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A Reliable Solvent-Free Transesterification Synthesis of Carbohydrate Fatty Acid esters: Optimization, Structure -Surface Activity Relationships and Antimicrobial Efficacy

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Abstract

A simple straight forward efficient method for the synthesis of sugar esters involving the transesterification of a sugar and fatty acid methyl ester is presented through a solvent -free alkali catalyzed procedure.

The influence of reaction temperature, reaction time, catalyst and molar ratio of the reactants were first screened to ensure the optimum conditions. After realizing the most suitable reaction media which achieve maximum conversion and yields, maltose, sucrose, and glucose fatty acid esters with acyl chains having 12 to 18 carbon atoms were chemically synthesized by following the base-catalyzed solvent- free transesterification of the sugar component and the methyl ester of the different fatty acids. In this study, the reaction afforded a total sugar ester (SE) yield over 88% with methyl fatty acid ester conversion of about 90% in most cases, by using K_2CO_3 catalyst under nearly ambient temperatures (40-50 ^oC) after a relatively short time (3 - 3.5 hrs.). The products were characterized by nuclear magnetic resonance (^1H NMR) and Fourier transform infrared (FTIR) spectroscopy. All the synthesized esters showed good solubility and distinct surface-active properties which depend on the balance between the length of the acyl chain and the hydrophilic head group (sugar the hydrophile-lipophile balance, HLB). The physicochemical characteristics were evaluated: surface tension values ranged from 38 to 44 mN/m, compared with 38.8 mN/m for sodium dodecyl sulfate (SDS). The critical micelle concentration (CMC) values were in the range $2.8x10^{-4}$ to 5.0×10^{-6} M/L. The longest the fatty acyl chain displayed the lowest CMC value. The variation of the molecular structure of the title compounds is reflected on certain of their important unique performance characteristics such as foamability, emulsifying and wetting potentialities, Moreover, the detergency capabilities were assessed in terms of their tendency of grease removal from wool substrates. Additionally, these esters also clearly display antimicrobial function against Gram-positive and Gram-negative bacteria as well as some fungi. Together, these findings imply that the synthesized esters from this work may be useful as foamers and emulsifiers as well as preservatives in dietary and other foods in the food and cosmetic industries.

***Key words*:** Sugar esters, Foaming properties, Antimicrobial activity, Interfacial properties, Sucrose stearate.

1.Introduction

Sugar esters are a fascinating set of chemicals that make up a significant class of sugar-based non-ionic surfactants [1–3]. They are made by combining a fatty acyl group produced from oleochemicals (fatty acids found in oils and fats) with a sugar's hydroxyl group.

Until now, both academic research and industry have mostly concentrated on glucose and sucrose-based surfactants as alternatives to petroleum-based surfactants [4–7]. Besides glucose, sucrose is the most abundant carbohydrate produced on a global basis, with 180 million metric tons generated in 2016/1017 [8]. It is therefore an important and desirable feedstock for sugar ester synthesis. Although food consumption accounts for the majority of demand, it is also useful as a raw material in the manufacture of emulsifying agents, detergents, and other derivatives [9]. Sugar ester surfactants have attracted the interest due to the fact that they can be created from fully renewable resources, affordable, from widely available raw materials, implying that they are environmentally friendly, compatible, non-toxic and completely biodegradable as well [10–14].

Consequently, this carbohydrate, has become a vital commodity chemical, particularly in the food,[15–18] nutraceutical, cosmetics, dental, and pharmaceutical industries, as well as other essential applications [19–26]. Sucrose esters in particular containing fatty acyl residues can be used as extremely effective nonionic surfactants and emulsifiers [27] , low-calorie food additives [28], and as drug delivery vehicles [29]. They can also, be used to make flavor oil emulsions in the aqueous phase to improve the taste of foods and beverages [30]. Furthermore, since these esters have good foaming ability, they can impart pleasant textures and mouth feel to food products [31,32], as well as whipping properties [28,33].

Many laboratories and industrial-based techniques aimed at the synthesis of carbohydrate esters have arisen in the intervening periods as a result of this extended field of applications. In general, there are two ways to make sugar esters: a) direct esterification of

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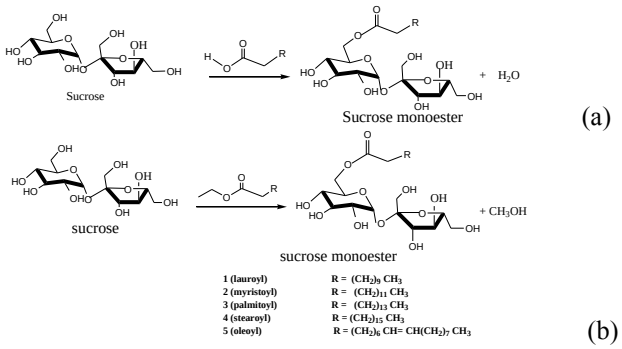
sucrose with fatty acyl components [14,23,34–36] and transesterification of sugar with methyl or ethyl esters of the fatty acid.

$C_n (H_2O)_n + RCOOH \rightleftharpoons C_n (H_2O)_{n-1}OCOR + H_2O$ (a)

$C_n (H_2O)_n + RCOOR' \rightleftharpoons C_n (H2O)_{n-1}OCOR + R'OH$ (b)



Several investigations have been published that try to synthesize sugar esters by direct interaction of fatty acid with sucrose [36–38]. In contrast to conventional polyols, sucrose decomposes near its melting point (186^0C) and undergoes glycoside bond cleavage, resulting in a combination of glucose and fructose [21]. To avoid overheating, various reaction procedures have been created, and numerous investigations have been dedicated towards the preference of synthesis of these esters via the interaction of sugar with anhydrides or fatty acid chlorides. As a result, acid chlorides were used to replace fatty acids [39]. However, it can't be utilized to make food additives because of its toxicity [40]. Despite the fact that some synthesis methods are straightforward, one of the most difficult aspects of sucrose esters creation is overcoming reactant incompatibility, as sucrose is a highly polar solid and fatty acids are non-polar.

To improve compatibility, articles have emphasized the benefits of using dimethyl sulfoxide DMSO or dimethyl formamide DMF as solvent in the transesterification of sucrose and methyl or ethyl esters of fatty acids [41,42]. , However, DMSO and DMF are hazardous solvents, and their residues make meeting conventional food, medicine, and cosmetic laws challenging. However, challenges persist since removing the high boiling solvents (153 ^{0}C for DMF and 189^0C for DMSO) is a difficult task.

Different techniques have been examined in recent years [5,43,44]. In this direction, a solvent-free transesterification of sugar and methyl ester was thought to be a reliable approach for synthesis of sucrose esters [10]. Other efforts have centered on enzymatic techniques, which have been proposed to be more favorable due to their simplicity and because they use less solvent, less hazardous, and less energy[19,45–47].

As a result, some basic research appears to be necessary to improve sugar ester synthetic methods and address the limitations that have previously been identified in this area. The main goal of this research was to determine the feasibility of manufacturing sugar esters without use of solvents via a direct transesterification of the sugar component with fatty methyl esters.

The main purpose of this procedure was to explore the impact of reaction parameters such as temperature, catalyst, sucrose to fatty acyl mol ratio and the reaction duration, on the basis of single factor studies, in order to assure appropriate reaction media. Following that, a variety of sugar esters were made by transesterifying glucose, maltose, and sucrose with different members of homologous series of long-chain fatty acyl methyl esters with chain lengths having12,14,16, and 18 carbons. The extent of the reactants transformation into esters and the creation of monoesters were assessed.

Fourier transform infrared (FTIR) and nuclear magnetic resonance (^{1}HNMR) spectroscopy were used to establish the successful synthesis of the esters. The title surfactants physicochemical properties and adsorption behavior were also studied. The surface tension and related interfacial phenomena, such as the fundamental features of surfactants at interfaces, were determined in a systematic manner. Biodegradability and antibacterial efficacy against major human diseases were also tested against important human pathogens.

2.Experimental

2.1. Materials:

All chemicals were of pure analytical grade, the fatty acids (lauric, myristic, palmitic, stearic, and oleic acids) were from Aldrich, glucose and maltose from AL-Nasr Pharmaceutical Chemical Co, Egypt, sodium hydroxide, potassium carbonate, NaH_2PO_4, acetone, methyl alcohol, ethyl alcohol, ethyl acetate, chloroform, and hexane, were analytical grade chemicals.

2.2Methodology

2.2.1Synthesis of fatty acid methyl esters:

The methyl esters of different selected fatty acids were prepared by refluxing the fatty acid in an excess of dry methanol for about 2hr in the presence of CH_3ONa as catalyst.

2.2.2 Synthesis of sucrose stearate:

In a 250 ml three- neck round- bottomed flask, sucrose 6.87g (0.02mol), and 5.96g (0.02mol) methyl stearate were mixed using a Teflon-coated magnetic stirrer for ½ hour. The flask was slowly heated to the desired temperature under reflux, then 0.25g of K_2CO_3 was added and heating was continued until the end of the reaction.

Once the reaction was completed, the flask was left to cool to ambient temperature, n-hexane (about 20ml) was added and the mixture stirred vigorously. (The n-hexane took up the unreacted methyl esters and precipitated the catalyst). The reaction was left overnight, and the n-hexane layer was separated quantitively. The solid sugar ester was washed three times with 10 ml portions of hexane, and the combined hexane extracts are subjected to saponification and titrated against exactly

0.1N HCl to determine the unreacted methyl esters. The precipitated product is treated with mixture of cyclohexane and butanol and the sugar ester was crystalized from ethyl acetate.

2.3. Methods of analysis

The structure of the synthesized sugar esters was assessed by nuclear magnetic resonance (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopy.

2.3.1. Infrared absorption spectroscopy:

The absorption spectra of the prepared compounds were examined using Nicolet iS10 spectrophotometer, Germany. Simple inspection and reference to generalized charts of characteristic group frequencies were used to assign bands to the various groups [48].

2.3.2Nuclear magnetic resonance (NMR) spectroscopy.

The (^{1}H NMR) spectra were recorded using Brucker Instruments, Karlsruhe, Germany, Inova 400 mg.HZ.

2.3.3. Thin-layer chromatography:

TLC was performed on silica gel coated plates (20 x 10 cm) and developed in Toluene: ethyl acetate: ethanol (2:1:1v/v). The spots were visualized by spraying the plates with sulfuric acid and heating at 110 ^{0}C for ½ hr.

2.4. Surface Active properties of the synthesized sugar esters:

Du Nouy tensiometer was used to measure surface tension (ST) for freshly prepared surfactant solutions in concentrations ranging from 10^{-1} to 10^{-7} mol/l. The critical micelle concentration (CMC) and the surface tension at the CMC (γ *CMC*) were determined using the values obtained from the point of intersection of the surface tension vs concentration curves

2.4.1. Critical micelle concentration (CMC)

The critical micelle concentration is the concentration at which surfactant molecules start to form aggregates (micelles) [49,50].

2.4.2. Efficiency (P_{C20})

The efficiency (P_{C20}) is the concentration (mol/L) of the surfactant solution capable of suppressing the surface tension by 20 mN/m [51].

2.4. 3. Effectiveness (π_{CMC})

The surface tension (γ CMC) values were utilized to compute the surface pressure (effectiveness) values.:

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

Where

$\gamma_{\square}$: the surface tension of pure water at 25 degrees Celsius.

γ_{CMC} :The surface tension of the measured solution at CMC [51].

2.4. 4. Maximum surface excess (Γ_{max})

The maximum surface excess (Γ_{max}) is defined as the efficiency of adsorption at the interface and was determined using of Gibbs adsorption equation from the slope of the straight line in the surface tension plot (dγ/d log C) below CMC:

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

Where: Γ_{max} is the highest surfactant ion surface excess concentration, and n is the number of species at the air-water interface whose concentration changes as surfactant concentration changes:

The gas constant is R (8.314 J/ (mol. k^{-1}):

T: is the absolute temperature (K).

(dγ/d log C) is the slope of the vs. – log c plot at room temperature [52,53].

2.4.5. Minimum surface area per molecule (A_{min})

The average minimum surface area (A_{min}) occupied by each molecule adsorbed at the contact (in square angstrom) is provided by. $A_{min} = 1/ (N_A \Gamma_{max})$

Where NA is Avogadro's number [11].

2.4.6. Standard free energy of micellization (ΔG^o_{mic}) and adsorption (ΔG^o_{ads})

Gibbs adsorption equation was used to compute the standard free energy of micellization (G^o_{mic}) and the standard free energy of adsorption (G^0 ads). as follow.

