



Original Research Article

View Article Online | View Journal

## Highly Efficient SO<sub>3</sub>H-Carbon Catalysed Solvent-Free Synthetic Protocol for Wax Esters *Via* Esterification of Long Chain Fatty Acids and Alcohols

B. L. A. Prabhavathi Devi\*, K. Vijayalakshmi, T. Vijai Kumar Reddy

Department of Oils, Lipid Science & Technology CSIR- Indian Institute of Chemical Technology, Tarnaka, Uppal Road, Hyderabad - 500007, India

### ARTICLE INFORMATION

Submitted: 10 May 2023  
 Revised: 30 May 2023  
 Accepted: 01 June 2023  
 Available online: 09 June 2023  
 Manuscript ID: [AJGC-2305-1390](#)  
 Checked for Plagiarism: [Yes](#)  
 Language Editor:  
[Dr. Fatimah Ramezani](#)  
 Editor who approved publication:  
[Dr. Ali Ramazani](#)  
 DOI: [10.22034/ajgc.2023.396739.1390](#)

### KEYWORDS

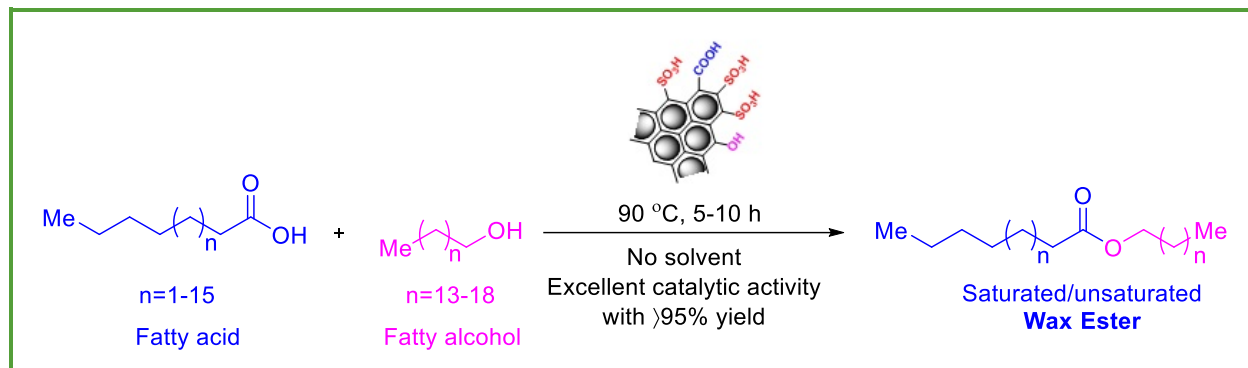
Cetyl esters  
 Oleic acid  
 Cetyl alcohol  
 Solid acid catalyst

### ABSTRACT

Solvent-free synthesis of saturated and monounsaturated wax esters (WEs), 3a-j with carbon chain ranging from C<sub>26</sub> to C<sub>38</sub> was successfully demonstrated through esterification of long chain fatty acids (LCFAs), **1a-g** (C<sub>10:0</sub>, C<sub>12:0</sub>, C<sub>16:0</sub>, C<sub>18:0</sub>, C<sub>18:1</sub>, C<sub>18:1,12-OH</sub>, C<sub>22:0</sub>, and C<sub>22:1</sub> acids) with long chain fatty alcohols (LCFAlc), **2a-d** (cetyl (C<sub>16</sub>), stearyl (C<sub>18</sub>), behenyl (C<sub>22</sub>) and erucyl (C<sub>22:1</sub>) alcohols) by SO<sub>3</sub>H-carbon catalyst derived from glycerol. The optimized reaction conditions for the efficient synthesis of WEs with excellent conversion and selectivity recorded in solvent free system are: 20 wt.% of SO<sub>3</sub>H-carbon catalyst, reaction time of 6-10 h, temperature of 90 °C and substrate (LCFA:LCFAlc) molar ratio of 1:1. All the synthesized WEs were purified by silica gel column chromatography and characterized by FTIR, <sup>1</sup>H-NMR, and GC-MS spectral studies. In addition, this methodology involves simple workup protocol, without use of dean stark or dehydrating agents compared to the reported homogeneous/heterogeneous catalysed methods. Furthermore, the resulting synthetic WEs can play a potential alternates for the commercial products extracted from natural sources of lesser availability, thus making this SO<sub>3</sub>H-carbon catalysed route very promising for further potential industrial implementation.

© 2023 by SPC (Sami Publishing Company), Asian Journal of Green Chemistry, Reproduction is permitted for noncommercial purposes.

## Graphical Abstract



## Introduction

Fatty acid methyl/ethyl esters (FAMEs/FAEEs) are suitable for use as biodiesel/biofuels as an environmentally attractive alternative to fossil diesel. Traditionally, these biofuels are industrially produced from plants, animals, or waste cooking oils by transesterification with alcohols in the presence of a base, an acid, or an enzyme catalyst [1].

Whereas, wax esters (WEs) are high-molecular weight long-chain fatty acid alkyl esters composed of long-chain fatty acids (LCFAs) and long-chain fatty alcohols (LCFAlc) with a number of carbon atoms ranging from C<sub>12</sub>-C<sub>32</sub> [2].

The vast majority of WEs are extracted from natural sources, either from vegetable oil/fat or animal origin, including honeycomb, jojoba seeds, carnauba, sperm whale, skin lipids, sheep wool, seafowl feathers, etc. They can be composed of saturated and unsaturated WEs, which determine the liquidity of the chemicals, constitute the WEs. Saturated WEs are predominant in beeswax, and sperm whale oil, whereas, jojoba oil is rich in unsaturated WEs.

