Synthesis of Sucrose Fatty Acid Esters by Using Mixed Carboxylic-fatty Anhydrides

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Abstract: Fatty acid sugar esters are non-ionic surfactant active agents with excellent performance and many uses. This work is devoted to the synthesis of sugar esters by the esterification reaction of sugar with mixed carboxylic-palmitic anhydrides using resin Amberlyst-15 as heterogeneous acid catalyst. These anhydrides should be stable and react as acylating agents. Influence of different reaction parameters, such as the molar ratio (sucrose/anhydride), the type of solvent and the reaction time on the yield of the esterification reaction were studied. The esterification reaction of sucrose with mixed palmitic benzoic anhydride leads to a mixture of sucrose esters of palmitic acid with a good percentage of conversion. The mixed anhydride was both reactive and selective for the preparation of fatty acid ester.

Key words: fatty acid, mixed anhydride, heterogeneous acid catalyst, resin Amberlyst-15, esterification, sucrose, acylation of sucrose, sucrose fatty acid esters (SEs)

1 Introduction
Sucrose fatty acid esters (SEs), commonly called sugar esters, are nonionic surfactants that have excellent emulsifying, stabilizing, detergency and other useful effect[1–4]. Sugar esters are attractive because of their ready biodegradability, low toxicity and low irritation to eyes and skin[5–7]. They have a large number of applications in industry such as the pharmaceutical, cosmetic, detergent and food[8–10]. In addition, their antimicrobial, antitumoral and insecticidal properties have been reported and might open new markets[11]. The sucrose esters (SEs) are consisted from natural raw materials: sucrose as hydrophilic group and fatty acids as lipophilic groups[12]. Sucrose has eight hydroxyl groups, which allow the formation of esters from monooesters to octaesters with different fatty acid[8–10]. Sucroesters can be synthesized either by using chemical or enzymatic processes[1, 2]. The chemical process is generally performed at high temperature in toxic solvents which leave traces in the products, which is accompanied by low selectivity toward the various hydroxyl groups in sugars and forming coloured derivatives as side-products[3–4, 11, 14, 15]. Product of chemical synthesis is often an undefined and complex mixture of mono-, di- and poly-esters, which is difficult to be characterized with respect to its physical properties and surfactive[1, 2, 14]. Sugar esters are synthesized by esterification of sugars or sugar alcohols with fatty acids[1]. Because the esterification is a reversible reaction, mixed anhydrides have been often employed in order to obtain a high yield of ester[16]. Mixed anhydrides obtained from two different carboxylic acids are molecules finding an increasing interest in the chemical industry due to their high reactivity[17, 18].

The objective in this work is to develop new techniques for the synthesis of sugar fatty acid esters by chemical means allowing the production of economic compounds (raw materials and manufacturing processes) and environmentally friendly.

This work is devoted to the development of new reaction pathways for obtaining a sucrose fatty acid ester using mixed carboxylic-fatty anhydride in the presence of ion exchange resins (Amberlyst-A15) as a catalyst.

2 Experimental
2.1 Synthesis of sucrose octaacetate
2.1.1 Acylation reaction of sucrose solvent-free
5 g (0.014 mol) of sucrose, 100 mL (1.055 mol) of acetic anhydride used as reactant and solvent in the reaction and 2 g (9.4 meq/g) of resin Amberlyst A-15 as catalyst were charged in a 250 mL flask. The reaction mixture was stirred for 6 hours in oil bath at 50–55 °C.

When the reaction was completed, the reaction mixture was filtered and the Amberlyst-15 washed 3 times with...
acetic anhydride (10 mL). The organic phase was slowly added to 600 mL of a mixture (water/ice) then allowed to stand for 12 hours. The syrup formed in this period was separated from the aqueous phase. The aqueous phase was extracted 3 times with 30 mL of chloroform. The chloroform separated from the aqueous phase. The aqueous phase was stand for 12 hours. The syrup formed in this period was

The acylation reaction was determined by calculating the ratio between the mass of sucrose octoaceate (after recrystallization) and the theoretical mass of ester formed.