ΔG^o_{mic} = n RT Ln CMC

$\Delta G^o_{ads} = \Delta G^o_{mic} - 6.023x\ 10^{-1} x\ \pi_{CMC} x\ A_{min}$

Where R is the gas constant, T is the absolute temperature of conventional surfactants (n=2), and CMC is the surfactant molarity.

2.5. Kraft point:

The kraft point was determined as the temperature at which a 1 % aqueous sample changes sharply to a clear solution on gradual heating. And it is a convenient measure of aqueous solubility [54].

2.6. Cloud point

The cloud point was determined by gradually heating a solution (1.0 % w/w) of the surfactant in a controlled temperature water bath. The temperature at which a clear or nearly clear solution becomes decidedly cloudy was recorded. Cooling the solutions until they become clear again verifies the temperature's repeatability [55].

2.7. Foaming properties:

Foaming was measured according to vigorous shaking of 25ml of sample solution (1wt%, 0.1wt%,0.01wt%,) in 100ml glass stoppered graduated cylinder for 20 seconds. The solution was allowed to stand for 30 seconds and the foam height was measured [56].

2.8. Wetting power.

The wetting was determined by immersing a sample of cotton skein 3g attached to a stainless-steel hook in a 0.1wt% solutions of sugar ester at 25 ^{0}C. The time recorded from the moment the cotton skein was put into the solution until the moment it started to sink is the wetting time [57].

2.9. Drop- penetration (D.P.T) method:

The drop penetration time was employed as a screening test and was applied on local commercial peatmoss ground in wiley mill to pass through about N^o 10 screen. About 1gm ground peatmoss was placed on a

watch glass to form a thickness of about 3-4 mm thick. Two drops of 0.1% solution of SE surfactant were applied from a medicine dropper to the surface and the time was recorded for the liquid to penetrate the peatmoss. Rewetting time was determined with distilled water after the samples had dried overnight at room temperature. The resulting values are the average of 5 determinations [58].

2.10. Emulsifying power:

The sugar ester solution (3ml,0.1wt%) and sunflower oil (2ml) solution were mixed in a 100 ml stoppered cylinder by giving the cylinder 20 strong shakes. The volume of the emulsion was measured at 0, 5, 15, and 30 minutes time intervals and the time taken for any phase separation was recorded [57].

2.11. Grease removal power:

A 10 g sample of the test cloth was soiled with olive oil (4%) and washed in 1 liter of the test solution. After washing, the test solution was extracted for 3 hours with benzene: ethanol (1:1,v:v) to assess the amount of olive oil left in the test fabric [59].

2.12. Antimicrobial activity

The antibacterial activity of the sugar esters was evaluated against some selected pathogenic Gram-positive and Gram-negative bacteria, as well as a fungus strain by nutrient agar method. Eight different organisms were examined, including *Staphylococcus aureus* (ATCC25923), *Bacillus subtilis* (RCMB015) (NRRL B-543), methicillin-resistant *Staphylococcus aureus* (MRSA) ATCC4330), as example of Gram-positive and *Candida albicans* (RCMB0005003 ATCC10231) as examples of fungi. Gram negative bacteria included *Escherichia coli* (ATCC25922), *Salmonella typhimurium* [60].

2.13. Biodegradability

The biodegradability was evaluated using the Dye-away in river water method by measuring the change in surface tension values versus time of biodegradation [61].

3. Results & Discussion

3.A. Synthesis of sucrose esters, optimization, and characterization.

3.A.1 Synthesis of sucrose stearate by transesterification of sucrose and methyl stearate

Despite the introduction of numerous procedures for the synthesis of carbohydrate fatty acid esters, there are few publications on a complete successful logical approach to finding the optimum reaction conditions that result in a high yield of sugar fatty acid esters. The synthesis of carbohydrate fatty acid esters using a solvent-free transesterification has given special consideration in this study, since it appears to have a great potential as a cost-effective and straightforward method.

For the synthesis of sugar esters, sucrose and the methyl ester of stearic acid were used as model substrates to optimize the transesterification reaction. In this synthesis, sucrose acted as acyl acceptor and stearic acid methyl ester was selected as a convenient model of an acyl donating molecule. The reaction is illustrated in (**Fig.1) .** The operating conditions were selected according to afore-mentioned literature reports [43,62,63]. Thus, in the preliminary investigations, the molar ratio of methyl stearate to sucrose was kept constant at 1:1 molar ratio althroughout the synthesis of sucrose stearate by the transesterification procedure.

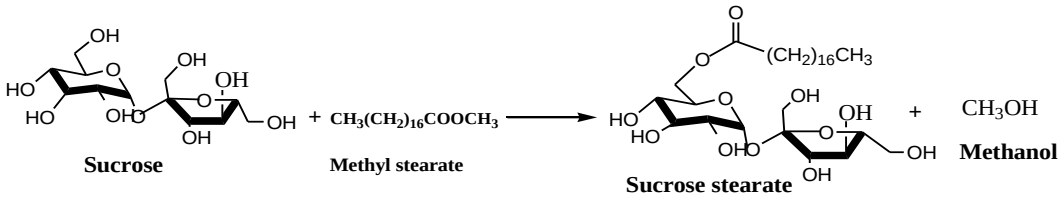


Fig.1. *Transesterification reaction of sucrose and methyl stearate.*

The reaction was performed at a temperature of 40-45 ^{0}C under strictly anhydrous conditions in a medium completely free from any solvent which seems to be essential for reproducibility [42] in the presence of K_2CO_3, (0.5 % g) as catalyst, which is regarded as the most widely used for this type of reactions [64].The mixture turned to a homogenous system after about 1hr., then after completion of the reaction. The product was purified by crystallization from ethyl acetate to yield a white amorphous powder. The reaction was monitored by thin- layer chromatography (T.L.C.). (**Fig.2)**

Fig.2. *A photograph of thin layer chromatography (TLC) of sucrose stearate as an arbitrary sample.*

3.A.2. Characterization of the synthesized sucrose esters

The molecular structure of the synthesized compounds was confirmed by Fourier-Transform Infrared (FTIR) and Proton Nuclear Magnetic Resonance

(^{1}H NMR) spectroscopy.

(Fig.3) shows a sample of the Fourier- Transform Infrared (FTIR) spectra measured at wave number from 500 cm^{-1} to 4000 cm^{-1} of methyl stearate, sucrose and sucrose stearate.

The characteristic new bands of sucrose stearate in (C) include the carbonyl ester group (C=O) which appears at 1740 cm^{-1} duo to stretching vibration ($V_{C=O}$) of the ester group. The presence of such a band of 1728 cm^{-1} was reported by Song et al. [65], in sucrose octanoate (ester obtained by transesterification of sucrose with ethyl caprylate). Thus, this band was shifted from the carbonyl group (C=O) of the fatty acid at 1695 cm ^{1}. The band at (2849-2918 cm^{-1}) is due to C-H for chain length of fatty acid ester stretching and the broad band at3340 cm^{-1} is due to OH group. In(B)at about 3340 cm^{-1} there is a wide asymmetric band duo to the stretching vibrations of the O-H group of the sucrose molecule. The stretching vibrations(C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1000 cm^{-1} and 1200 cm^{-1} as well as at 920 cm^{-1} pyranose ring confined the formation of a sugar esters, The two sharp peaks at 720 cm^{-1} or 730 cm^{-1} in all products also confirmed the formation of sugar esters, these are related to a sequence of at least 4 methylene groups in a linear hydrocarbon chain as shown in the case of the sugar esters synthesized here [66]. Furthermore, in (C) the peak around 1051 cm^{-1} assigned the carbon- oxygen (-C-O-) single bond [66], a peak at 1376 cm^{-1} due to the methyl group ($-CH_3$) at the end of the long hydrocarbon chain, and an absorption around 1466 cm^{-1} corresponding to the methylene groups($-CH_2-$) in sucrose and the fatty acyl part. the spectra included several bands in some regions specific to carbohydrates.

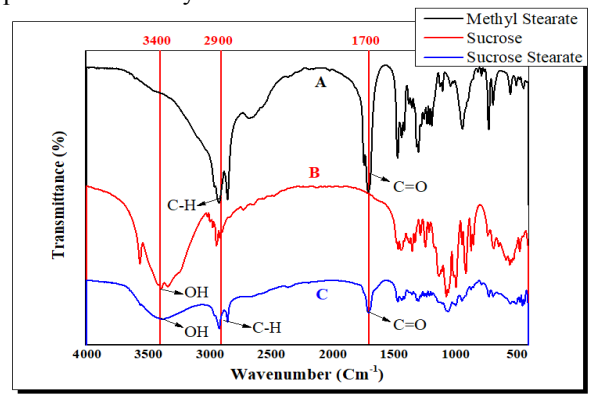


Fig.3.*Fourier Transform Infrared Spectroscopy (FTIR)of, (A) methyl stearate (B) sucrose and (C) synthesized sucrose mono stearate.*

Proton Nuclear Magnetic Resonance (^{1}H NMR) Spectroscopy.

In the *^{1}H NMR* spectrum sucrose stearate two regions can be distinguished in the range (0-3.0) ppm, which is typical for methyl and methylene protons from the aliphatic long -chain acyl substituent and (3.0-6.0)ppm, which as typical for protons of the sucrose moiety. Chemical displacement for protons of the methyl groups of sucrose stearate are observed as usual at (0.87-0.99) ppm. The proton signals from the ($-CH_2$) methylene groups were in the range of (1.17-2.02) pp. Glucose protons of glucopyranose are observed in the range of (3.34-5.40) ppm and fructose protons of fructofuranose at (3.5-4.5) ppm.

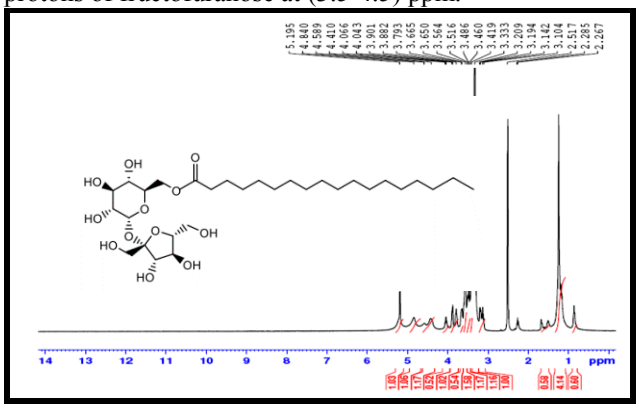


Fig.4.*^{1}H NMR* spectra of sucrose stearate

Stearoyl sucrose : (δ, ppm) δ 5.18 (d, 1H), 4.84 (s, 1H), 4.58 (s, 1H), 4.42 (s, 1H), 4.13 – 3.94 (m, 2H), 3.88 *J* = 7.7 Hz, (m, 2H), 3.79 (d, 2H), 3.71 *J* = 58.7 Hz, (d, 1H), 3.60 *J* = 32.0 Hz, (dd, 3H), 3.46 *J* = 22.2, 12.9 Hz, (t, 1H), 3.27 – 3.00 (m, 6H), 2.26 (m, 2H,- CH_2-CO-), 1.68 (m, 2H,-CH_2-CH_2-CO-), 1.28 (m, 28H,-CH_2 – chain), 0.86 (t, 3H) CH_3.

3.B. Optimization of factors affecting the synthesis of sucrose esters

3.B.1*Selection of the reaction conditions*

By the single factor experiments, a number of small-scale experiments was carried out to establish the effect of temperature, time of the reaction, catalyst and molar ratio of the reactants. Initially, the influence of the reaction temperature on the process of transesterification was evaluated at temperature varying between 40 ^{0}C and 70 ^{0}C. In these experiments, the maximum temperature tested was 70 ^{o}C, since over these limits overheating of the media and degradation of the sugar could occur. The results shown in **(table 1)** Indicate that the reaction may proceed favorably nearly ambient conditions. Maximum yield (about 83%) was attained at (40 -45) ^{o}C, however, above this temperature, further increase a reduction in the percentage of conversion of sucrose and yield of only about 69% were observed which is probably because higher temperature promotes sucrose and sucroesters decomposition as well as other side reactions, leading to decrease in the optimum yield.

The influence of the time of the reaction assessed using the previously determined optimum temperature (45) ^{o}C showed that increasing time favors formation of sucrose esters, where a maximum yield (88.5%) was attained at a 3 hr reaction period. However, longer periods did not further enhance the yield of the products. It was noteworthy that, under these conditions of temperature and time of reaction, the product obtained was enriched with monoesters (about 91%).

***Table* (1)** Effect of temperature and time on solvent -free synthesis of sucrose stearate by transesterification of sucrose and methyl stearate.