WEs are fine chemicals, which are produced in low volume with high value and are widely used as base materials in pharmaceuticals,

lubricants, paints, wood coatings, and cosmetics [3].

Specific novel characteristics of WEs such as biodegradability, non-toxicity, good fat soluble properties, and excellent emollient behavior have maximized their usage in the formulations of numerous personal care products [4].

Seafowl feathers contain a C<sub>24:0</sub>-WE, cetyl octanoate (C<sub>16</sub>-C<sub>8</sub>) as one of the main WEs, which help in protecting the birds from becoming wet and also make the feathers flexible. Due to its excellent moisture retaining ability and non-greasy feeling on the skin, the C<sub>24:0</sub>-WE has wide industrial applications as an oil base in cosmetic formulations [5].

The WEs extracted from sperm whale oil, mostly composed of a C<sub>32:0</sub>-WE, cetyl palmitate (C<sub>16</sub>-C<sub>16</sub>, Figure 1) and is widely used as oil lamp fuel, lubricant, or ingredient for cosmetics. Due to the ban on whale hunting, availability of this oil was stopped, and then Jojoba oil was found to be the main alternative WEs from natural source for commercial applications.

The jojoba oil extracted from the nut of the jojoba bush is mainly composed of WEs with chain length ranging from C<sub>38</sub>-WE to C<sub>44</sub>-WE having monounsaturated fatty alcohol (MUFAlc) and monounsaturated fatty acid (MUFA) moieties. The jojoba-like WEs are highly enriched in >70% oleyl nervonate having C<sub>18:1</sub>-C<sub>24:1</sub>-WE. Hence, jojoba WEs became the

most suitable substitute for the cosmetics sector, mainly in the formulations of moisturizers, shampoos, and conditioner [6]. However, the main obstacles to large-scale use of jojoba WEs in pharmaceuticals and cosmetics are the cost and availability.

Concerning the growing demand for WEs in the food, pharmaceutical and cosmetic industries, methods for chemical or enzymatic synthesis of WEs have been developed. Among the several biocatalytic methods reported so far, the lipase-catalyzed synthesis of WEs by the esterification of fatty acids and alcohols has drawn much attention [4, 7].

Even though, the enzymatic processes are environmentally benign, they suffer from several drawbacks in terms of productivity, scale-up challenges, designing of reactors for selectivity, and catalyst stability.

Generally, the conventional chemical catalyzed production of WEs use homogeneous mineral acids (HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, etc.) and

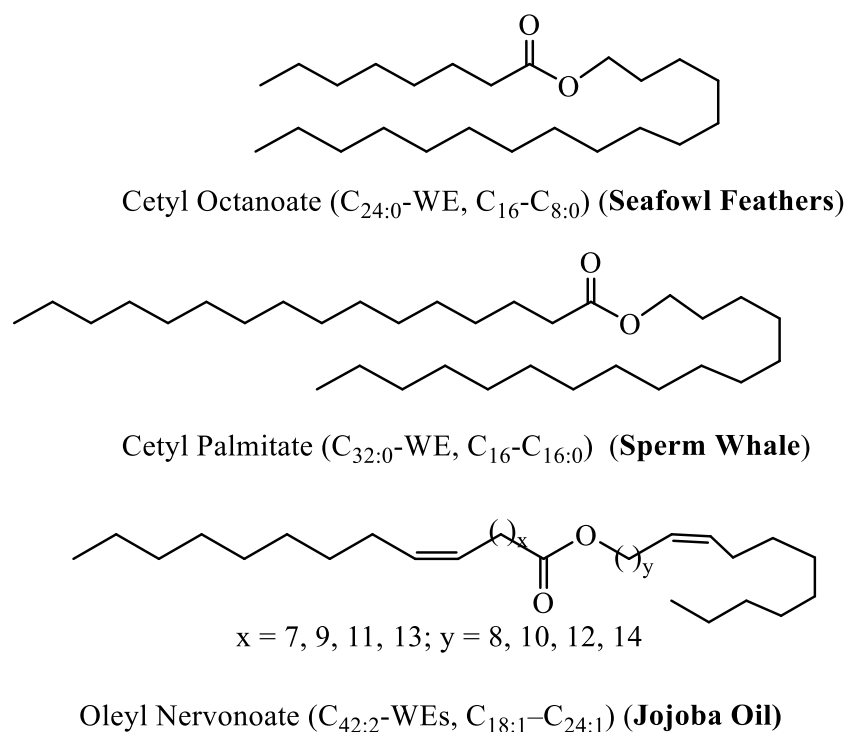
organic acids like (*p*-TSA, CH<sub>3</sub>SO<sub>3</sub>H, ClSO<sub>3</sub>OH, etc.) as catalysts [8].

Lewis acids are further largely employed for the esterification reactions, because they allow mild reaction conditions when compared to Brønsted acids [9].

Recently, Nguyen *et al.* reported homogeneous ruthenium-catalyzed methodology for the WEs synthesis by consecutive hydrogenation-dehydrogenation reactions of fatty acid methyl esters [10].

However, most of these homogeneous acid catalysts have inherent drawbacks and hence, the present tendency is to replace the traditional homogeneous acid catalysts by heterogeneous catalysts as they are environmental friendly with respect to corrosiveness, safety, waste disposal problem, and the ease of separation and recovery.

Several heterogeneous catalysts have been reported for the synthesis of industrially important esters [11].