### 2.1.2 Acylation reaction of sucrose in solvent

5 g (0.014 mol) of sucrose, 20 mL (0.527 mol) of acetic anhydride and 2 g (9.4 meq/g) of resin Amberlyst A-15 as catalyst were added in a 250 mL flask. The reactants were placed in an organic solvent such as dichloromethane, diethyl ether, hexane and chloroform. The mixture was then stirred under refluxing of the solvent. At the end of the reaction, the mixture reaction obtained was treated in the same manner as before until a dry product was obtained. The products recrystallized were weighed and analyzed by IR and $^{13}$C NMR spectroscopy. The yield of the acylation reaction was determined by calculating the ratio between the mass of sucrose octoaceate (after recrystallization) and the theoretical mass of ester formed.

### 2.2 Synthesis of sucroesters by mixed benzoic-palmitic anhydride

3 g (8.33 $10^{-3}$ mol) of crude mixed benzoic palmitic anhydride, 2 g, 0.5 g then 0.3 g of sucrose corresponding respectively to the molar ratios (sucrose/anhydride) (1:1.5), (1:6) and (1:10) and 2 g (9.4 meq/g) of Amberlyst-15 were stirred under reflux of organic solvent such as hexane and cyclohexane. After completion of the reaction, the reaction mixture was filtered and the Amberlyst-15 resin was washed with the organic solvent (20 mL). The solvent was then evaporated to dryness and the crude product was weighed and analyzed by IR, $^{1}$H NMR and $^{13}$C NMR.

### 2.3 Spectroscopic analysis

The FT-IR spectra of the crude products were recorded on a spectrometer type Perkin Elmer Spectrum version 10.

The NMR spectra of the crude products were recorded in solution in CDCl$_3$ on a spectrometer type Bruker Avance III HD ($^1$H at 400 MHz and $^{13}$C at 100 MHz).

### 3 Results and Discussion

In a previous work, we have studied the synthesis of fatty esters by the esterification with mixed carboxylic palmitic anhydrides. These anhydrides characterized by the general formula C$_{15}$H$_{31}$COOCOR can be easily prepared by the reaction of palmitic acid with aliphatic or aromatic acid chloride in the presence of triethylamine and in organic solvent$^{18}$. The esterification reaction of primary, secondary and tertiary alcohols with mixed aliphatic palmitic anhydride and mixed aromatic palmitic anhydride was realized in the presence of resin Amberlyst-15 as heterogeneous acid catalyst. We have showed that the palmitic group of the mixed carboxylic palmitic anhydride was the most involved in the esterification reaction and the leaving of the alkyl or aryl group of the mixed anhydride. The preferential esterification of alcohol was realized by the palmitic group of mixed carboxylic palmitic anhydride and the obtained palmitic esters were produced with good yields. We have found that the mixed aliphatic palmitic anhydrides were less reactive and less selective than their mixed aromatic palmitic anhydrides$^{19, 20}$. Among tested mixed aromatic palmitic anhydrides, we have chosen the mixed benzoic palmitic anhydride in the esterification reaction of sucrose using resin Amberlyst-15 as heterogeneous acid catalyst.

#### 3.1 Synthesis of sucrose octoacetate

We have taken first, as a simple model of anhydride: acetic anhydride in the acylation reaction of sucrose in the presence of a catalyst. We have studied the influence of the main experimental parameters such as the molar ratio (sucrose/acetic anhydride) and the type of solvent on the yield of the acylation reaction.

##### 3.1.1 Effect of type of solvent

We have studied the effect of type of solvent on the yield of sucroesters. The acylation reaction involves the exchange of the (OH) group of the sucrose by the (OCOCOR) group of the acetic anhydride in the presence of an ion exchange resin Amberlyst-15 as heterogeneous catalyst. The reaction mixture was stirred for 6 hours at a temperature of 50-55°C (without solvent) or under reflux of solvent as indicated in Scheme 1.

