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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Green recyclable SO₃H-carbon catalyst for the selective synthesis of isomannide-based fatty acid monoesters as non-ionic bio-surfactants

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

A series of novel isomannide-based fatty acid monoesters **3(a-f)** were synthesized by employing a highly active, water resistant and easily recoverable carbon-based solid acid catalyst derived from glycerol. The mannitol was reacted with decanoic, lauric, myristic, palmitic, stearic and oleic acids in presence of carbon acid catalyst under solvent free conditions to obtain corresponding isomannide fatty acid monoesters involving *in situ* dehydration of mannitol to isomannide followed by acylation. The optimized reaction conditions for obtaining isomannide monoesters are: fatty acid to mannitol mole ratio (1:1.5), catalyst 20 wt% of mannitol, temperature 180 °C and reaction time of 12 h. The carbon acid catalyst was recovered by filtration and reused for five cycles without losing its catalytic activity. The use of a recyclable solid acid catalyst makes this method more convenient, simple, and cost effective in addition to high selectivity with good yields. All the synthesized compounds were further evaluated for their surface active properties such as, critical micelle concentration (CMC), surface tension at the CMC (γ_{CMC}), surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m (pC_{20}), maximum surface excess (τ_{max}), and the interfacial area occupied by the surfactant molecules (A_{min}) using surface tension measurements. The micellization ($\Delta G^{\circ}_{\text{mic}}$) and adsorption free energies ($\Delta G^{\circ}_{\text{ads}}$) were calculated. Isomannide monomyristate (**3c**) and isomannide monolaurate (**3b**) exhibited superior surface active properties followed by isomannide monopalmitate (**3d**) compared to other isomannide monoesters.

1. Introduction

In the early 20th century, the application of synthetic surfactants has continuously increased and, as a result, surfactants are currently among the highest volume synthetic chemicals produced globally. Surfactants are produced using either petrochemical or oleochemical feedstocks, favoring petrochemicals which account for roughly two thirds of the organic carbon embodied in the final product.¹ In recent years, oleochemicals and other renewable substrates, such as carbohydrates, organic acids, and amino acids, have been of increasing interest as feedstocks for surfactant production. Nowadays, growing consumer demand for “green” products has increased attention on the utilization of carbohydrates as raw materials for specialty chemicals.²⁻⁶

Sugar-fatty acid ester based bio-surfactants have gained lot of significance because they consist of two inexpensive, renewable and readily available starting agricultural materials such as sugars and fat/oil.⁷⁻¹¹ As surfactants showing high stabilizing, detergent, and emulsifying properties, they find applications in various fields like, food, cosmetic, oral-care products, cleaning and pharmaceutical industries.¹²⁻¹⁷ In addition,

these type of bio-surfactants are odorless, nontoxic, tasteless, non skin irritant, and fully biodegradable.¹⁸ Further they can be easily digested by the stomach as a carbohydrate-fatty acid mixture.¹⁹ The hydrophilic-lipophilic balance (HLB) of these products can be modulated over a wide range by varying the different chain length, the number of hydrocarbon chains of the sugar molecule, or the degree of unsaturation of the chains.²⁰

Generally, sugar esters are synthesized by chemical routes.²¹⁻²³ Osipow et al. reported the synthesis of sugar esters by transesterification of sugars with fatty acid methyl ester in DMF employing acid/base catalyst at high temperatures and reduced pressure.²⁴ Use of homogeneous acid/alkaline catalysts, toxic solvents and high temperature may result in the formation of toxic by-products and also decolouration of the product. Some of the by-products are allergenic and conceivably carcinogenic. In addition, industrial processes are not selective and they can form different product mixtures differing in the number of esterified hydroxyls or in the acylation position.²⁵ In case of sugar alcohols, the process encompasses the formation of dehydrated products.²⁶ Although di- and triesters are opportune for many applications, chemical reactions that produce monoesters selectively in prudent ways open interesting perspectives in new applications.