**Figure 1.** Wax esters found in nature

Most of the reported esterification reactions have been limited to esters with carbon chain <C<sub>10</sub> in either carboxylic acid or alcohols. In addition, various methods have been explored to find novel solid acid catalysts for the WEs preparation. Many researchers have explored several metal chloride salts [12], multi-valent metal salts, ionic liquid choline-chloride.2ZnCl<sub>2</sub>, and acid activated Indian bentonite as catalysts for the WEs synthesis with the use of either dehydrating agent (MgSO<sub>4</sub>) or azeotropic solvent to remove water [13].

On the other hand, the classical chemical/synthetic approaches are typically energy intensive and waste-generating processes. For instance, Sn(IV)-based catalysed process used for the industrial production of WEs requires high temperature, and extensive downstream purification process [14].

Although most of these solid acid catalysts offer distinct advantages over conventional methods in terms of product separation and recycling, they suffer from certain drawbacks such as high cost, long reaction times, poor selectivity, and lower yields of the desired products. Hence, there is a need for the implementation of a novel, selective, and environmentally benign processes for the WEs production from readily available bio-sourced compounds.

Even though there are large number of solid acid catalyzed methodologies reported, 'green' protocols for the WEs synthesis is still in demand. In continuation to our investigations for the applications of developed glycerol/glycerol-pitch based SO<sub>3</sub>H-carbon and SO<sub>3</sub>Na-carbon catalysts for different acid/base catalyzed esterification/ transesterification of fatty acids/triglycerides to biodiesel [15], and other organic transformations [16], the present study reports a begin SO<sub>3</sub>H-carbon catalyzed methodology for the direct ester condensation of equimolar amounts of LCFAs (1a-g) with

LCFAlc (2a-d) to corresponding WEs (3a-j), in excellent yields (90-98%) under solvent free conditions (Table 2).

## Experimental

### Materials and Methods

The chemicals used for the research work are of AR grades and were purchased from SD Fine Chemicals and used without any extra purification. The raw materials needed for the study, such as capric acid, lauric acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, erucic acid, cetyl alcohol, stearyl alcohol, erucyl alcohol, and behenyl alcohol were purchased from Fluka, Switzerland.

Silica gel (60-120 mesh) for column chromatography was purchased from M/s Acme's synthetic chemicals (Mumbai, India) and pre-coated TLC plates (silica gel 60 F<sub>254</sub>) from Merck (Darmstadt, Germany). IR spectra were recorded on a Perkin Elmer (Model: Spectrum BX) FT-IR spectrometer using CH<sub>2</sub>Cl<sub>2</sub> or KBr. All <sup>1</sup>H-NMR spectra were recorded on Varian 200 MHz NMR spectrometer. GC-MS spectra were recorded on Agilent GC-MS 5973 Mass Spectrometer in the EI mode and are given in mass units (*m/z*).

### Preparation of glycerol-based SO<sub>3</sub>H-carbon catalyst

As per our reported method [15], a mixture of glycerol (10 g) and con. H<sub>2</sub>SO<sub>4</sub> (30 g) were taken in a 500 mL glass beaker and gently heated on a hotplate to 180-220 °C for 20 min, to facilitate *in situ* partial carbonization and sulfonation. The reaction mixture was allowed at that temperature for about 20 min till the foaming ceases and the resultant black crystalline carbon material was washed with hot water under agitation till the wash water becomes neutral to pH.

The partially crystalline carbon material was filtered and dried in an oven at 120 °C for 2 h to ensure free of moisture to obtain glycerol-based SO<sub>3</sub>H-carbon catalyst (4.67 g). The catalyst was evaluated for its esterification activity for the preparation of methyl palmitate in quantitative yields at 65 °C in 5 h. The SO<sub>3</sub>H-carbon catalyst was found to have 2.98 mmol/g acid density and 1.5 m<sup>2</sup>/g surface area.

#### General procedure for the preparation of wax esters (WEs)

Equimolar amounts (5 mmol) of palmitic acid (1.28 g) and cetyl alcohol (1.21 g) were taken and SO<sub>3</sub>H-carbon catalyst (0.50 g, 20 wt.% of substrates i.e. FA + FAlc) was added and the resultant reaction mixture was heated at 90 °C under stirring for the specified period of time. After completion of the reaction, the reaction mixture was cooled and ethyl acetate was added and the catalyst was separated by filtration.

The filtrate was concentrated and dried under vacuum to obtain the crude product and was further purified on a silica gel (60-120 mesh) column chromatography eluting with 10% EtOAc in hexane to afford C<sub>32:0</sub> WE cetyl palmitate (2.32 g) in 97% yield. The same procedure was employed for the synthesis of all the WEs (**3a-j**), as listed in Table 1 and yields were found to be varying from 90 to 98% depending on the substrates.

#### Selected spectral data

The prepared wax esters were characterized using different spectral techniques such as FT-IR, <sup>1</sup>H-NMR, IR and GC-MS techniques and the data of most of the esters matches with those reported in the literature [7, 8, 13]. All Proton chemical shifts (δ) are relative to tetramethyl silane (TMS, δ = 0.00) as an internal standard, and coupling constants (*J*) are given in Hz. The

spectral data of some of the WEs prepared (Table 1) are represented as follow.