The acylation reaction was carried out with a large excess of acetic anhydride used as reactant and solvent. Then, we introduced an organic solvent in the reaction medium to facilitate the contact between the reactants and to ensure the better reactivity. Solvents of different polarities were used while keeping the same procedure. The yields of recrystallized products were resumed in the Table and the structure of these products was confirmed by IR and $^{1}$H and $^{13}$C NMR analysis.

The IR spectra of recrystallized products show the disappearance of the C = O absorption bands characteristic of the acetic anhydride and also the disappearance of the OH absorption band of the sucrose at 3400 cm$^{-1}$. These
spectra show the appearance of new C = O absorption band corresponding to sugar ester at 1756 cm⁻¹. The ¹³C NMR spectrum is in agreement with the structure of the desired compound. The 8 peaks corresponding to 8 carbonyls (C = O) are observed between 165 and 167 ppm which proves that all the OH groups of sucrose are acylated. The analysis by ¹H NMR confirmed also that the recrystallized product is sucrose octaacetate. The ¹H NMR spectrum shows the signals between 4 and 5.7 ppm corresponding to 14 protons of the sucrose molecule and a multiplet at 2.1 ppm corresponding to 24 protons relative to 8 CH₃ groups.

The yield of the recrystallized product obtained by the acylation of sucrose with acetic anhydride without solvent is 37% (Table 1, entry 1). Solvents of different polarities were introduced into the reaction mixture to facilitate the contact between the reactants. From the results given in the Table 1, the yield obtained in the case of acylation with acetic anhydride, catalyzed by the Amberlyst-15 resin, does not exceed 43% after treatment and the purification of the crude product. The best yield of sucrose octaacetate is obtained in the case where the reaction is carried out in hexane followed by the reaction in chloroform (Table 1, entry 2: 43% and entry 5: 38%). A low yield is obtained in the case of where the reaction is carried out in dichloromethane and diethyl ether (Table 1, entry 3: 25% and entry 4: 22%).

However, it is pertinent to note that the acylation in hexane results in a significant yield than when performed in chloroform. Chloroform and hexane are solvents of different polarities. This led us to keep the same experimental protocol, and try to improve the ester yield, by acting on the polarity of the reaction medium. We carried out a series of acylation reactions in a 20 mL mixture of the solvent (hexane:chloroform) as shown in Table 2.

It is found that the variation in the volume ratio of the solvent mixture (chloroform:hexane) in the acylation reaction did not improve the yield of sucrose octaacetate (Table 2, entry 2: 21%, entry 3: 27% and entry 4: 22%). The best yield of sucroester is obtained in the case where the reaction is carried out in 20 mL of hexane (Table 2, entry 1: 43%).

3.1.2 Effect of the molar ratio (sucrose/anhydride)

We have studied the effect of the molar ratio (sucrose/anhydride)
Table 3 Effect of molar ratio (sucrose/anhydride) on the yield of acylation.

| Entry | Solvent     | Volume of acetic anhydride (mL) | Molar ratio (sucrose/anhydride) | Yields (%) |
|-------|-------------|---------------------------------|---------------------------------|------------|
| 1     | Chloroform  | 10                              | 1:19                            | –          |
| 2     | Chloroform  | 20                              | 1:38                            | 38         |
| 3     | Chloroform  | 30                              | 1:57                            | 32         |
| 4     | Chloroform  | 10                              | 1:19                            | –          |
| 5     | Hexane      | 20                              | 1:38                            | 43         |
| 6     | Hexane      | 30                              | 1:57                            | 34         |

anhydride) on the yield of sucroesters. We have varied the molar ratio (sucrose/anhydride) fixing the other experimental conditions such as the volume solvent at 20 mL, time reaction and temperature to improve the yield of sucrose octaacetate. Spectroscopic analysis IR and (1H and 13C) NMR show that the recrystallized products are sucrose octaacetate. The yields of sucrose octaacetate were resumed in the Table 3.