Temperature °C	Time (hr.)	Yield %	Conversion %	Composition of sucrose stearate	
				Monoester %	di-esters %
40	1.0	82.57	83.00	83.89	5.90
45	1.0	82.97	83.03	96.40	3.21
50	1.0	69.73	69.59	90.34	6.42
60	1.0	69.65	69.43	91.30	7.72
70	1.0	70.92	74.33	89.12	6.51
45	1.0	81.74	82.85	83.89	15.90
45	2.0	81.90	88.42	96.40	3.40
45	2.5	81.58	81.88	90.34	6.42
45	3.0	85.49	88.09	91.30	8.15
45	3.5	85.81	81.49	91.66	8.02
45	4.0	84.81	88.42	91.23	6.87

The influence of mole ratio of Sucrose to fatty acid methyl esters (FAME).

The mole ratio of the reactants is one of the most important factors that affects sugar ester synthesis. In general, it is known that increasing the mole ratio of surfactants improves the reaction of S_N2 type mechanism by increasing the collisions between reaction molecules [67,68].

In this solvent-free transesterification process, it was revealed (**table 2)** that increasing sucrose ester ratio enhanced methyl ester conversion resulting in a relatively greater yield concurrently, as expected, with higher proportions of monoesters. The higher percentage of monoesters was reached with a sucrose: methyl esters ratio of (1.5: 1.0), where the product constituted nearly 98% monoesters. Thus, greater ratio of sucrose to FAME, apparently promote selective transesterification towards monoester formation.

***Table* 2.** Effect of mol ratio on the alkali- catalyzed synthesis of sucrose stearate by transesterification of sucrose and methyl stearate.

Mole ratio of sucrose/ methyl ester	Wt ratio of sucrose/ methyl ester	Yield %	Conversion %	Composition of sucrose stearate	
				Monoester %	di-esters %
0.01/0.01	3.42/2.98	81.80	81.15	91.94	3.26
0.0125/0.01	4.27/2.98	85. 36	84.96	95.89	0.96
0.0150/0.01	5.13/2.98	85.88	85.62	98.45	0.14
0.020/0.01	6.84/2.98	87.66	86.78	94.20	1.99
0.025/0.01	8.55/2.98	89.97	87.56	95.08	1.33

The influence of catalyst on the yield & sucrose stearate formation was also examined. Since sucrose hydrolyses with extreme ease under acidic conditions, but reasonably stable in the presence of strong bases, thus, the preparation of sucrose derivatives is largely restricted to basic media. As suggested by the outcomes of certain experiments, the choice of the base employed in sucrose transesterification can have a significant influence on the yield of such process. Therefore, in establishing suitable transesterification conditions in this solvent- free procedure, some basic compounds such as Na_2CO_3, K_2CO_3, K_2HPO_4 and Al_2O_3 were tested for their catalytic effect on sucroester production **(table 3,4).**

***Table* 3.** Effect of type of the catalyst on the solvent- free synthesis of sucrose stearate by transesterification of sucrose and methyl stearate

Catalyst type	M. wt. of the catalyst	Catalyst used (g)	Catalyst used (mol)	Yield %	Conversion %	Composition of sucrose stearate	
						Monoester %	di-esters %
Na_2CO_3	106	0.254	0.0024	70.72	80.40	96.77	0.609
K_2CO_3	138	0.3312	0.0024	71.54	91.12	98.19	0.139
K_2HPO_4	174	0.4176	0.0024	70.29	92.05	91.47	1.99
Al_2O_3	102	0.2448	0.0024	68.26	87.95	77.58	0.14

***Table* 4.** Effect of catalyst (K_2CO_3) concentration on the solvent- free synthesis of sucrose stearate by trance- esterification of sucrose and methyl stearate

Catalyst	No. moles of catalyst	Wt. Of Catalyst (g)	Mole ratio of sucrose/ methyl ester	Yield %	Conversion %	Composition of sucrose stearate	
						Monoester %	di-esters %
K_2CO_3	0.0012	0.165	0.02/0.02	67.68	67.74	94.30	2.21
K_2CO_3	0.0024	0.33	0.02/0.02	68.98	68.91	98.19	0.14
K_2CO_3	0.0048	0.662	0.02/0.02	72.37	72.40	91.94	3.26
K_2CO_3	0.0096	1.325	0.02/0.02	81.74	82.86	96.63	3.37
K_2CO_3	0.0192	2.649	0.02/0.02	82.58	83.09	96.53	3.13

On the basis of the comparative analysis of the data (**table 3, 4**), it can be observed that the carbonates of sodium and potassium are relatively more suitable catalysts. The use of di potassium hydrogen phosphate do not lead to any significant increase in the yield. Furthermore, under the chosen reaction conditions, the increase in the catalyst concentration results in a significant increase in yield. In general, salts of the more basic nature are better catalysts for transesterification, which has a logical consistency with the S_N^2reaction mechanism [69].

In this context, an important challenge of the solvent-free transesterification procedure arises from the incompatibility of sugars (solid) with the fatty methyl esters. According to traditional viewpoints, sucrose cannot dissolve in methyl esters and due to the immiscibility and interfacial barrier of the reactants, the reaction cannot be accomplished. However, the achievement of this reaction under these conditions of incompatibility may be explained by the fact that actually, there is no absolute incompatibility since it was observed that the equilibrium solubility of sucrose in methyl stearate, for example, varies from (0.09/100 g to 0.19g/100g) depending on temperature [42]. Then, if sucrose can partly dissolve in FAME phase, the reaction system become homogenous, therefore some free sucrose molecules and fatty acid esters can be adsorbed on the surface of catalyst and form intermediate- state molecule complex. Briefly, sucrate ions generate irreversibly by the reaction of sucrose and the basic catalyst [70]. After wards, the sucrate ions nucleophiles attack the carbonyl carbon of fatty acid esters and a nucleophile is ejected as a leaving group producing sucrose monoesters. The latter reaction have been described by the process which is a typical example of SN^2 mechanism. [71].

a) $(Sucr)-OH + CO_3^- \rightleftharpoons (Sucr)-O^- + HCO_3^-$

b) $(Sucr)-O^- + RCOOCH_3 \rightleftharpoons (Sucr)-O-COCH_3 + CH_3O^-$

c) $CH_3O^- + (Sucr)-OH \rightleftharpoons (Sucr)-O^- + CH_3OH$

Further, after the optimization of the reaction conditions for the solvent-free transesterification sucrose with methyl stearate was established, it has become a focus to expand this study by investigation of sucrose carbohydrate esters from other inexpensive renewable sugar substrates, the transesterification of maltose, glucose in addition to sucrose with therefore, fatty methyl esters embodying 12-18 carbon acyl chain length was performed at the optimized reaction conditions previously established.

Typically, the products recovered from sucrose, maltose and glucose esters of varying homologous fatty acids reached almost more than 80% as determined from the yield and the percentage of conversion of the starting reactants. Of special importance, is the observation that over 90% weight ratio of monoesters to diesters are usually obtained,. higher substitution products were rarely present in minor proportions. **(Table 5).**

***Table* 5.** Synthesis of different sugar esters of homologous series of long-chain fatty acids by solvent- free base- catalysed transesterification methyl esters with sucrose, maltose and glucose.

Sugar	Sugar ester	Acyl donr (methyl Ester)	M.WT of methyl ester of F.A	Formula of sugar ester	M.WT of sugar ester	M.P(^{0}C)	Yield %	Conversion %	Composition of sucrose stearate	
									Monoester %	di-esters %
Sucrose	SS	Stearate	298	$C_{30}H_{56}O_{12}$	608	76	82.60	81.20	91.09	1.82
	SP	palmitate	270	$C_{28}H_{52}O_{12}$	580	52	81.89	86.20	97.06	2.83
	SM	myristate	242	$C_{26}H_{48}O_{12}$	552	47	80.76	86.02	94.03	2.64
	SL	laurate	214	$C_{24}H_{44}O_{12}$	524	45	80.85	81.76	96.15	3.00
	SO	oleate	296	$C_{30}H_{54}O_{12}$	606	55	80.11	86.65	92.41	1.64
Maltose	MS	Stearate	298	$C_{30}H_{56}O_{12}$	608	70	80.59	76.30	91.09	1.82
	MP	palmitate	270	$C_{28}H_{52}O_{12}$	580	57	81.89	83.15	97.06	2.83
	MM	myristate	242	$C_{26}H_{48}O_{12}$	552	50	80.76	77.45	94.03	2.63
	ML	laurate	214	$C_{24}H_{44}O_{12}$	524	45	78.85	75.28	96.15	3.00
	MO	oleate	296	$C_{30}H_{54}O_{12}$	606	53	80.11	72.65	97.91	1.64
Glucose	GS	Stearate	298	$C_{24}H_{46}O_7$	446	78	82.67	84.49	96.72	2.18
	GP	palmitate	270	$C_{22}H_{42}O_7$	418	59	87.66	86.26	94.10	2.24
	GM	myristate	242	$C_{20}H_{38}O_7$	390	53	80.11	84.45	97.42	1.74
	GL	laurate	214	$C_{18}H_{34}O_7$	362	72	80.15	89.96	94.65	1.56
		oleate	296	$C_{24}H_{44}O_7$	444	63	87.78	82.35	98.83	1.04

For instance, the chemical structure of the different synthesized (glucose, maltose& sucrose) esters was characterized by FTIR as well as ^{1}H NMR spectroscopic investigation.

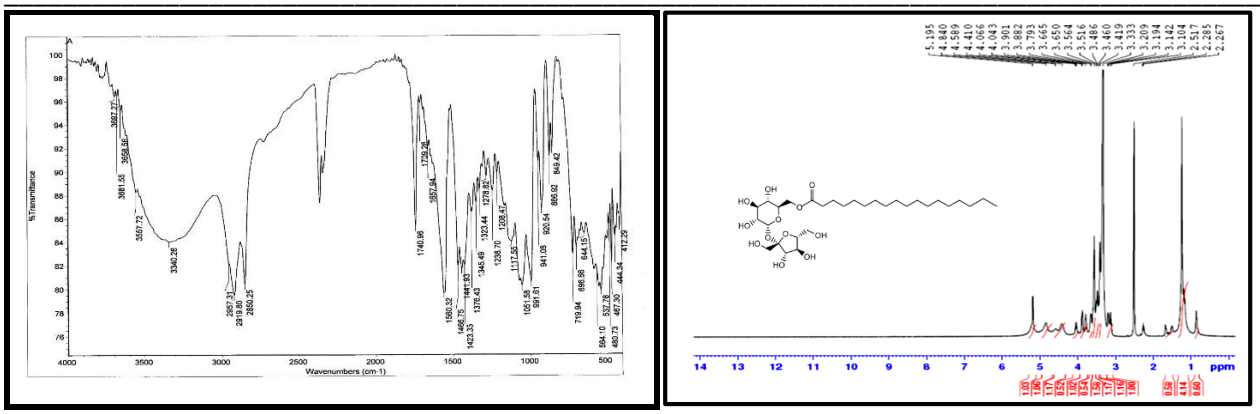


Fig. 5. FTIR& ^{1}H NMR spectra of sucrose monostearate ester.

Sucrose mono stearate (SMS). 6-O-stearoylsucrose *FTIR band* at 3300 cm^{-1} (OH),),(2850-2957 cm^{-1}) C-H for chain length of fatty acid ester stretching bands of O-C bond at 1316 cm^{-1} and 1015 cm^{-1} , 1740 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1050 cm^{-1} and1238 cm^{-1} , (920 cm^{-1}) pyranose ring . ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 5.18 (d, 1H), 4.84 (s, 1H), 4.58 (s, 1H), 4.42 (s, 1H), 4.13 – 3.94 (m, 2H), 3.88 *J* = 7.7 Hz, (m, 2H), 3.79 (d, 2H), 3.71 *J* = 58.7 Hz, (d, 1H), 3.60 *J* = 32.0 Hz, (dd, 3H), 3.46 *J* = 22.2, 12.9 Hz, (t, 1H), 3.27 – 3.00 (m, 6H), 2.26 (m, 2H,- CH_2-CO-), 1.68 (m, 2H,-CH_2-CH_2-CO-), 1.28 (m, 28H,-CH_2 – chain), 0.86 (t, 3H) CH_3.