#### Cetyl palmitate (**3c**, C<sub>32</sub>H<sub>64</sub>O<sub>2</sub>, C<sub>32:0</sub>-WE, entry 3)

FT-IR (KBr, cm<sup>-1</sup>): ν 1734 (-C=O), 1182 (-O-CH<sub>2</sub>-); <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 0.86-0.89 (6 H, br t, CH<sub>2</sub>-CH<sub>3</sub>), 1.24-1.30 (50 H, br s, alkyl-CH<sub>2</sub>-), 1.55-1.65 (4 H, br m, CH<sub>2</sub>-CH<sub>2</sub>-C=O, CH<sub>2</sub>-CH-O-), 2.28 (2H, t, CH<sub>2</sub>-C=O-), and 4.04 (2 H, t, *J* = 6.6 Hz, -O-CH<sub>2</sub>-). Mass (GC-MS): *m/z*, 480 [M]<sup>+</sup>.

#### Cetyl oleate (**3e**, C<sub>34</sub>H<sub>66</sub>O<sub>2</sub>, C<sub>34:1</sub>-WE, entry 5)

FT-IR (KBr, cm<sup>-1</sup>): ν 1735 (-C=O), 1182 (-O-CH<sub>2</sub>-). <sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>): δ 0.86-0.90 (6H, br t, CH<sub>2</sub>-CH<sub>3</sub>), 1.25 (48H, br s, alkyl-CH<sub>2</sub>-), 1.58-1.61 (4H, br m, CH<sub>2</sub>-CH<sub>2</sub>-C=O, CH<sub>2</sub>-CH-O-); 2.13 (2H, m, *J* = 7.5 Hz, CH<sub>2</sub>-HC=CH-CH<sub>2</sub>-), 2.23 (2H, t, CH<sub>2</sub>-C=O), 4.04 (2H, t, *J* = 6.6 Hz, -O-CH<sub>2</sub>-), and 5.28 - 5.32 (2H, br m, -HC=CH-). Mass (GC-MS): *m/z*, 506 [M]<sup>+</sup>.

#### Cetyl ricinoate (**3f**, C<sub>34</sub>H<sub>66</sub>O<sub>3</sub>, C<sub>34:1(12-OH)</sub>-WE, entry 6)

FT-IR (KBr, cm<sup>-1</sup>): ν 3344 (OH), 1737 (-C=O), 1174 (-O-CH<sub>2</sub>-). <sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>): δ 0.88 (6H, br t, CH<sub>2</sub>-CH<sub>3</sub>), 1.21-1.39 (42H, br s, alkyl-CH<sub>2</sub>-), 1.43 (2H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O), 1.64 (4H, br m, -CH<sub>2</sub>-CH<sub>2</sub>-C=O, -CH<sub>2</sub>-CH-O), 2.02 (2H, q, -CH<sub>2</sub>-HC=CH-), 2.09 (1H, s, -OH), 2.23 (2H, t, *J* = 7.5 Hz, OH-CH-CH<sub>2</sub>-HC=CH-), 2.32 (2H, t, *J* = 7.5 Hz, -CH<sub>2</sub>-C=O), 3.50 (1H, m, OH-CH-), 4.02 (2H, t, *J* = 6.6 Hz, -O-CH<sub>2</sub>-), 5.32-5.40 (1H, m, -HC=HC-CH<sub>2</sub>-), and 5.47-5.56 (1H, br m, -HC=HC-CH<sub>2</sub>-OH); Mass (GC-MS): *m/z*, 523 [M]<sup>+</sup>.

#### Cetyl erucate (**3g**, C<sub>38</sub>H<sub>74</sub>O<sub>2</sub>, C<sub>38:1</sub>-WE, entry 7)

FT-IR (KBr, cm<sup>-1</sup>): ν 1722 (-C=O), 1181(-O-CH<sub>2</sub>-). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz): δ 0.86-0.90 (6H, br t, *J* = 6.5 Hz, -CH<sub>2</sub>-CH<sub>3</sub>), 1.25 (56H, br s, alkyl-CH<sub>2</sub>-), 1.58-1.61 (4H, br m, CH<sub>2</sub>-HC=CH-



CH<sub>2</sub>), 2.13 (2H, t,  $J = 7.5$  Hz, CH<sub>2</sub>-CH<sub>2</sub>-C=O), 2.23 (2H, t,  $J = 7.5$  Hz, CH<sub>2</sub>-C-O), 4.02 (2H, t,  $J = 6.6$  Hz, -O-CH<sub>2</sub>), 5.27-5.33 (2H, br m, -HC=CH-). Mass (GC-MS):  $m/z$ , 563 [M]<sup>+</sup>.

*Behenyl palmitate (3i, C<sub>38</sub>H<sub>76</sub>O<sub>2</sub>, C<sub>38:0</sub>-WE, entry 9)*

FT-IR (Neat, cm<sup>-1</sup>):  $\nu$  1736 (-C=O), 1182, (-O-CH<sub>2</sub>-). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  0.88 (6H, br t, CH<sub>2</sub>-CH<sub>3</sub>), 1.21-1.39 (62H, br s, alkyl-CH<sub>2</sub>-), 1.55-1.65 (4H, br m, -CH<sub>2</sub>-CH<sub>2</sub>-C=O), 2.23 (2H, t,  $J = 7.5$  Hz, -CH<sub>2</sub>-C-O), and 4.02 (2H, t,  $J = 6.6$  Hz, -O-CH<sub>2</sub>-). Mass (GC-MS):  $m/z$ , 565 [M]<sup>+</sup>.

## Results and Discussion

The present study investigated the application of SO<sub>3</sub>H-carbon catalyst for the direct esterification of LCFAs with LCFAlc under solvent free conditions to obtain corresponding WEs in excellent yields.