Enzymatic synthesis is an alternative route for the synthesis of sugar-based fatty acid esters, which avoids only a few

problems raised in the chemical synthesis.²⁷ Extensive literature reported on lipase mediated synthesis of carbohydrate fatty acid esters.²⁸⁻³⁰ However, one of the major complication of this process is the poor solubility of the sugars leading in some cases to low product yield due to long reaction times.³¹⁻³⁸ Another factor is, sugars have low solubility in non-polar solvents, in which lipases exhibit esterification activity, whereas, vice versa most of the lipases lose their activity in polar solvents, in which sugars are soluble.³⁹

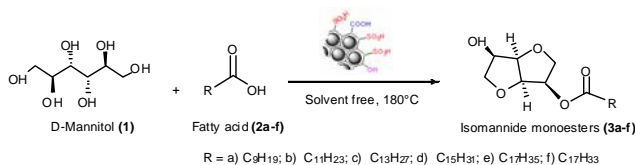
Isomannide monooleate has been extensively used as emulsifiers in many veterinary vaccines.⁴⁰ Very few reports are available in the literature towards the direct synthesis of isomannide monooleate from mannitol by esterification with fatty acid under strong acidic conditions.⁴¹⁻⁴⁴ Major drawbacks of these methods are low product yield without selectivity, difficulty in separation and purification of the product apart from the generation of huge quantities of effluents and lack of recovery and reusability of the catalyst. Recent years, carbon-based solid acid catalysts have gained importance due to their significant advantages over homogeneous mineral acids, such as increased activity and selectivity, longer catalyst life, negligible equipment corrosion, ease of product separation, and reusability.⁴⁵

Recently, we have reported a sustainable methodology for the preparation of SO₃H-carbon catalyst with an excellent esterification activity from bioglycerol (biodiesel by-product), glycerol pitch (waste from fat splitting industry) and commercial glycerol by involving *in situ* partial carbonization and sulfonation in a single pot.⁴⁶⁻⁴⁸ This carbon catalyst has showed outstanding catalytic properties by demonstrating its effectiveness for different transformations⁴⁹⁻⁵² due to its high thermal stability, recyclability and strong acid sites of sulfonic acid functional groups. In continuation of our ongoing research towards exploring the applications of the glycerol-based carbon acid catalyst, here we disclose a simple and highly efficient green solvent free synthetic approach for the preparation of a novel series of isomannide-based fatty acid monoester compounds at 180 °C in 12 h with high selectivity in good yields.

2. Results and discussion

2.1 Synthesis of isomannide monoesters

SO₃H-Carbon catalyst is demonstrated for the selective synthesis of isomannide-based fatty acid monoesters involving *in situ* dehydration of mannitol followed by acylation with fatty acid with varying hydrophobic chain lengths (C₁₀, C₁₂, C₁₄, C₁₆, C₁₈ and C_{18:1}) under solvent free conditions (Scheme 1) in a single



pot.

Scheme 1 SO₃H-Carbon catalyzed synthesis of isomannide-based fatty acid monoesters.

The reaction was carried out by heating a mixture of D-mannitol and fatty acid in presence of carbon acid catalyst in ACE pressure tube under stirring at 180 °C for 12 h to obtain isomannide fatty acid monoesters **3(a-f)** in good yields.

Esterification of oleic acid with D-mannitol was selected as a model reaction for optimization of the various reaction parameters namely, substrate mole ratio, loading of the catalyst (5-20 wt% of D-mannitol), temperature (140-180 °C) and reaction period (4-16 h) for the selective formation of isomannide monooleate in maximum yield. Using these optimized reaction parameters, the scope of this methodology was further extended to different fatty acids by varying chain lengths from C₁₀-C₁₈. All the synthesized isomannide-based fatty acid monoesters were purified by silica gel column chromatography and fully characterized by IR, ¹H NMR, ¹³C NMR, ESI-MS, HRMS and optical rotation data analysis.

2.2 Effect of substrate mole ratio

Molar ratio of substrates would affect the reaction progress and the composition of products. The effect of mannitol: oleic acid mole ratios (1:1-1:2) on the yield of isomannide monooleate was studied for the esterification of mannitol with oleic acid in presence of 20 wt% of carbon acid catalyst at 180 °C for 12 h and the results are given in Table 1. The data clearly indicates that, with the increase of mole ratio of mannitol to oleic acid from 1 to 1.5 increases the yield of isomannide monooleate (84%). Further increase of mannitol mole ratio from 1.5 to 2.0, resulted in decrease in the yield of isomannide monooleate from 84 to 61% with increase in the formation of isomannide from 2-31%. Therefore, 1:1.5 molar ratio was found to be the optimum for the maximum conversion of mannitol to isomannide monooleate in 84% yield.