The best yield of sucroester is obtained in the case where the reaction is carried out in hexane with a molar ratio (sucrose/anhydride) that equal to 1:38 (Table 3, entry 5: 43%). Less important yield is obtained in the case where the reaction is carried out in chloroform (Table 3, entry 2: 38%). When the molar ratio (sucrose/anhydride) is increased to (1:59), the yield of sucrose octaacetate decreases in the case where the reaction is carried out in hexane and chloroform (Table 3, entry 3: 32% and entry 6: 34%). The variation in molar ratio (sucrose/anhydride) in the sucrose acylation reaction did not improve the yield of sucroesters.

Acylation of sucrose with acetic anhydride in the presence of an ion exchange resin Amberlyst-15 as heterogeneous catalyst leads to a sucrose octaacetate with a yield of 43%. The reaction is carried out in 20 mL of hexane and with molar ratio (sucrose/anhydride) (1:38).

It is found that the best acylation yield exceeds slightly 40% (entry: 1) after treatment and purification of the crude reaction. This is probably due to side reactions that can occur in parallel with acylation as hydrolysis and sucrose polymerization. Although we worked in an anhydrous medium with well-dried reagents and distilled solvents (to remove all traces of water), the risk of these reactions is always maintained.

3.2 Synthesis of sugar esters by mixed benzoic-palmitic anhydride

In the second part, the esterification reaction is carried out by the action of the benzoic palmitic anhydride already prepared as indicated in the article9,20 on sucrose in the presence of an ion exchange resin A-15 as a catalyst in an organic solvent. The main experimental parameters such as the type of solvent, the reaction time and the molar ratio (sucrose/anhydride) have been varied to find the best conditions which favor the progress of this reaction.

Sucrose contains three primary and five secondary hydroxyl groups. We have assumed that the esterification of the OH groups of sucrose by the palmitic group. The palmitic group of the mixed carboxylic palmitic anhydride was the most involved in the esterification reaction of primary and secondary alcohols and the leaving of the aryl group of the mixed benzoic palmitic anhydride. In addition, the formation rate of benzoic ester was much slower than that of aliphatic acid ester when we used the mixed anhydrides as reagents of esterification9,20.

3.2.1 Effect of molar ratio (sucrose/anhydride) and reaction time in hexane

The action of mixed benzoic-palmitic anhydride on sucrose with the molar ratios (sucrose/anhydride) (1:1.5) and (1:6) in the presence of resin Amberlyst-15 was stirred under reflux hexane for 16 hours. During this period, Samples are taken at different times (6 h, 8 h, 10 h, 12 h and 16 h) for both reactions. Each sample is analyzed by IR. The IR spectra show no difference for each sample at (6 h, 8 h, 10 h, 12 h and 16 h) for both reactions (Fig. 1 and Fig. 2).

The IR spectra (Fig. 1 and Fig. 2) show the disappearance of the C=O absorption bands of the mixed benzoic palmitic anhydride at 1725 and 1795 cm⁻¹ and the disappearance of the OH absorption band at 3400 cm⁻¹ of sucrose. These spectra also show the appearance of two new C=O absorption bands at 1744 cm⁻¹ of sugar ester of the palmitic acid and at 1685 cm⁻¹ of palmitic acid and benzoic acid. It has a OH broad band absorption between 2550 and 2670 cm⁻¹ of acid and a C-O absorption band between 1150 and 1300 cm⁻¹ of the sucroester.

These spectra show, in fact, just traces of palmitic acid sugar ester. It is found that increasing the ratio (sucrose/anhydride) from (1:1.5) to (1:6) causes a slight increase in the C=O absorption band characteristic of the sugar ester of the palmitic acid.

3.2.2 Effect of molar ratio (sucrose/anhydride) in cyclohexane

To improve the yield of the sucroester, the hexane organic solvent was changed by cyclohexane. The esterifi-
cation reaction of sugar is carried out with a molar ratio (sucrose/anhydride) \(1:6\) to \(1:10\) for 6 h. The products obtained at the end of the reactions are analyzed by IR as shown in Fig. 3 and Fig. 4.