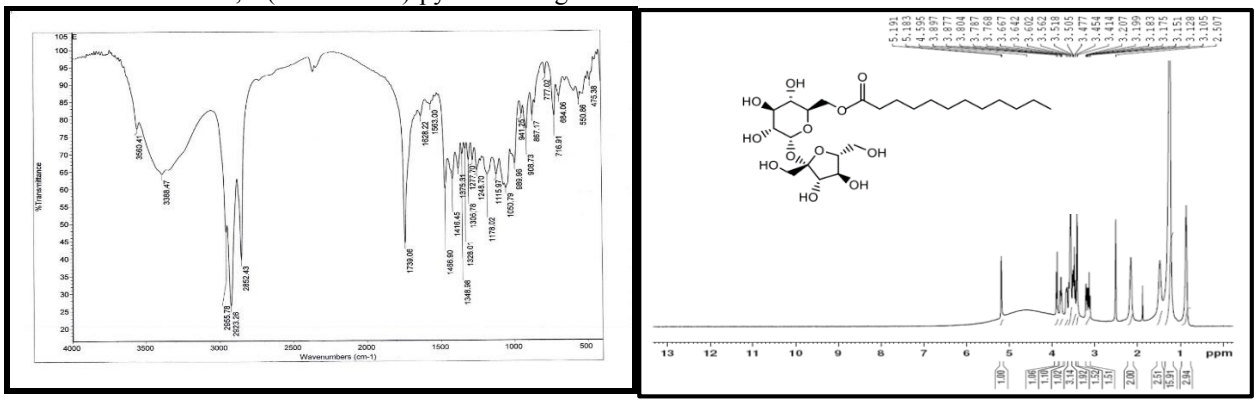


Fig.6. FTIR& ^{1}H NMR spectra of sucrose monolaurate ester.

Sucrose mono laurate (SML) 6-O-lauroylsucrose *FTIR band* at 3388 cm^{-1} (OH),),(2852-2955 cm^{-1}) C-H for chain length of fatty acid ester stretching bands of O-C bond at 1305 cm^{-1} and 1050 cm^{-1} , 1739 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1051 cm^{-1} and1248 cm^{-1} , (908 cm^{-1}) pyranose ring. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 5.19 (d,1H, *J* = 3.3 Hz,), 3.89 (dd, *J* = 8.0 Hz, 3H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.84 – 3.71 (t, 2H), 3.82 – 3.73 (t, 1H), 3.66 (m, *J* = 6.7 Hz, 3H), 3.65 (m, *J* = 9.8 Hz, 2H), 3.62 (m, *J* = 23.7, 7.4 Hz, 6H), , 3.48 (d, 2H),3.16 (m, 6H), (m, 2H, *J* = 7.4 Hz -CH_2-CO-), 1.47 (m, 2H, CH_2-CH_2-CO-), 1.24 (m, 16H,-CH_2 – chain), 0.86 (t, 3H, *J* = 7.0 Hz CH_3)

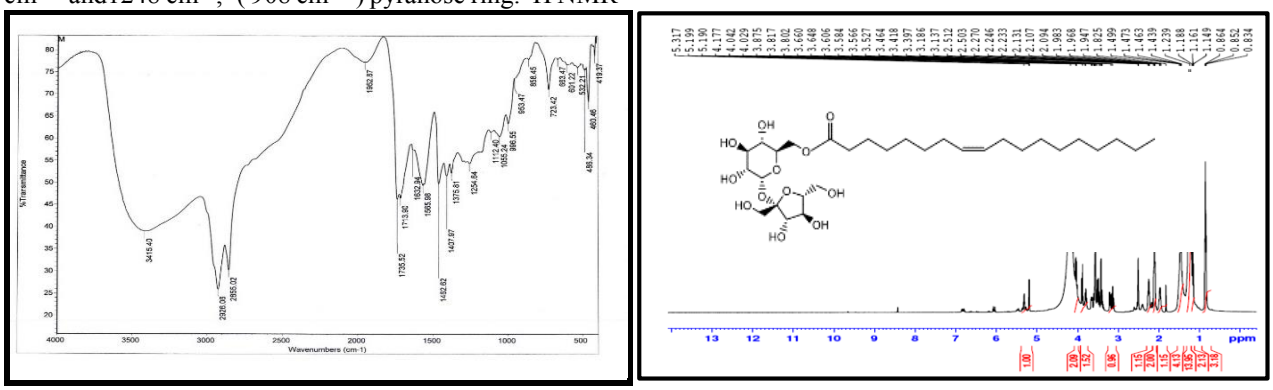


Fig.7. FTIR& ^{1}H NMR spectra of sucrose monooleate ester.

Sucrose mono oleate (SML) 6-O-oleaiosucrose *FTIR band* at 3415 cm^{-1} (OH), (2855-2926 cm^{-1}) C-H for chain length of fatty acid ester. stretching bands of O-C bond at 1357 cm^{-1} and 1112 cm^{-1} , 1735 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1055 cm^{-1} and1254 cm^{-1} , (953 cm^{-1}) pyranose ring. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 5.19 (d, 1H *J* = 3.6 Hz,), 4.18 (s, 3H), 4.03 (dd, , 3H *J* = 14.2, 7.1 Hz), 3.89 (d, 2H, *J* = 8.1 Hz,), 3.50 (d, , 1H *J* = 9.4 Hz), 3.46 (dd, , 3H *J* = 31.3, 5.8 Hz), 3.42 (t, , 2H *J* = 2.2 Hz), 3.27 – 3.04 (m, 6H), 2.25 (t, , 2H *J* = 7.2, 4.5 Hz, -CH_2-CO-), 2.11 (m, , 4H *J* = 6.2 Hz CH_2 CH = CH -CH_2), 1.35 (m, , 2H *J* = 91.0 Hz, CH_2-CH_2-CO-), 1.23 (m, 20H, ,-$(CH_2)_n$ – chain), 0.86 (t, , 3H *J* = 13.0 Hz) CH_3. δ 5.31 (t, 2H), CH = CH

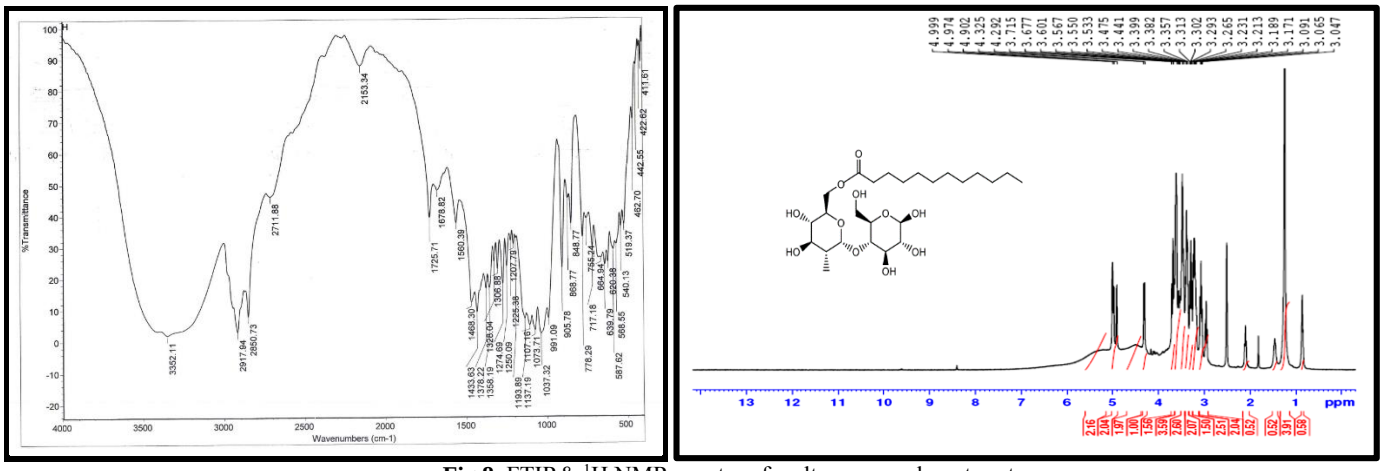


Fig.8. FTIR& ^{1}H NMR spectra of maltose mono laurate ester.

Maltose mono laurate (MML) 6-O-lauroylMaltose *FTIR band* at 3352 cm^{-1} (OH),), (2850-2917 cm^{-1}) C-H stretching for chain length of fatty acid ester. stretching bands of O-C bond at 1306cm^{-1} and 1073 cm^{-1} , 1725 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1037 cm^{-1} and1225 cm^{-1} , (905 cm^{-1}) pyranose ring. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 4.99 (dd,1H, *J* = 11.2, 2.8 Hz,), 4.91 (d, 1H, *J* = 2.7 Hz,), 4.31 (d, 1H, *J* = 7.6 Hz), 3.74 – 3.65 (m, 4H), 3.61 (s, 1H), 3.54 (t, 1H *J* = 12.2, 5.3 Hz,), 3.46 (t,1H, *J* = 10.0 Hz,), 3.42 – 3.33 (m, 3H), 3.32 – 3.24 (m, 1H), 3.25 – 3.15 (m, 5H), 3.07 (t, 1H, *J* = 8.9 Hz), 2.96 (t, 1H *J* = 8.3 Hz,), 2.10 (t,2H, *J* = 7.2 Hz, -CH_2-CO-), 1.81 (m, 2H, CH_2-CH_2-CO-), 1.24 (m, , 16H,-CH_2 – chain), 0.85 (t, 3H *J* = 6.7 Hz, CH_3).

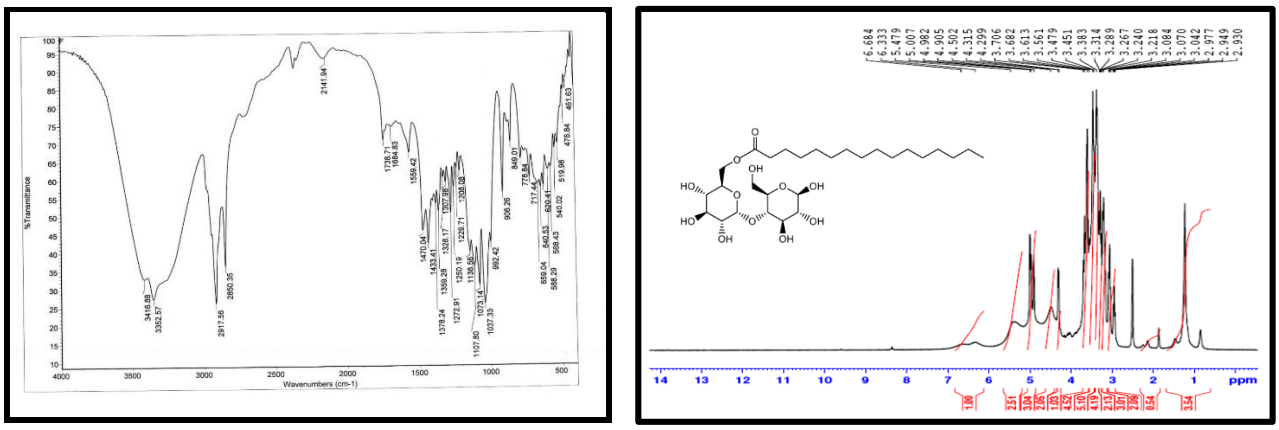


Fig.9. FTIR& ^{1}H NMR spectra of maltose monopalmitate ester.

Maltose mono palmitate (MMP) 6-O-palmitoyl Maltose *FTIR band* at 3416 cm^{-1} (OH), (2850-2917 cm^{-1}) C-H stretching for chain length of fatty acid ester. stretching bands of O-C bond at 1307cm^{-1} and 1073 cm^{-1}, 1738 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1037 cm^{-1} and1206 cm^{-1} ,(906 cm^{-1}) pyranose ring. ^{1}H NMR (400 MHz, DMSO) δ 4.99 (d,1H, *J* = 8.8 Hz,), 4.91 (d, 1H), 4.49 (s, 1H), 4.31 (d, 4H *J* = 7.4 Hz,), 3.69 (t,1H, *J* = 10.0 Hz,), 3.61 (s, 1H), 3.46 (t, 1H *J* = 9.8 Hz,), 3.38 (d, 3H *J* = 6.5 Hz,), 3.28 – 3.17 (m, 1H), 3.25 – 3.15 (m, 5H), 3.07 (t, 1H *J* = 8.6 Hz,), 2.95 (t, 1H *J* = 8.1 Hz,), 2.14 (t, 2H, *J* = 7.3 Hz -CH_2-CO-), 1.47 (m, 2H CH_2-CH_2-CO-), 1.24 (m, 24H- CH_2 – chain), 0.85 (t, 3H, *J* = 6.9 Hz CH_3).