Esterification of palmitic acid (PA, **1c**, C<sub>16:0</sub>) with cetyl alcohol (**2a**, C<sub>16</sub>) was chosen as a model reaction to optimize the reaction parameters such as the catalyst amount, temperature and reaction period for the complete esterification to obtain the saturated C<sub>32:0</sub>-WE cetyl palmitate (**3c**, C<sub>16</sub>-C<sub>16</sub>) in excellent yield (Figure 2).

Initially, the reaction was carried with 1:1 mole ratio of palmitic acid (**1c**) and cetyl alcohol (**2a**) by varying catalyst amount from 0 to 25 wt.% (5, 10, 15, 20 and 25 wt.%) of the substrates at 90 °C for 6 h and the results are given in Table 1.

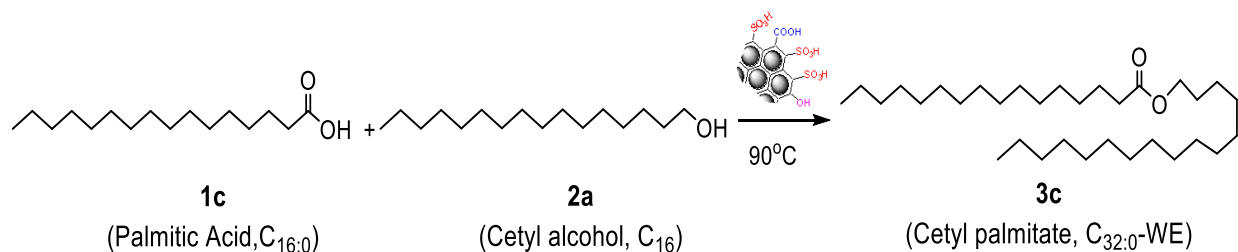
When the esterification was conducted without catalyst, the esterification reaction was found to be very slow and ~10% of cetyl palmitate (**3c**) formation was observed by TLC even after 12 h, whereas in the presence of 5 wt.% of catalyst resulted **3c** in 60% isolated yield in 6 h. This study shows that SO<sub>3</sub>H-carbon catalyst is essential for driving the esterification reaction towards the formation of the WE **3c**. It

was also observed that the overall conversion increased from 60 to 88% with increasing catalyst amount from 5 to 15 wt.% and a maximum conversion of 97% has been achieved with 20 wt.% catalyst. Further increase of the amount of catalyst to 25 wt.% did not show a significant increase in the % conversion and hence, 20 wt.% of SO<sub>3</sub>H-carbon catalyst was found to be optimum for the maximum ester condensation to **3c** in 97% yield in 6 h. Next, to investigate the effect of temperature and reaction period, esterification reaction was conducted at various temperatures ranging from 60 to 100 °C and reaction periods ranging from 6 to 12 h. It was observed that the formation **3c** increased with the increase of temperature and time. When the reaction was conducted at 60 °C only 67% of **3c** was obtained even after 12 h, whereas a maximum 97% of isolated yield of **3c** was observed at 90 °C within 6 h. This study demonstrated that the operating temperature played a significant role in obtaining the WE **3c** in higher yield. The final optimized reaction conditions for the complete esterification of the PA (**1c**) with cetyl alcohol (**2a**) to obtain C<sub>32:0</sub> WE **3c** in the maximum yield of 97% are: 20 wt.% of catalyst, 90 °C temperature and 6 h of reaction period.

The reaction progress was monitored by TLC and after completion of reaction the WE **3c** formed was isolated from the reaction product mixture after the catalyst separation by filtration.

The isolated crude product was subjected for silica gel column chromatographic separation to obtain pure C<sub>32:0</sub> -WE **3c** and was further characterized by spectral techniques.

Formation of saturated C<sub>32:0</sub>-WE cetyl palmitate (**3c**) was confirmed by the presence of a peak at  $\delta$  4.02 ppm as triplet, integrating for two protons assigned to ester methoxy group (-OCH<sub>2</sub>-), a characteristic ester carbonyl (-C=O) and ester methoxy (-OCH<sub>2</sub>-) groups absorption



**Figure 2.**  $\text{SO}_3\text{H}$ -Carbon catalyzed synthesis of cetyl palmitate (**3c**)

**Table 1.** Effect of  $\text{SO}_3\text{H}$ -carbon catalyst

Entry	Catalyst (wt.%)	Isolated Yield (%)
1	0	10 <sup>b</sup>
2	5	60
3	10	77
4	15	88
5	20	97
6	25	98

<sup>a</sup>Reaction conditions: Palmitic acid (5 mmol), cetyl alcohol (5 mmol), temperature (90 °C), and time (6 h)

<sup>b</sup>After 12 h

bands at 1736 and 1182  $\text{cm}^{-1}$  in FT-IR and a molecular ion peak ( $m/z$ ) 480  $[\text{M}]^{++}$  in GC-MS spectra (Figure S1a-c, supporting information).

Initially, cetyl alcohol (**2a**) was esterified with different saturated and unsaturated fatty acids with chain lengths ranging from  $C_{10}$  to  $C_{22}$  (entries 1-8) and all the substrates reacted smoothly to give the corresponding cetyl WEs **3a-g** in excellent yields. Esterification of short chain fatty acids namely, decanoic (**1a**,  $C_{10:0}$ ) and lauric (**1b**,  $C_{12:0}$ ) acids (entries 1 and 2) with cetyl alcohol (**2a**) resulted the corresponding  $C_{26:0}$  and  $C_{28:0}$ -WEs **3a** and **3b**, in a high yield of 98% within a short period of 5 h.

