ± 0.58 to 18.33 ± 1.53 mm for fungi, respectively, which prove their antimicrobial activity [100]. Compound **7**exhibted the strongest inhibition of *Gram +ve B. cereus* where the inhibition zone reached 21.00 ± 1.00 mm compared with 25.00 ± 0.10 for *Penicillin G*. Further, *Staph. aureus* was specially affected by **2, 7** and **9** whereas, *E. coli* and *E. cloacae* were significantly inhibited by all tested esters. In general, all tested carboxyl compound shows MIC between 3.91 - 62.5 µg/ml. The variability of the inhibitory effect found in this study is in agreement with previous work [101,102]. The antibacterial inhibition effect is usually referred to disruption of microbial cell membranes [103].

Table 8. Preliminary examination of chelation ability of Ca^{++} and Mg^{++} hardness for anionic- nonionic novel sugar-based surfactants (1-9):

Surfactants	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**EDTA**
Metals	Monomethyl carboxy						Mono- carboxy	Di- carboxy		
Vol. of (0.1M) metal complexed										
Ca^{++}	**10**	**7**	**6**	**12.5**	**8**	**6**	**6**	**9**	**8**	**7**
Mg^{++}	**16.5**	**17**	**18**	**17.5**	**16**	**16**	**9.5**	**13.5**	**17.5**	**12**

Table 9. Effect of pH, time and temperature on tolerance capacity of Ca^{++} and Mg^{++} hardness for anionic- nonionic novel sugar-based surfactant (1-9):

a- Effect of pH on tolerance capacity of compounds (1-9) for hardness of water

Metals	**pH**	**Surfactants**									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**EDTA**
Ca^{++}	***pH=11***	7.5	4	3.5	4.5	3.5	2.5	3	4	3	2
	pH=12	8.5	5.5	4.5	8	6.5	5	4	6	5.5	4
	pH=14	10	7	6	12.5	8	6	6	9	8	7
Mg^{++}	***pH=11***	6	4	4	6.5	4	4	4	4.5	3.5	3
	pH=12	11	6	7	9	8	7.5	7	6.5	11	6
	pH=14	16.5	17	18	17.5	16	16	9. 5	13.5	19.5	12

b- Effect of time on tolerance capacity of compounds (1-9) for hardness of water

Metals	**Time(min.)**	**Surfactants**									
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**EDTA**
Ca^{++}	**Zero**	10	7	6	12.5	8	6	6	9	8	7
	5	12	8	7	13.5	9	7	8	10	9	8
	10	13	9	9	15.5	10	8	10	12	11	9.5
	20	13.5	10	11	16.5	11	10	12.5	14	13	11
	40	-	-	-	17	12	-	-	-	-	11.5
Mg^{++}	**Zero**	16.5	17	18	17.5	16	16	13.5	9.5	17.5	12
	5	17.5	17.5	18.5	18.5	17	17	14.5	10.5	18.5	12.5
	10	18	18	19.5	19.5	18	18.5	16	12.5	19.5	13.5
	20	-	19	21	21	18.5	20	17	15	-	15
	40	-	-	23	23	19	20.5	-	17	-	15.5

c- Effect of temperature on tolerance capacity of compounds (1-9) for hardness of water

	Temperature ◦C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**EDTA**
Ca^{++}	**25 ◦C**	13.5	10	11	17	12	10	12.5	14	13	11.5
	40 ◦C	16	13	16.5	19	15.5	16	17	15.5	14.5	14
Mg^{++}	**25 ◦C**	18	19	23	23	19	20.5	17	17	19.5	15.5
	40 ◦C	18.5	21.5	27	24.5	22	26.5	20	21	21.5	18

Table 10. Tolerance capacity of Ca^{++} and Mg^{++} hardness for anionic- nonionic sugar-based surfactant (1-9), *at PH=1, (20-40) min. and 40* ◦C.

Surfactants	1	2	3	4	5	6	7	8	9	EDTA
	Monomethyl carboxy						**Mono- carboxy**	**Di- carboxy**		
Ca^{++}	16	13	16.5	19	15.5	16	17	15.5	14.5	14
Mg^{++}	18.5	21.5	27	24.5	22	26.5	20	21	21.5	18

Table 11. Inhibition zone diameter (mm) of mono-(1-3,7), and dicarboxylic compounds (8,9) *against* some selected bacteria and fungi.

Surfactants	**Gram (+) Bacteria**		**Gram (-) Bacteria**		**Fungi**	
	B. cereus	***Staph. aureus***	***E. coli***	***E. cloacae***	***S. cerevisiae***	***C. albicans***
Inhibition Zone diameter (mm)						
1	16.33 ±1.15	9.33 ± 1.53	16.67 ± 0.58	11.33± 1.16	8.0 ± 0.00	6.67 ± 0.58
2	16.67 ±2.31	14.67 ± 2.52	19.67 ±0.58	12.33 ± 1.16	12.0 ± 1.73	10.0 ± 0.00
3	14.0 ± 0.00	10.0 ± 0.00	16.0 ± 0.00	18.0 ± 1.73	12.33± 0.58	15.0 ± 0.00
7	21.0 ± 1.00	17.67 ± 1.53	23.67 ± 1.53	20.0 ± 1.16	15.0 ± 2.00	18.33 ± 1.53
8	13.33 ± 1.53	10.0 ± 0.00	18.0 ± 0.00	16.33 ± 1.16	10.33 ± 1.53	10.67 ± 0.58
9	11.0 ±1.00	13.0 ± 0.00	13.33 ± 2.08	17.0 ± 1.73	8.0 ± 1.73	13.33 ± 1.16
Penicillin G	25.0 ±0.10	24.0 ± 0.00	-	-	-	-
Ciprofloxacin	-	-	29.0 ± 0.00	23.0 ± 0.00	-	-
Ketoconazole	-	-	-	-	22.0 ± 0.10	23.0 ± 0.00