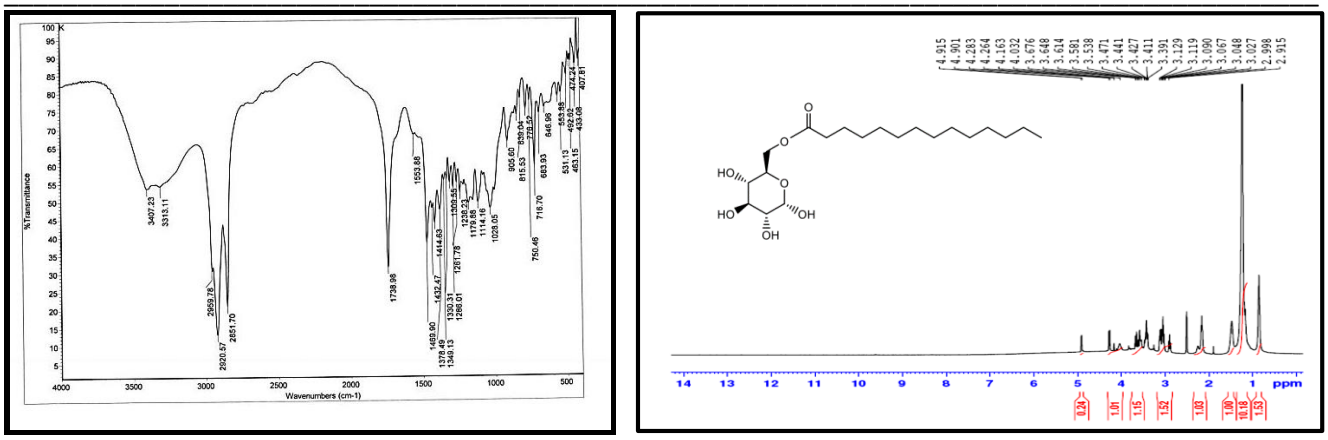


Fig.10. FTIR & ^{1}H NMR spectra of Glucose mono myristate ester.

Glucose mono myristate (GMM) . 6-O-myrestoylglucose *FTIR band* at 3313 cm^{-1} (OH)), (2885-2959 cm^{-1}) C-H for chain length of fatty acid ester stretching bands of O-C bond at 1330cm^{-1} and 1114 cm^{-1} , 1739 cm^{-1} due to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1029 cm^{-1} and1238 cm^{-1} , (905cm^{-1}) pyranose ring. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 4.91 (d, 2H J = 3.2 Hz,), 4.27 (d, 1H J = 7.7 Hz,), 4.16 (s, 1H), 3.66 (d, 1H J = 11.8 Hz,), 3.49 – 3.32 (t, 2H), 3.20 – 2.93 (m, 3H), 2.89 (t, 1H), 2.16 (t, 2H J = 6.6 Hz, -CH_2-CO-), 1.48 (m,, 2H, CH_2-CH_2-CO-), 1.20 (m, 20H J = 28.0 Hz, -CH_2 – chain), 0.85 (t, , 3H, CH_3).

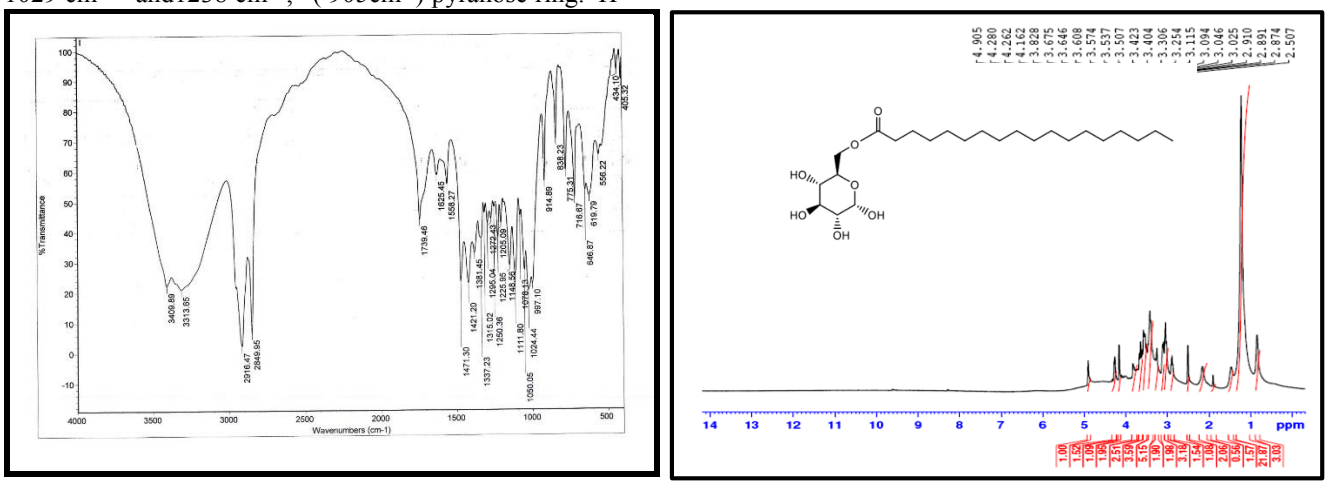


Fig.11. FTIR & FTIR, ^{1}H NMR spectra of Glucose mono stearate ester.

Glucose mono stearate (GMS) . 6-O-stearoylglucose *FTIR band* at 3409 cm^{-1} (OH),),(2849-2916 cm^{-1}) C-H for chain length of fatty acid ester stretching bands of O-C bond at 1295 cm^{-1} and 1078 cm^{-1} , 1739 cm^{-1} duo to stretching vibration (V $_{C=O}$) of the ester group, The stretching vibrations (C-C), (C-O), (C-O-C) of the pyranose moiety of sucrose are observed between 1024 cm^{-1} and1205 cm^{-1} , (914cm^{-1}) pyranose ring ^{1}H NMR (400 MHz, DMSO) (δ, ppm) δ 4.90 (d, 2H), 4.27 (d, 1H J = 7.2 Hz,), 3.56 (d,1H, J = 15.1 Hz,), 3.42 (t, 2H), 3.25 (s, 1H), 3.07 (dd, 3H J = 27.4, 8.4 Hz,), 2.96 – 2.81 (t, 1H), 2.16 (t, 2H ,- CH_2-CO-), 1.47(m, 2H,-CH_2-CH_2-CO-), , 1.23 (m, 28H,-CH_2 – chain), 0.84 (t, 3H, CH_3).

3. B.2.Surface Active Properties of The Sugar ester.

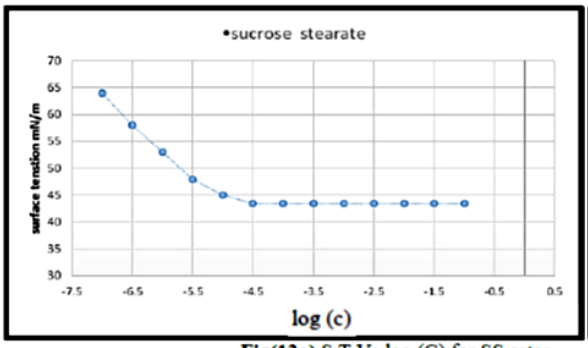
3.B.2.1. Air-water surface tension properties

Because of the amphiphilic chemical structure, which is characterized by combination of hydroxyl groups in the sugar head with hydrophobic acyl chain tail within the same molecule, sugar esters with 12 or more carbon acyl groups are expected to have surface active features. The variation of surface tension vs.log concentration of the different sugar esters at 25 ^{0}c are shown in (**fig 12,13,14).** The results reveal that the surface tension of aqueous solution of all esters was reduced significantly as compared with the surface tension of water 72mN/m. Generally, surface tension decreased with increase concentration until a specific value, known as the critical micelle concentration (CMC) is reached at which the molecules of these compounds aggregate to form micellar particles. The value of CMC is of great particular importance since it is the concentration required to solubilize insoluble molecules in water or other hydrophilic solvents. It can be observed from the tables that the CMC values decrease with increasing the acyl chain length of the acyl substituent. The CMC of the sucrose esters ranged from 3.7 x10^{-4} to about 5.12x10^{-6} m/l for C_{12} to C_{18} compounds, indicating an obvious decrease of CMC values as the length or the acyl side chain increased. Once again, values determined for

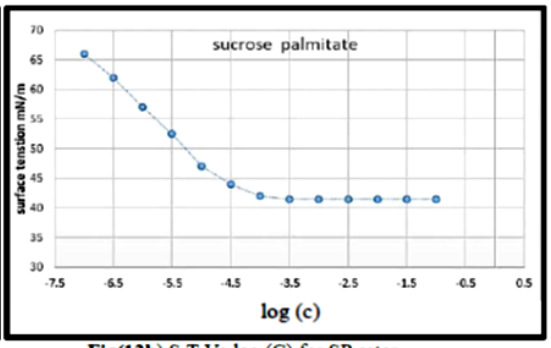
sucrose esters are nearly similar to those of maltose and glucose esters counterparts having the same acyl chain length. This may suggest that the surface properties are not significantly affected by the structure of the head groups. Such a trend and data are consistent with literature reports[11,72,73].

All the synthesized sugar esters in this study were found to display distinctive surfactant behavior. The relation between structure and property of these esters showed that for this type of structure, the length of the acyl chain play an important role in the different characteristics of the sugar ester molecule. For instance, when the acyl chain increases, the water solubility, critical micelle concentration (CMC) as well as hydrophile lipophile (HLB). balance decrease. The surface-active properties of sugar esters (as judged by their HLB values, water solubility, cloud and kraft points as well as CMC were investigated. The higher hydrophilicity of the ester would be expected in higher HLB values for the corresponding ester. The longer the acyl chain associated with the fatty acyl-derived sugar has the higher HLB.

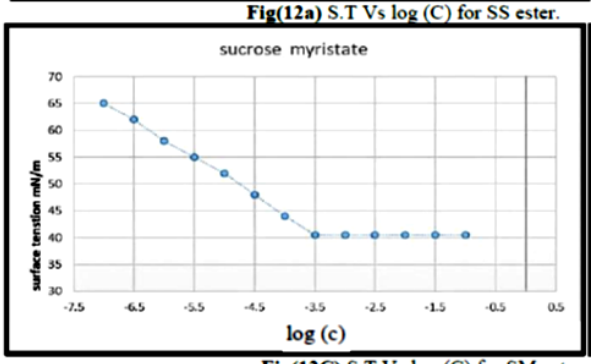
Broadly speaking, all 15 esters of (glucose, maltose & sucrose) can be considered hydrophilic (their measured HLB about 7.79-13.05) indicating they could serve as oil in water emulsifiers [74]. The molecular structure is directly related to certain important unique performance characteristic such as foamability, emulsifying, wetting potentialities and other peculiar properties include their antimicrobial potentialities. The structure-surface activity performance of the synthesistized sucrosters are described in the following.



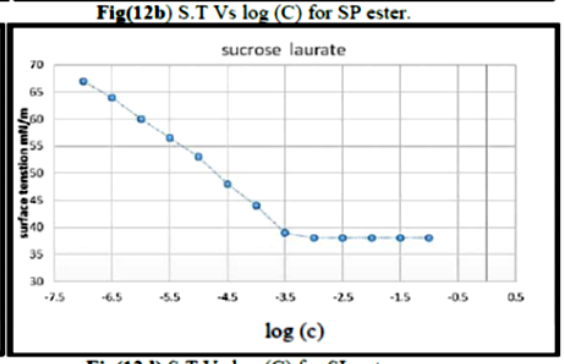
Fig(12a) S.T Vs log (C) for SS ester.



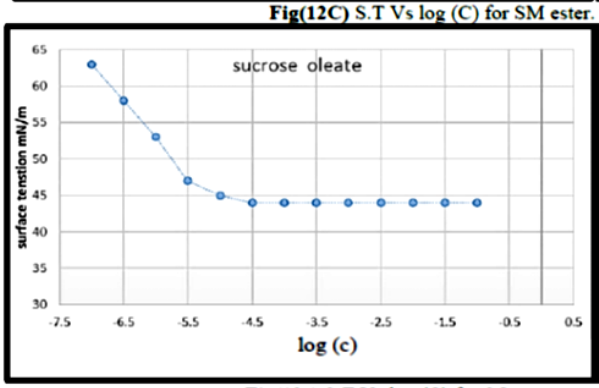
Fig(12b) S.T Vs log (C) for SP ester.



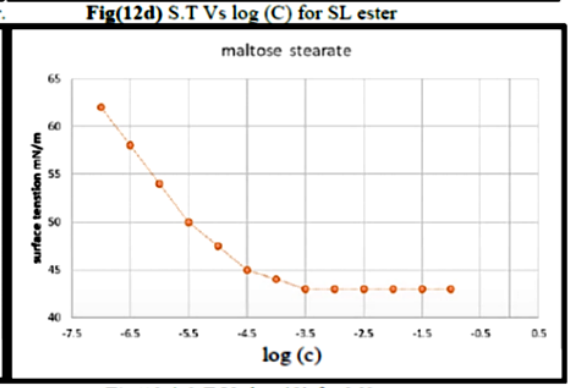
Fig(12C) S.T Vs log (C) for SM ester.