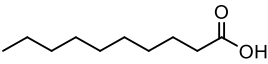
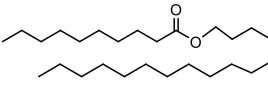
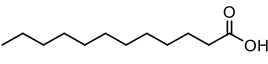
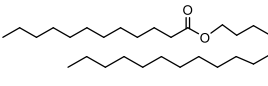
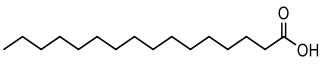
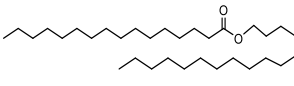
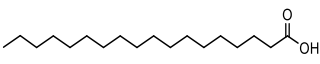
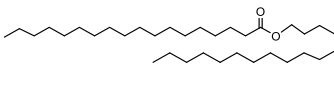
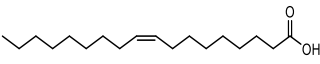
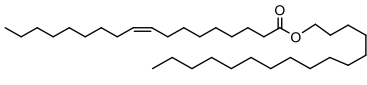
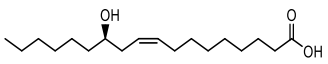
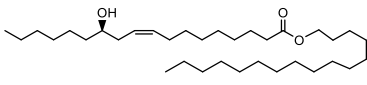
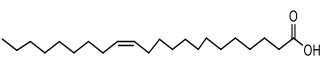
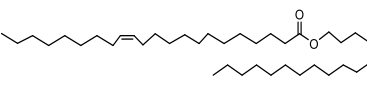
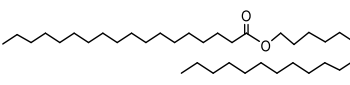
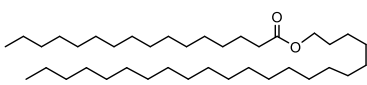
Whereas, esterification of unsaturated fatty acids; namely, oleic (**1e**,  $C_{18:1}$ ) and erucic (**1g**,  $C_{22:1}$ ) acids with saturated cetyl alcohol (**2a**) and unsaturated erucyl alcohol (**2d**,  $C_{22:1}$ ) required longer reaction time of 10 h in resulting corresponding unsaturated  $C_{34:1}$  and  $C_{38:1}$ -WEs **3e**, **3g**, and **3j** (entries 5, 7 and 10) in 95% yields. Formation of unsaturated  $C_{34:1}$ -WE, cetyl oleate (**3e**) was confirmed by the presence of a peak at  $\delta$  4.04 ppm as triplet integrating for two protons assigned to ester methoxy group (-

$\text{OCH}_2$ -) and a multiplet at  $\delta$  5.27-5.35 ppm integrating for two protons of the double bond (- $\text{HC}=\text{CH}$ -), a characteristic ester carbonyl (- $\text{C}=\text{O}$ ) and ester methoxy (- $\text{OCH}_2$ -) groups absorption bands at 1735 and 1182  $\text{cm}^{-1}$  in FT-IR and a molecular ion peak ( $m/z$ ) 506  $[\text{M}]^{++}$  in GC-MS spectra (Figure S2a-c, supporting information).

In the case of esterification of unsaturated hydroxy fatty acid, ricinoleic acid (**1f**,  $C_{18:1(12\text{-OH})}$ ) with cetyl alcohol (**2a**), yield of the corresponding unsaturated hydroxyl  $C_{34:1(12\text{-OH})}$ -WE (**3f**, entry 6) is observed to be only 90%. Involvement of hydroxyl functionality in the estolide formation as by-product by the intramolecular esterification may be reducing the yield of WE **3f**.

Further investigations are in progress to study the reaction kinetics to improve the yield of WE **3f** by controlling the estolide formation. Esterification of PA (**1c**) with steryl (**2b**,  $C_{18}$ ) and behenyl (**2c**,  $C_{22}$ ) alcohols also required longer reaction time of 8 and 10 h to obtain the corresponding long chain  $C_{34:0}$  and  $C_{38:0}$ -WEs (**3h** and **3i**, entries 8 and 9) in >95% yields.

**Table 2.** SO<sub>3</sub>H-Carbon catalyzed synthesis of wax esters<sup>a</sup>

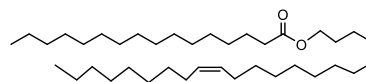
Entry	Fatty Acid (1)	Fatty Alcohol (2)	Wax Ester (3)	Result <sup>b</sup>
1	 <b>1a</b> (Decanoic acid, C <sub>10:0</sub> FA)	<b>2a</b>	 <b>3a</b> (Cetyl decanoate, C <sub>26:0</sub> -WE)	5 h 98%
2	 <b>1b</b> (Laruic acid, C <sub>12:0</sub> FA)	<b>2a</b>	 <b>3b</b> (Cetyl laurate, C <sub>28:0</sub> -WE)	5 h 98%
3	 <b>1c</b> (Palmitic acid, C <sub>16:0</sub> FA)	<b>2a</b>	 <b>3c</b> (Cetyl palmitate, C <sub>32:0</sub> -WE)	6 h 97%
4	 <b>1d</b> (Stearic acid, C <sub>18:0</sub> FA)	<b>2a</b>	 <b>3d</b> (Cetyl stearate, C <sub>34:0</sub> -WE)	8 h 96%
5	 <b>1e</b> (Oleic acid, C <sub>18:1</sub> FA)	<b>2a</b>	 <b>3e</b> (Cetyl oleate, C <sub>34:1</sub> -WE)	8 h 96%
6	 <b>1f</b> (Ricinoleic acid, C <sub>18:1(12-OH)</sub> FA)	<b>2a</b>	 <b>3f</b> (Cetyl ricinoleate, C <sub>34:1(12-OH)</sub> -WE)	10 h 90%
7	 <b>1g</b> (Erucic acid, C <sub>22:1</sub> FA)	<b>2a</b>	 <b>3g</b> (Cetyl erucate, C <sub>38:1</sub> -WE)	10 h 95%
8	<b>1c</b>	<b>2b</b>	 <b>3h</b> (Stearyl palmitate, C <sub>34:0</sub> -WE)	8 h 96%
9	<b>1c</b>	<b>2c</b>	 <b>3i</b> (Behenyl palmitate, C <sub>38:0</sub> WE)	10 h 95%