Value = mean ±SD, *n*=3

Table 12. Minimum inhibitory concentrations (MIC, in µg/ml) of mono-(1-3,7) and dicarboxylic compounds (8,9) against some selected bacteria and fungi. a: Gram-positive pathogens; b: Gram-negative pathogens; c : Fungi

MIC (µg/ml)						
Surfactants	***B. cereus*** [a]	***Staph. aureus*** [a] ***(ATCC25923)***	***E. coli*** [b] ***ATCC-25955***	***E. cloacae*** [b] ***ATCC-23355***	***S. cerevisiae*** [c] ***ATCC- 9763***	***C. albicans*** [c] ***ATCC-10231***
1	31.3	62.5	31.3	62.5	125	62.5
2	31.3	125	7.81	15.6	62.5	125
3	62.5	62.5	15.6	31.3	62.5	125
7	7.81	31.3	3.91	15.6	31.3	15.6
8	15.6	125	15.6	31.3	250	125
9	62.5	62.5	31.3	31.3	125	31.3

Conclusions

Surfactant molecules that adhere to interface (e.g. water -oil, solid -liquid or gas, liquid -gas) and lower their surface energy have numerous applications in every day human lives including foods, cosmetics, pharmaceuticals, medicines, cleaners, textile processing and other auxiliaries. There surface functionality is due to their peculiar molecules structure consisting of separated lipophilic and hydrophilic domains. The present work relates to a novel composition of chemical structure in a homologous series of amphiphilic molecules consisting of water-soluble anionic-nonionic sugar-based surfactants bearing a lipids fatty acyl hydrophobic chain merged to a primary hydroxyl group in various sugars (sucrose, maltose and glucose) to form nonionic molecule. These were modified by incorporating an additional anionic chemical function (carboxyl or methyl carboxylic group) into a hydroxylic functionality of the sugar part to furnish anionic- nonionic molecular surfactant configuration. In particular, 6-*O*-octadecanoyl or hexadecanoyl chain constituting the lipophilic tail while the sugar back bone with the additional carboxyl functionality at the end of sugar act as the head moiety of this amphiphilic structure. These anionic-nonionic compounds were synthesized using successful operational simple and high-yielding procedure. The molecular structure of these anionic-nonionic amphiphiles is characterized by possessing a hydrophilic anionic carboxylic functionality at the end of the sugar molecule besides nonionic hydroxyl groups in the sugar moiety bearing a lipophilic acyl-side chain substituent. Accordingly, this unique molecular structure enabled to display both anionic and non-ionic properties [104-106].

Thus, all candidates of this study were found to exhibit distinct surface activities including their excellent capability of surface tension lowering effect, and considerably low CMC nearly close to (SDS). Also, foamability and stability of foam which are important phenomena particularly in light duty detergency were nearly in parallel to SDS. More significantly the carboxyl-modified sugar esters have excellent emulsifying efficiency compared to some traditional commercial surfactants. In addition, rapid wetting efficiency in another major important advantage of these molecular structure. Furthermore, besides remarkable surface-active properties they possess good detersive power, especially soil cloth cleansing, dish washing in addition to potential lime-soap dispersing power. In this context the carboxylic acid functionality showed enhanced detergency and sequestering properties, in accordance with the literature as most of the calcium chelators are carboxylic acid-containing product. It is noteworthy that, the structure of the title surfactants was built in accordance with its ability to form complexes with metal cations as well as for environmental and economic considerations. Thus, all the tested compounds synthesized in this study were used from the cheapest available sugars (sucrose, maltose and glucose).

Furthermore, because the sugars are not sufficient enough as complexing agent, an additional complexing COOH functionality was added to develop the structure of sugar ester configuration. Accordingly, batch experiments on the tolerance capabilities of the tittle compounds to chelate Ca^{+2} and Mg^{+2} metal ions indicated this molecular structure to possess an additional potent sequestering functionality and may be helpful in hard water detergency process. Besides good surfactants, including foaming, wetting and emulsifying properties, they possess autonomous sequestering ability.

The results obviously indicate that this amphiphilic molecular structure can be considered as excellent potential substitutes of petroleum- based products in cosmetic detergency, medicine and many other fields. Additionally, the study of biodegradability proved that the synthesized compound are normally biodegradable and consequently considered ecofriendly useful products.

On the other hand, these compounds were obviously capable to inhibit the growth of certain pathogenic Gram +Ve and Gram -Ve as well as fungi especially Gram +Ve microorganism. The structure prosperity profile evaluated through this work, together with the continued efforts to a chive new application for these novel sugar ester derivatives should help to expand the utility of such compounds of multipurpose applications including detergency medicinal, nutritional and soil remediation fields. Therefore, these results combine with other important knowledge of sugar-based surfactants and are sustainable to continue the development of this particular type of promising amphiphilic structures for future work.

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