The IR spectra (Fig. 3 and Fig. 4) show the absence of the \(\text{C}=\text{O}\) absorption bands of the mixed benzoic palmitic anhydride at 1725 and 1795 cm\(^{-1}\) and the absence of the OH absorption band at 3400 cm\(^{-1}\) of sucrose. These spectra also show the appearance of two new \(\text{C}=\text{O}\) absorption bands at 1744 cm\(^{-1}\) of sugar ester of palmitic acid and at 1685 cm\(^{-1}\) of palmitic acid and benzoic acid. They present a OH broad band absorption between 2550 and 2670 cm\(^{-1}\) of acid and a C-O absorption band located between 1150 and 1300 cm\(^{-1}\) of sucrester.

The IR spectra (Fig. 3 and Fig. 4) of the crude products obtained at the end of the reaction, when the molar ratio (sucrose/anhydride) of \(1:6\) to \(1:10\) is increased, show an increase in the \(\text{C}=\text{O}\) absorption band at 1744 cm\(^{-1}\) of the sugar ester of palmitic acid.

The crude product obtained with a molar ratio (sucrose/anhydride) \(1:10\) in cyclohexane is then purified by column chromatography to obtain the sugar ester of palmitic acid. The crude product dissolved in the minimum of the dichloromethane solvent is deposited at the top of the column.
The column is washed with a solvent mixture (dichloromethane/ethanol) (90/10, v/v). The palmitic acid sugar ester obtained is a white solid and then analyzed by IR, $^1$H and $^{13}$C NMR as shown in Fig. 5, Fig. 6 and Fig. 7.

The IR spectrum of the sugar ester of palmitic acid (Fig. 5) shows the disappearance of the C=O absorption band at 1685 cm$^{-1}$ of benzoic acid and palmitic acid and the absence of the OH absorption band at 3400 cm$^{-1}$ of sucrose. It also shows the appearance of the C=O absorption band at 1742 cm$^{-1}$, the C-O absorption band at 1162 cm$^{-1}$ relating to the function of the sugar ester of palmitic acid and the C-H absorption band between (2850-2950 cm$^{-1}$) arising from the palmitic acid chain.

The $^{13}$C NMR spectrum of the palmitic acid sucrose ester (Fig. 6) shows, in particular, peaks between 14 and 35 ppm which correspond to the carbons of CH$_3$ and CH$_2$ groups of the palmitic acid, peaks between 55 and 110 ppm which correspond to the carbons of sucrose, peaks between 125 and 135 ppm which correspond to –C=O and 8 peaks corresponding to C=O groups between 170 and 175 ppm. It appears that in our operating conditions all OH groups available in the molecule of sucrose have been esterified.

The $^1$H NMR spectrum of sucrose ester of palmitic acid...
(Fig. 7) shows the protons of sucrose coming of the esterification of mixed benzoic palmitic anhydride. This spectrum shows that the purified product is a mixture of palmitic acid sucroesters. It shows the presence of three doublets of a single proton of hydrogen atom ($^1$H) of sucrose skeleton at 5.9, 6.4 and 6.6 ppm. The polyfunctionality of sucrose plays a very important role in the reaction complexity. The physicochemical properties of sucrose are complex. The multifunctional structure posed difficulties in the experimental study.

4 Conclusion
This paper describes the new techniques for the synthesis of sugar fatty acid esters by chemical means. We have studied the synthesis of sucrose esters by esterification of sucrose using two types of anhydride: symmetrical anhydride (acetic anhydride) and mixed anhydride (mixed palmitic benzoic anhydride) in the presence of an ion exchange resin Amberlyst-15 as a heterogeneous catalyst. We have improved the yield of the sugar ester by varying several experimental parameters such as solvent type, reaction time and molar ratio (sucrose/anhydride). IR and ($^1$H and $^{13}$C) NMR spectroscopic analysis show that the esterification reaction of sucrose with acetic anhydride leads to a
single product sucrose octaacetate. On the other hand, the esterification reaction of sucrose with mixed palmitic benzoic anhydride leads to a mixture of sucrose esters of palmitic acid.

Supporting Information
This material is available free of charge via the Internet at http://dx.doi.org/jos.69.10.5650/jos.ess19239

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