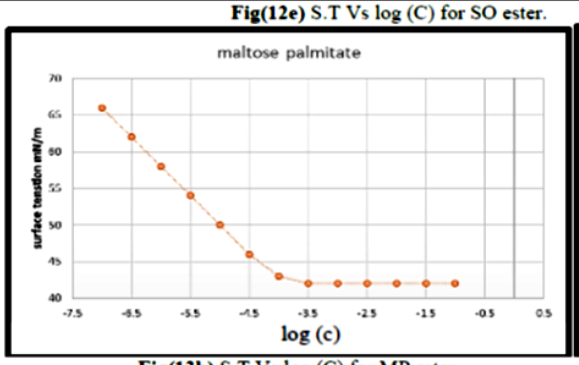
Fig(12d) S.T Vs log (C) for SL ester



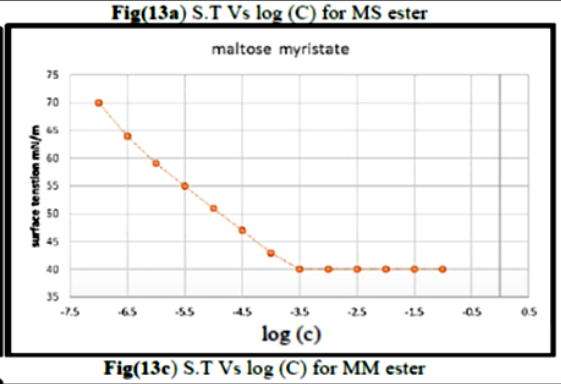
Fig(12e) S.T Vs log (C) for SO ester.



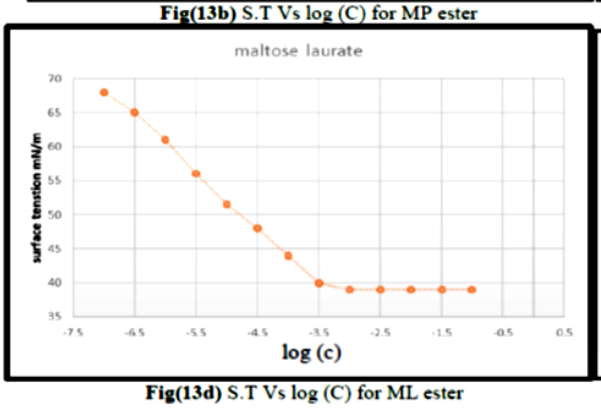
Fig(13a) S.T Vs log (C) for MS ester



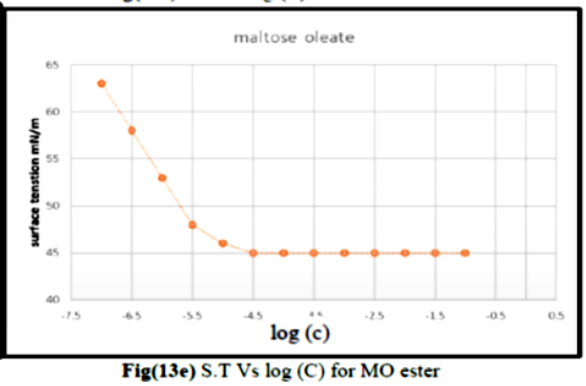
Fig(13b) S.T Vs log (C) for MP ester



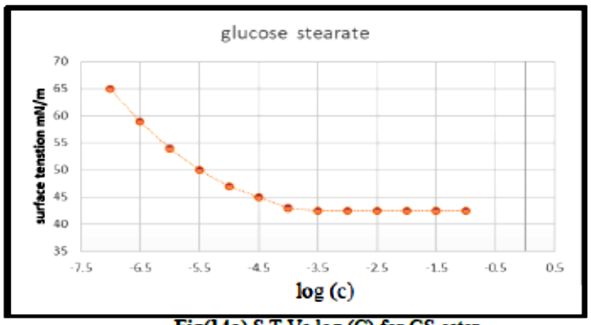
Fig(13c) S.T Vs log (C) for MM ester



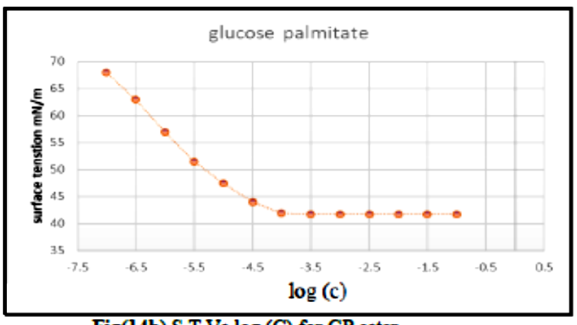
Fig(13d) S.T Vs log (C) for ML ester



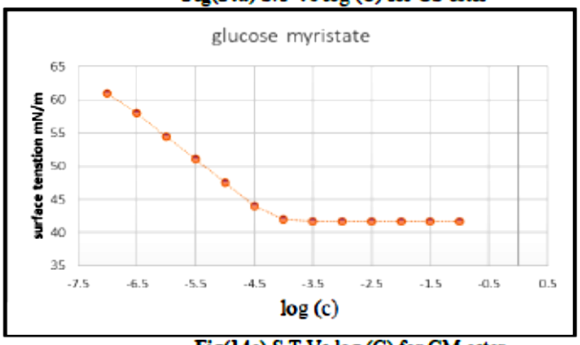
Fig(13e) S.T Vs log (C) for MO ester



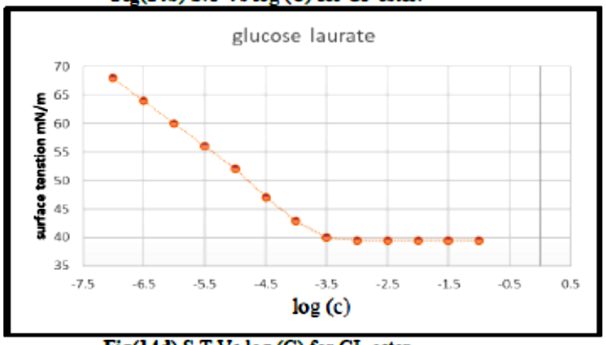
Fig(14a) S.T Vs log (C) for GS ester



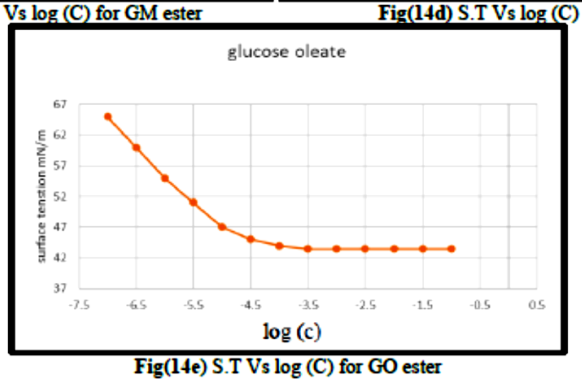
Fig(14b) S.T Vs log (C) for GP ester.



Fig(14c) S.T Vs log (C) for GM ester



Fig(14d) S.T Vs log (C) for GL ester



Fig(14e) S.T Vs log (C) for GO ester

Maximum surface excess concentration (Γ_{max}), *and Minimum surface area* (A_{min}) *of the sugar esters molecule*.

The surface tension data for each surfactant were treated in terms of Gibbs adsorption equation to calculate the amount of surfactant adsorbed per unit area at air-water surface. The maximum adsorption concentration (Γ_{max}), in mol.m^{-2} the min area per surfactant molecule at the air-water interface ($\AA_1$ in $\AA^2$, area determined for the relations : [75]

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

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

The calculated values of the maximum surface excess concentration revealed a general linear increasing trend with increasing carbon chain length of acyl substituent as shown from the slope of the curve before the CMC region of the surface tension profile **(fig 12,13,14)**, which indicates that an increasing in the amount of the surfactant molecule adsorbed at the air/ liquid interface, and consequently the area occupied by molecule A_{min} decrease **(table 6)**

Area occupied per molecule (A) at the saturated water – air interface

With respect to the influence of the alkyl chain length for a given headgroup. The general behavior described for conventional surfactants is a decrease when the alkyl chain increases. Due to a more closed- packed arrangement favored by hydrophobic interaction between these chains. With respect to the sugar fatty acyl derivatives, has been found in this study to a great extent.

For instance, a value of 20 $\AA^2$ is given for the cross-sectional area (A_{min}) of the aliphatic side chain when it is oriented perpendicular to the interface. However, the calculated values of A_{min} calculated ((45.31 A^2 – 66.51 A^2) obtained for A_{min} sugar esters. In this study, suggest that the acyl side- chain are not oriented perpendicular to the air- water interface but they are oriented slightly titled with respect to the interface. It may be imagined that the progressive increase of chain molecules at the interface can promote changes in the area per molecule $A_{min.}$ in some cases, growing up, either by a larger projection on the interface of the oriented chain, or by chain coiling. However, in other cases lower values in the result of a more compact packing is attained as a consequence of hydrophobic bonds established between acyl chains. **(Table 6)** also include the PC_{20} parameter while is the

negative logarithm of the molar concentration (called C_{20}) needed to decrease the surface tension of the solvent by 20mN/m. the higher the PC_{20} , the more of the efficiency of the surfactant is.

***Table* 6.** Critical micelle concentration (CMC) , surface tension at CMC(ϒCMC) , efficiency (PC_{20}), surface excess concentration (Γ_{max}), minimum area/molecule (A_{min}) , standard free energy of adsorption (ΔG^0_{ads}) of sugar fatty acid surfactant.

Surfactant	CMC (M/L)	ϒCMC (m N/m)	Γ_{max} (10^{-10}) (mol/cm^2)	A_{min} (nA^{o2})	PC_{20}	$-\Delta G^o_{ads}$ (Kjmol^{-1})
SL	$3.7x10^{-4}$	38	3.36	45.72	4.95	20.51
SM	$2.8x10^{-4}$	40.5	2.497	66.51	5.15	21.53
SP	$2.2x10^{-5}$	41.5	1.816	91.457	5.29	27.93
SS	$5.12x10^{-6}$	43.5	3.66	45.31	5.94	30.96
SO	$5.01 x10^{-6}$	44	4.08	40.698	5.95	30.92
ML	$3.38x10^{-4}$	39	2.59	64.0199	4.94	21.07
MM	$2.57x10^{-4}$	40	2.21	75.24	5.1	21.93
MP	$2.19x10^{-5}$	42	2.51	66.098	5.3	27.77
MS	$5. 37x10^{-6}$	43	3.39	49.054	5.94	30.92
MO	$5.25x10^{-6}$	45	2.74	60.69	5.96	31.11
GL	$3.31x10^{-4}$	39.5	4.54	36.54	4.92	20.57
GM	$1.99x10^{-4}$	41	2.92	56.95	5.2	22.173
GP	$2.14x10^{-5}$	41.7	3.82	43.44	5.4	27.43
GS	$4.78x10^{-6}$	42.5	5.19	32.00	5.85	30.92
GO	$4.89x10^{-6}$	43.5	5.34	31.095	5.9	30.83

3.B.2.2. Performance characteristic
Cloud and kraft point

The cloud point is, a reliable measure of solubility, especially for nonionic surfactants. As expected, the solubility of sugar esters is a function of molecular weight, with lower values being the most soluble. The data given in **(Table7)** clearly show that the (C.P) increases with increasing the hydrophobic moiety. Within the same homologous series, the cloud point are related to their CMC values, it increases with increasing in HLB numbers.

On the other hand, the kraft point (K.P.) determines the minimum temperature at which the sugar esters can form micelles, it increases with increasing the chain length of the hydrophobic acyl part.

Foaming properties

The creation of foam is an aspect of great importance in food, cosmetics, and other industrial applications. Sugar esters are foam- producers as a result of their tendency of facilitating aeration during agitation or shearing [76]. The foam height illustrated in **(fig.15,16,17)** clearly revealed that all these candidates are excellent foam generators. Foam height measured for 0.01%,0.1%and 1%w/w concentrations showed that above the CMC, the foam height persists almost unchanged for long periods of time which means that they exhibit good stability as indicated by only a slight decrease in the height was noticed even after standing for more than 30 minutes. Obviously, the data showed a modest positive relation between foamability and concentration of the particular sugar ester, Generally, the greater concentration produces exhibited high foaming ability of a given ester.