10

1c

2d



3j

(Erucyl palmitate, C<sub>38:1</sub>-WE)

10 h

95%

<sup>a</sup>Reaction conditions: fatty acid (5 mmol), fatty alcohol (5 mmol), SO<sub>3</sub>H-carbon catalyst (20 wt.%), and temperature (90 °C).

<sup>b</sup>Time (h) and isolated yield.

This study also revealed that the glycerol-based SO<sub>3</sub>H-carbon catalyst is an efficient catalyst for the LCFAs esterification with LCFAlc under solvent free condition at moderate temperature of 90 °C in shorter reaction.

Periods of 5 to 10 h in excellent yields. This study also shows that the conversions increase with the increase of reaction time as the chain length of either fatty acid or fatty alcohol increases.

In addition, the SO<sub>3</sub>H-carbon is a potential green catalyst due to its high catalytic activity and can be recovered by simple filtration for reuse at least for 5 times without any significant loss of esterification activity [15].

## Conclusion

The present study successfully demonstrated SO<sub>3</sub>H-carbon derived from glycerol as an effective, environment friendly, and productive greener heterogeneous solid acid catalyst for the synthesis of saturated and unsaturated wax esters **3a-j** in excellent yields (>95%) by the direct ester condensation of long chain fatty acids (LCFAs) and fatty alcohols under solvent-free condition. The present method has the following practical and environmental advantages over existing methods for WEs synthesis: (a) the SO<sub>3</sub>H-carbon catalyst is easy to prepare from sustainable raw material glycerol/glycerol-pitch compared to other catalysts, (b) catalyst can be separated very easily from the reaction mixture by simple filtration, and (c) can be reused without significant loss of activity as the

catalyst is moisture tolerant, there is no need to remove water produced during the esterification reaction.

## Disclosure Statement

No potential conflict of interest was declared by the authors.

## Funding

The authors are grateful to the Director, CSIR-IICT for providing the facilities to carry out the work and DKIM for providing plagiarism check software and CSIR-IICT Communication No. (IICT/Pubs./2023/181).

## Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the article and agreed to be responsible for all the aspects of this work.

## Orcid

B. L. A. Prabhavathi Devi

<https://orcid.org/0000-0002-4689-2898>

## Supporting Information

Supporting information file contains <sup>1</sup>H-NMR, IR and GC-MS spectra of the WE **3c** (Figure S1) and WE **3e** (Figure S2).

## References

- [1]. a) Goma-Doncescu N., Legoy M.D. *J. Am. Oil Chem. Soc.*, 1997, **74**:1137 [Crossref], [Google Scholar], [Publisher]; b) Dennis Y.C., Leung

- D.Y.C., Wu X., Leung M.K.H. *Appl. Energy*, 2010, **87**:1083 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [2]. a) Misra S., Ghosh A. *Analysis of epicuticular waxes in Essential Oils and Waxes*, Linskens H.F., Jackson J.F. New York: Springer-Verlag Berlin Heidelberg, 1991, 205 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Kolattukudy P.E. *Wax Esters: Chemistry and Biosynthesis in Lipids and Skin Health*; Pappas A. New York: Springer Science + Business Media, 2015, **11**:159 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [3]. a) Hallberg M.L., Wang D., Harrod M. *J. Am. Oil Chem. Soc.*, 1999, **76**:183 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Doan C.D., To C.M., De Vrieze M., Lynen F., Danthine S., Brown A., Dewettinck K., Patel A.R. *Food. Chem.*, 2017, **214**:717 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [4]. a) Petersson A.E.V., Gustafsson L.M., Nordblad M., Borjesson P., Mattiasson B., Adlercreutz P. *Green Chem.*, 2005, **7**:837 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Thum O. *Tenside. Surfactants. Deterg.*, 2004, **41**:287 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [5]. a) Kuo C.H., Chen H.H., Jiann-Hwa Chen J.H., Yung-Chuan Liu Y.C., Shieh C.J. *Int. J. Mol. Sci.*, 2012, **13**:11694 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Kuo C.H., Ju H.Y., Chu S.W., Chen J.H., Chang C.M.J., Liu Y.C., Shieh C.J. *J. Am. Oil Chem. Soc.*, 2012, **89**:103 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [6]. a) Miwa T.K. *J. Am. Oil Chem. Soc.*, 1984, **61**:407 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Sánchez M., Avhad M.R., Marchetti J.M., Martínez M., Aracil J. *Energy Convers. Manag.*, 2016, **129**:293 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [7]. a) Jaiswal K.S., Rathod V.K. *SN Appl. Sci.*, 2019, **1**:949 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Khan N.R., Jadhav S.V., Rathod V.K. *Ultrason. Sonochem.*, 2015, **27**:522 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; c) Deng L., Wang X., Nie K., Wang F., Liu J., Wang P., Tan T. *Chin. J. Chem. Eng.*, 2011, **19**:978 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; d) Alves M.D., Cren E.C., Mendes A.A. *J. Mol. Catal. B: Enzym.*, 2016, **133**:S377 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; e) Radzi S.M., Basri M., Salleh A.B., Ariff A., Mohammad R., Abdul Rahman M.B., Abdul Rahman R.N.Z.R. *Electronic J. Biotechnol.*, 2005, **8**:292 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8]. a) Kolah A.K., Asthana N.S., Vu D.T., Lira C.T., Miller D.J. *Ind. Eng. Chem. Res.*, 2007, **46**:3180 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Al-Arafi N., Salimon J. *E-Journal. Chem.*, 2012, **9**:99 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [9]. a) Barbosa S.L., Hurtado G.R., Klein S.I., Lacerda Jr V., Dabdoub M.J., Guimarães C.F. *Appl. Catal. A*, 2008, **338**:9 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Liu Y., Lotero E., Goodwin Jr J.G. *J. Catal.*, 2006, **242**:278 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [10]. Nguyen D.H., Raffa G., Morin Y., Desset S., Capet F., Nardello-Rataj V., Dumeignil F., Gauvin R.M. *Green Chem.*, 2017, **19**:5665 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [11]. a) Kantam M.L., Bhaskar V., Choudary B.M. *Catal. Lett.*, 2002, **78**:185 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Ramu S., Lingaiah N., Prabhavathi Devi B.L.A., Prasad R.B.N., Suryanarayana I., Sai Prasad P.S. *Appl. Catal. A Gen.*, 2004, **276**:163 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [12]. a) Ishihara K., Ohara S., Yamamoto H. *Science* 2000, **290**:1140 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Ishihara K., Nakayama M., Ohara S., Yamamoto H. *Tetrahedron*, 2002, **58**:8179 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; c) Bartoli G., Boeglin J., Bosco M., Locatelli M., Massaccesi M., Melchiorre P., Sambri L. *Adv. Synth. Catal.*, 2005, **347**:33 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; d) Mantri K., Komura K., Sugi Y. *Green Chem.*, 2005, **7**:677 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)];