Table 1 Effect of mannitol: oleic acid mole ratio on the yield of isomannide monooleate^a

Oleic Acid: Mannitol (Mole ratio)	Composition (wt%) of the product by GC		
	Oleic Acid	Isomannide	Isomannide monooleate
1:1	32	4	64
1:1.5	14	2	84
1:2	8	31	61

^a Reaction conditions: oleic acid (1 g), catalyst (20 wt% of mannitol), temperature (180 °C) and time (12 h).

2.3 Effect of catalyst loading

Catalyst concentration relates to the reaction rate, at certain ranges, an increase in catalyst concentration amounts leads to increase of reaction rate. A detailed study was conducted by varying SO₃H-carbon catalyst loading from 5-20 wt% of D-mannitol, keeping the reaction temperature at 180 °C and taking the oleic acid to mannitol molar ratio as 1:1.5 and the results are depicted in Fig.1. The study indicates that, the yield of isomannide monooleate increased from 50 to 84% with the increase of the catalyst loading from 5 to 20 wt%. Even at lower catalyst loading (5 wt%), considerable amount of product formation was observed containing about 50% of isomannide

monooleate along with ~10% of isomannide. Whereas, 20 wt% of catalyst resulted a maximum yield 84% of isomannide monooleate and attempts on further increase of catalyst amount didn't result any significant increase in the product yield. Therefore, 20 wt% of catalyst was found to be the optimum for obtaining the maximum yield of isomannide monooleate by *in situ* dehydration of mannitol (1.5 mmol) to isomannide and acylation with oleic acid (1 mmol) at 180 °C in 12 h.

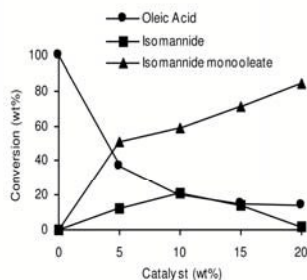


Fig. 1 Effect of catalyst loading on the yield of isomannide monooleate. Reaction conditions: oleic acid (1 g), mannitol (0.97 g), temperature (180 °C), time (12 h).

2.4 Effect of reaction temperature

Reaction temperature is of paramount importance in the esterification reaction, especially for the heterogeneous catalysts. Effect of reaction temperature on the condensation of D-mannitol with oleic acid to obtain maximum yield of isomannide monooleate was conducted at different temperatures ranging from 140 to 180 °C for 12 h (Fig. 2). This study revealed that, with the increase of the reaction temperature from 160 to 180 °C, the formation of isomannide monooleate increased drastically from 15 to 84% may be due to the complete melting and dehydration of D-mannitol at 180 °C. Hence, 180 °C was found to be optimum for the maximum condensation of mannitol and oleic acid to isomannide monooleate.

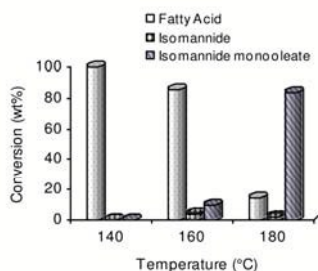


Fig. 2 Effect of reaction temperature on the yield of isomannide monooleate. Reaction conditions: oleic acid (1 g), mannitol (0.97 g), catalyst (0.19 g), time (12 h).

2.5 Effect of reaction time

Condensation reaction of mannitol with oleic acid at 180 °C using 20 wt% catalyst was conducted to study the effect of reaction period varying from 4-16 h and the results are given in Fig. 3. The study indicates that, the yield of isomannide monooleate

increased from 10 to 84% with the increase of reaction time from 4 to 12 h. Further increase to another 4 h resulted only marginal increase in the product yield and hence 12 h was found to be optimum reaction period for the maximum conversion of mannitol to isomannide monooleate.