Once again, for the same hydrophilic portion (sucrose, maltose or glucose), the foamability is affected by the chain length of the hydrophobic chain, the myristoyl ($C_{14:0}$) derivatives possessed exclusively the best foam inducing ability. The presence of the unsaturation within the acyl side chain had little impact on foaming properties of a particular sucrose ester. This can be observed by comparing foam height obtained from both the stearoyl ($C_{18:0}$) embodying a saturated side chain with its counterpart, the unsaturated, oleate($C_{18:1}$) acyl derivatives.

It is conceivable that the foam stability of such system arises althrough the operation of a variety factors, including the adsorption capacity of the surfactants at the air/ water interface and the rate of diffusion of the gas captured in the foam [77] .

In general, taken together, the present results reinforce the notation that, sucrose, maltose, and glucose esters embodying appropriate acyl moiety of (12-18) carbon atoms can act as excellent foaming agents and so, they may have real potential in food, cosmetics and other industries.

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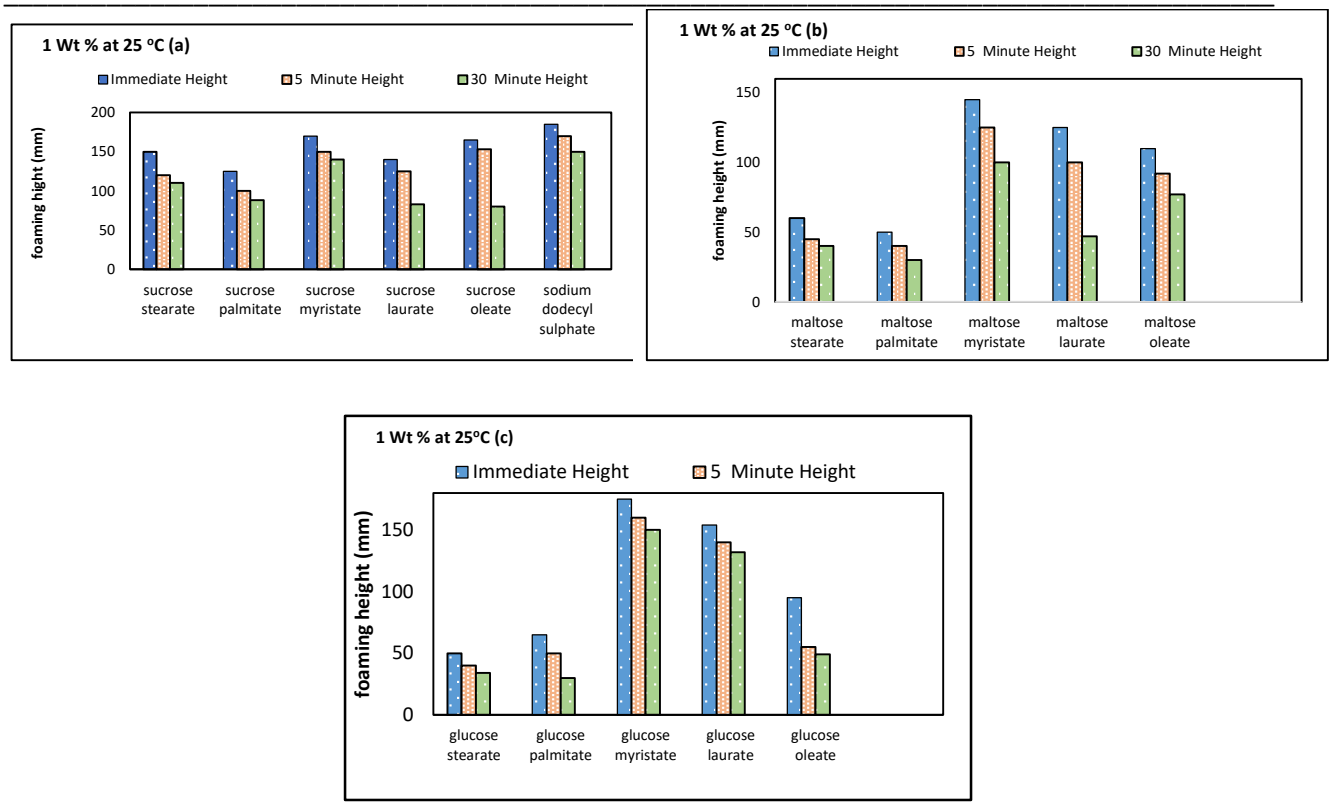

Fig.15. (a, b, c) Foaming height of sucrose, maltose, and glucose fatty acid ester at concentration (1wt%) and 25°C

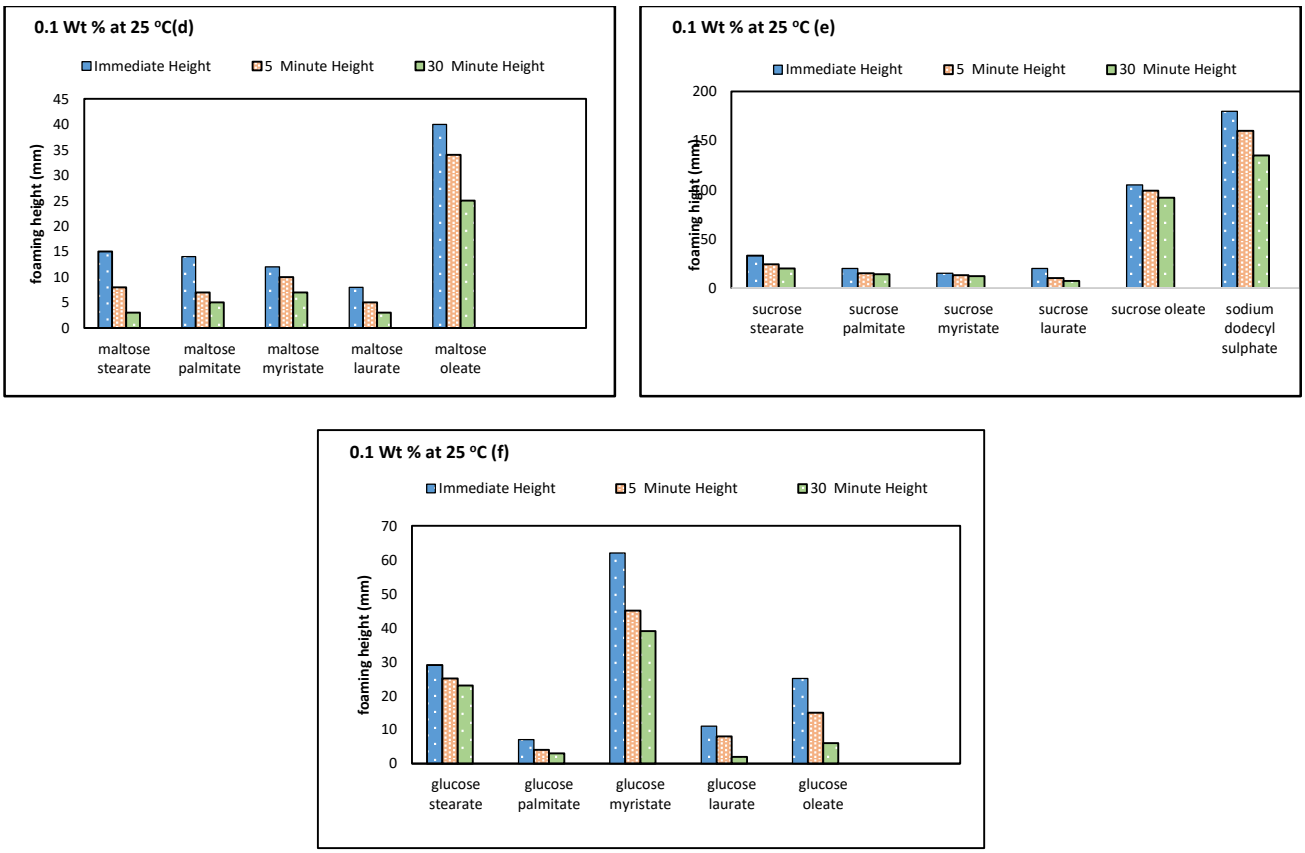

Fig. 16. (d, e, f) Foaming height of maltose, sucrose, and glucose fatty acid ester at concentration (0.1wt%) and 25°C

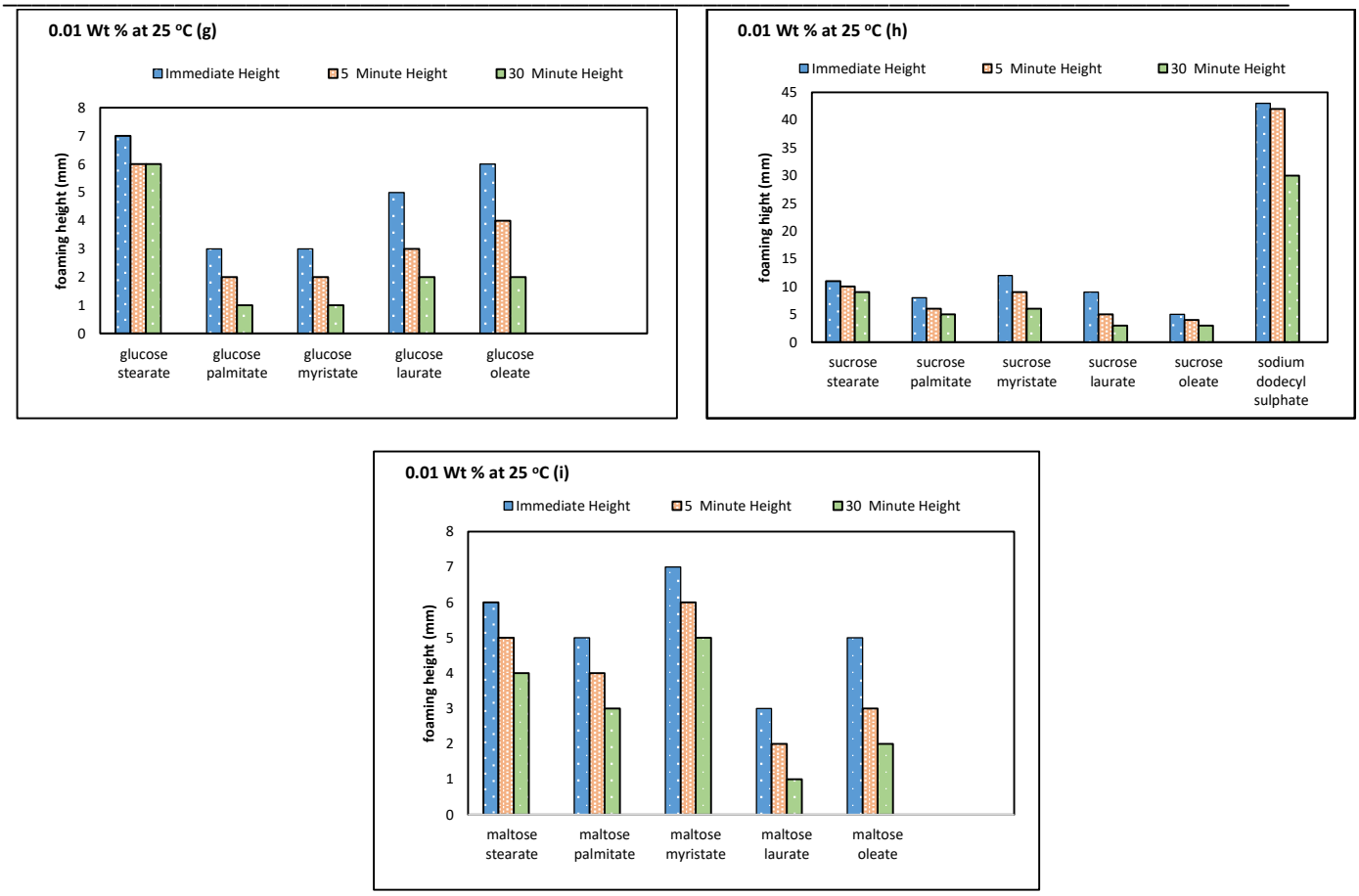

Fig. 17. (g, h, i) Foaming height of glucose ,sucrose, and maltose fatty acid ester at concentration (0.01wt%) and 25°C

Wetting power

Working properties of the sugar esters in this study, were examined using the modified Draves test [57] . Again, the drop penetration test developed by Savage et.al[58] was also employed as a screening method for a valuation of wetting capabilities. The data (**Table 7)** indicates that all sugar esters displayed effective wetting at both concentration (0.1% and 0.01% w/w) of the test samples compared with distilled water. These compounds have great ability to reduce the time of wetting of cotton skein to about 60-48 seconds at 0.1% w/w concentration at 25^0C, compared with water (185 seconds). Rewet values, which served to confirm these results showed that, as expected, rewet times were shorter than the wetting periods, although they follow the same trend. Again wetting efficiency increased with shorter chain length of the hydrophobic acyl substituent, irrespective of the structure of the hydrophilic (sugar) head group. This is parallel to the ability of these products to decrease the surface and interfacial tension by decreasing the hydrophobic chain length. Also, it was early reported [79] that wetting properties are attributed to the hydrophobic part and not improved by the structure of the polar head group. Generally, esters embodying a twelve-carbon acyl chain substituent displayed the best wetting properties.