- e) Ieda N., Mantri K., Miyata Y., Ozaki A., Komura K., Sugi Y. *Ind. Eng. Chem. Res.*, 2008, **47**:8631 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [13]. a) Mantri K., Komura K., Sugi Y. *Chem. Lett.*, 2005, **34**:1502 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Sunitha S., Kanjilal S., Srinivasa Reddy P., Prasad R.B.N. *Tetrahedron Lett.*, 2007, **48**:6962 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; c) Vijayakumar B., Nagenrdappa G., Jai Prakash B.S. *Ind. J. Chem. Technol.*, 2009, **16**:377 [[Google Scholar](#)], [[Publisher](#)]
- [14]. Meneghetti M.R., Plentz Meneghetti S.M. *Catal. Sci. Technol.*, 2015, **5**:765 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Ferreira A.B., Cardoso A.L., da Silva M.J. *ISRN. Renew. Energy.*, 2012, **2012**:142857 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [15]. a) Prabhavathi Devi B.L.A., Gangadhar K.N., Sai Prasad P.S., Jagannadh B., Prasad R.B.N. *ChemSusChem*, 2009, **2**:617 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Prabhavathi Devi B.L.A., Gangadhar K.N., Kumar K.L.N.S., Shanker K.S., Prasad R.B.N., Sai Prasad P.S. *J. Mol. Catal. A Chem.*, 2011, **345**:96 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; c) Prabhavathi Devi B.L.A., Vijai Kumar Reddy T., Vijaya Lakshmi K., Prasad R.B.N. *Bioresource Technol.*, 2014, **153**:370 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; d) Prabhavathi Devi B.L.A., Vijaya Lakshmi K., Gangadhar K.N., Prasad R.B.N., Sai Prasad P.S., Jagannadh B., Kundu P.P., Kumari G., Narayana C. *ChemistrySelect.*, 2017, **2**:1925 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [16]. a) Karnakar K., Murthy S.N., Ramesh K., Reddy K.H.V., Nageswar Y.V.D., Chandrakala U., Prabhavathi Devi B.L.A., Prasad R.B.N. *Tetrahedron Lett.*, 2012, **53**:3497 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; b) Rao B.M., Reddy G.N., Reddy T.V.K., Prabhavathi Devi B.L.A., Prasad R.B.N., Yadav J.S., Reddy B.V.S. *Tetrahedron. Lett.*, 2013, **54**:2466 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; c) Vijay M., Prasad R.B.N., Devi B.L.A.P. *J. Oleo. Sci.*, 2013, **62**:849 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; d) Chandrakala U., Prasad R.B.N., Devi B.L.A.P. *Ind. Eng. Chem. Res.*, 2014, **53**:16164 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; d) Reddy T.V.K., Rani G.S., Prasad R.B.N., Devi B.P. *RSC. Adv.*, 2015, **5**:40997 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]; e) Sandhya Rani G., Jyotsna A., Prabhavathi Devi B.L.A. *Asian. J. Green. Chem.*, 2019, **3**:125 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

**How to cite this manuscript:** B. L. A. Prabhavathi Devi\*, K. Vijayalakshmi., T. Vijai Kumar Reddy. Highly Efficient SO<sub>3</sub>H-carbon Catalysed Solvent-Free Synthetic Protocol for Wax Esters Via Esterification of Long Chain Fatty Acids and Alcohols. *Asian Journal of Green Chemistry*, 7(4) 2023, 239-249. DOI: 10.22034/ajgc.2023.396739.1390