Emulsification

Sugar esters reduce the surface and interfacial tension, between immiscible liquids so, facilitating the generation of emulsion through the formation of dispersed oil droplets in water as dispersion medium, in case of oil in water emulsion type. [76]. The synthesized sugar esters displayed distinct emulsifying abilities, as shown by longer emulsion persisting times **(Table7)**. Generally, sugar ester become more hydrophobic as the carbon number of the acyl chain increases and therefore its solubility in oils and fats increased. For instance, those embodying saturated, or mono-unsaturated18 carbon side-chain length can produce emulsions that remain stable for 17 and 19 days, respectively. Overall, the data of this study indicate that the candidates bearing long-acyl chain exhibit better emulsifying. Thus, this study suggests that the results obtained may serve as a guide for the development of esters with appropriate emulsifying properties with desirable stability for the particular type of food or cosmetic preparations by selecting the sugar with appropriate length of acyl chain.

Grease removal properties

The performance characteristics of sugar esters including wetting, foaming and emulsification are collectively factors contributing to the detergency process.

In this study, a grease removal test was developed as a typical method for examination of house- hold cleaning and detergency processes. The synthesized esters evaluated with respect to their tendency for removing of oil from wool samples soiled with olive oil. **Table 8** clearly revealed that they possess a great potential in grease removal. This effect was particularly obvious when these products were compared with sodium dodecyl sulphate (SDS) a well-known detergent ingredient. The percentage oil removal from wool ranged from 55% to 88% compared with that from SDS (about 94%).

More specifically, lauroyl and myristoyl derivatives of either sucrose, maltose or glucose possess the greater capability in grease removal reaching 88.24%-85.29%: 87.65% -76.47and 82.35-70.59%, respectively.

The results suggest that they can be used as efficient and safe cleaning ingredients in house- hold detergents and cosmetic preparations as they are synthesized from natural and non-irritable substrates.

Biodegradation

Biodegradation is the breakdown of complex organic materials into environmentally acceptable simpler molecules, such as water, carbon dioxide and biomass by the action of naturally available living microorganisms (bacteria and fungi) under normal environmental conditions eventually, returning the molecules into environment. The course of biodegradation in this study, was followed by measurement of the increase in surface tension as a function of time [61](**Table 9).**The rate of biodegradation of sugar esters bearing 12 to 18 carbon atoms was compared with sodium dodecyl sulphate (SDS) control. Complete loss of surface activity of the prepared sucrose esters was attained within 5-6 days, which prove the accomplishment of the period required for biodegradation. There is virtually no significant difference in the rate of biodegradation between the varying candidates of these homologous series of sugar esters.

***Table* 7.** Wetting time, emulsification stability, cloud point, kraft point and HLB of different sugar esters.

Samples no.	Wetting 0.1% sec.	Re wetting 0.1% sec.	Wetting0.01%	Re wetting 0.01%	wetting	Re wetting	Emulsion stability											Kraft point	Cloud point	HLB
							0	5 min	15	30	1 h	2 h	3 h	4 h	5day	16day	17day	19 day			
Dis. H2O	194	96			24 sec																
SS	60	31	62	33	14	7	6.5ml	6	5.5	5.5	5	2	1.5	1	0.5	disappear			58	46	11.25
SP	54	27	55	29	13	6	6.5	5	5	5	2.5	2.5	2.5	2.5	2.5	disappear			55	40	11.78
SM	51	17	52	18	12	6	6.5	4.5	3	3	3	2.5	1	disappear after 36 hours					48	39	12.39
SL	49	15	50	16	10	5	6	4	1	0.5				disappear					44	37	13.05
SO	55	28	56	29	11	7	6.5	6	4.5	3	2.5	2	2	2	1			disappear	32	19	11.29
MS	55	22	56	23	15	10	6 ml	4	4	3.5	2	2	1.5	1	0.5	disappear			55	40	11.25
MP	52	20	54	21	16	9	5.5	4	3.5	2	1.5	1.5	1.5	2.5	2.5	disappear			54	37	11.78
MM	50	14	53	16	15	8	6.5	5	3.5	3	2	2	2	0.5	disappear				48	36	12.39
ML	48	11	50	13	11	7	6	5	1	0.5				disappear					45	32	13.05
MO	53	19	55	20	15	9	6.5	4.5	3.8	3.4	3.3	3.3	3.3	3.3	disappear				37	18	11.29
GS	54	18	55	20	15	9	6.5ml	4.5	4.5	4.5	4.5	4.5	4.5	4.5	3	disappear			47	37	8.07
GP	51	13	53	17	11	8	5.5	3	3	3	2.5	2		disappear					42	36	8.61
GM	50	15	53	19	9	5	5.5	5	4	4	4	3		2	disappear				39	32	9.23
GL	51	14	54	16	10	5	5.5	4	3.5	3.5	1			disappear					38	30	9.94
GO	51	17	53	22	12	6	6	5	5	4.5	4.5	4		disappear					36	16	7.79
SDS	13	7 sec	15	8 sec	6	4															

***Table.* 8** grease removal power of different sugar esters

Acyl radical	Grease removal %			
	Sucrose	**Maltose**	**Glucose**	**SDS**
S	52.94 %	54.7 %	55.88 %	94.12 %
P	58.82 %	73.53 %	64.71 %	
M	85.29 %	76.47 %	70.59 %	
L	88.24 %	87.65 %	82.35 %	
O	55.88 %	56.47 %	58.82 %	

S= stearate, P= palmitate, M= myristate, L= laurate, O= Oleate, SDS= sodium dodecyl sulphate

Table. 9 *Biodegradability of different sugar esters.*

Sugars	Acyl radical	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
Sucrose	Stearate	45	50	56	60	65	71	71	71
	Palmitate	44	50	55	59	65	69	69	69
	Myristate	43	51	57	62	65	71	71	71
	Laurate	42	49	55	61	67	71	71	71
	Oleate	46	53	56	62	67	69	69	69
Maltose	Stearate	46	52	58	63	68	70.5	70.5	70.5
	Palmitate	45	51	56	61	67	69.5	69.5	69.5
	Myristate	44	52	57	60	65	70	70	70
	Laurate	42	49	56	64	69	71	71	71
	Oleate	47	53	58	64	69	70	70	70
Glucose	Stearate	47	55	59	63	68	69	70	70
	Palmitate	46	53	58	62	67	69	69	69
	Myristate	44	55	59	65	68	70	71	71
	Laurate	45	54	58	64	69	70	71	71
	Oleate	48	53	59	63	69	70	70	70

Where (R.W) river water

Antimicrobial Activity

The study of the of sugar esters is a feature that can be exploited in the preservation of food[16] this activity is believed to be due to the capability of sugar esters to rupture bacterial cell membranes [80].

In order to ascertain the antimicrobial efficiency against pathogenic microorganisms, the in vitro antimicrobial activity of the synthesized sugar esters was evaluated by measuring the inhibition zone. Different Gram positive and Gram-negative bacteria were tested including the Gram-positive bacteria *Bacillus subtilis, Staphylococcus aureus* as well as the Gram-negative *Salmonella typhimurium*, *klebsiella pneumonia* and *pseudomonas aeruginosa*. Together with the fungus, *candida albicans.* The results presented in (**Table 10)** showed that the synthesized sugar esters possess varying antimicrobial effects against the tested microorganisms, Gram -positive bacteria were found to be the most vulnerable, which is in agreement with other reports. [80,81]. In general, sugar fatty acid esters tested, showed greater inhibition activity especially against Gram -positive bacteria.

On the other hand, the Gram-negative bacteria were more or less resistant to some esters of this study probably due to the structure of the outer cell membrane of these bacteria which restrict diffusion of these molecular structures through their liposaccharides covering membrane. The data obtained revealed that the shorter length of the side-chain displayed the greater inhibition activity especially against *Staphylococcus aureus*. The inhibition zone reached 12,25,30 mm in lauroyl sucrose, maltose and glucose esters, respectively. Similarly , it was reported that the antimicrobial effects of fructose esters decreased as the aliphatic side chain increase [82] .This is consistent with our findings that sugar esters with the smaller carbon chain length (lauroyl derivatives C_{12}) had greater potential inhibition activity. Thus, it seems that the carbon chain length of the side group was the most important factor influencing the surface properties [83].

Given the foregoing results, The antimicrobial properties in addition to the emulsifying and foaming performance. The synthesized sucroesters may have promising future in food preservation and cosmetic manufacturing industries.

Table. 10 *ANTIMICROBIAL ACTIVITY*

Sample ID / Microorganism used	SL	ML	GL	SM	MM	GM
Inhibition Zone (mm)						
Escherichia coli (ATCC25922)	15	non	20	non	non	non
Salmonella typhimurium (ATCC14028)	9	non	8	non	non	non
Klebsiella pneumonia (ATCC13883)	16	17	18	non	non	non
Pseudomonas aeruginosa (ATCC17853)	non	non	non	non	non	non
Bacillus subtilis (NRRL B-543)	15	13	14	non	non	non
MRSA Staphylococcus (ATCC4330)	11	8	10	non	non	non
Staphylococcus aureus (ATCC25923)	12	25	30	non	non	non
Candida albicans (ATCC10231)	non	non	non	non	non	non

Where: (SL) Sucrose laurate ester, (ML) Maltose laurate ester, (GL) Glucose laurate ester, (SM) Sucrose myristate ester, (MM) Maltose myristate, (GM) Glucose myristate. *Non: No activity

Conclusions

In this study, a reliable efficient procedure involving a base-catalyzed transesterification of sugar and methyl esters of long- chain fatty acids was presented for a solvent-free synthesis of sugar esters. However, since in process design the operation parameters should be optimized, the first goal of this work was to investigate the effect of reaction temperature, time, mol ratio of the reactants as well as the catalyst on the production of sugar esters. A total sugar esters (SE) yield of about 85% with a methyl ester conversion of near 90% could be obtained using K_2CO_3 as a catalyst when the reaction was performed at nearly ambient temperature (40-45°C) for 3 hrs. After realizing that the reaction media were successful enough for the esterification, then homologous series of acyl sucrose, maltose and glucose monoesters incorporating side- chains of varying lengths 12-16 carbon atoms were synthesized, using operationally the same optimum conditions. The structure of the different sugar esters was characterized and confirmed by Fourier transform infrared (FTIR) and Proton magnetic resonance (^{1}HNMR) spectroscopic examination.

The air- water surface tension vs sugar ester concentration were measured and surface active parameters, critical micelle concentration (CMC), minimum area per molecule (A_{min}), efficiency (PC_{20}) and surface excess concentration (Γ_{max}),were calculated from the Gibbs equation. Other surface-active performance such as foamability, wetting power and emulsifying characteristics were evaluated. It was found that such sugar esters embodying appropriately hydrophobic acyl side-chain display excellent surfactant effects, especially as oil water emulsifiers and high foamability. and unique wetting power. The performance of these sugar esters as surfactants is largely determined by the length of the associated acyl chain. The structure-property profile, as established in the present study indicated that, when the length of the acyl chain increased, their HLB values, CMC and water solubilities (as indicated by the cloud point and kraft point) decreased. Furthermore, esters with medium acyl chains (those embodying 12or14carbons) display the best foamability and foaming stability. The stability of emulsion increased as the acyl chain became longer.

In addition, all sugar esters bearing a side chain of 12 carbon atoms inhibited the growth of various microorganism, in particular Gram-positive bacteria.

The results of this study clearly summarize that the protocol applied for the synthesis of the sugar esters using the solvent-free transesterification of the carbohydrate moiety with methyl fatty acid ester is efficient, simple and reliable.

There are distinct advantages associated with such approaches, given that they are green, less energy-demanding and produced from low-cost renewable substrate. In addition to their easy biodegradability, antimicrobial and biological activities, such compounds are likely believed to be useful as food additives, drug carriers, cosmetics, and cleaning agents.

Conflicts of interest "There are no conflicts to declare".
Funding sources "There are no funding sources to be listed".

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