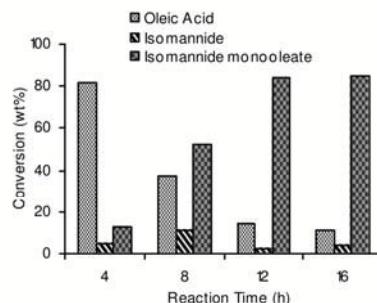
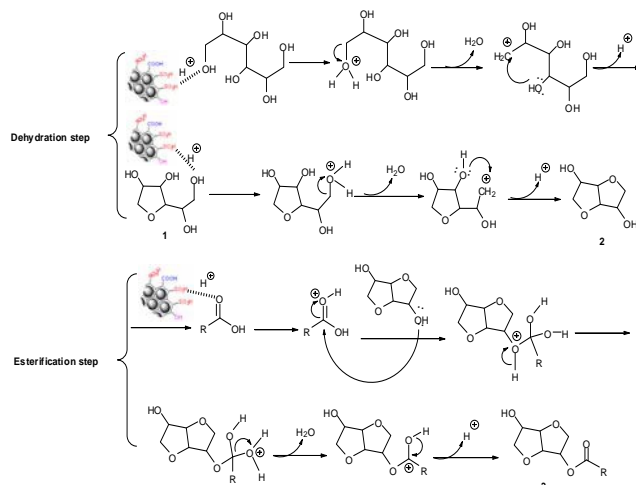


Fig. 3 Effect of reaction time on the yield of isomannide monooleate. Reaction conditions: oleic acid (1 g), mannitol (0.97 g), catalyst (0.19 g), temperature (180 °C).

We proposed a plausible mechanism for the synthesis of isomannide-based fatty acid monoesters as shown in Scheme 2. The reaction involves simultaneous dehydration and esterification of mannitol with fatty acid to isomannide monoester. During dehydration step, initially protonation occurs at the primary hydroxy group of D-mannitol by the release of proton from SO₃H-carbon catalyst leading to dehydration (-H₂O) between 1 and 4 hydroxy position for the formation of 1,4-monoanhydromannitol (**1**). This on subsequent elimination of second water molecule from 3 and 6 hydroxy position leads to the formation of isomannide (**2**). During esterification step, protonation of carbonyl group of the fatty acid by the SO₃H-carbon catalyst leads to the formation of carbocation which on nucleophilic attack with isomannide followed by dehydration results in isomannide fatty acid monoester (**3**).



Scheme 2 The plausible mechanism for the synthesis of isomannide-based fatty acid monoesters employing SO₃H-carbon catalyst.

2.6 Reusability of the catalyst

In the case of heterogeneous catalysis, the most important factor is the deactivation and reusability of the catalyst. The efficiency of the catalyst was compared upon reuse. After completion of the reaction, the catalyst was easily separated by filtration, washed with water and followed by methanol, dried in oven at 120 °C for 1 h. The catalyst was reused for 5 cycles and it was found that the catalytic activity maintained with ~84% conversion in first two cycles and marginally reduced from 83% to 80% in the last three cycles (Fig. 4), which may be due to the mass loss of the catalyst during the recovery process. The thermal stability, easy recovery and reusability without any deactivation and leaching indicates that the carbon acid catalyst holds great potential for the green chemical processes.

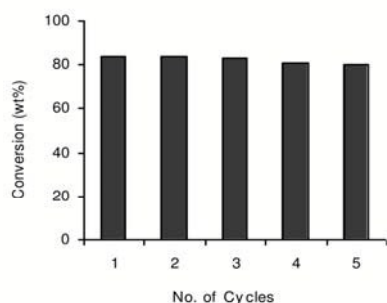


Fig. 4 Reusability of SO₃H-carbon catalyst. Reaction conditions: oleic acid (1 g), mannitol (0.97 g), catalyst (0.19 g), temperature (180 °C), time (12 h).

2.7 Comparative study of SO₃H-carbon catalyst with other solid acid catalysts

A detailed comparative study of the SO₃H-carbon catalyst against commercially available solid acid catalysts namely, Kieselguhr G, ZSM-5 and Amberlyst-15 was conducted for the synthesis of isomannide monooleate by varying the reaction period from 4 to 16 h and the results were summarized in Fig. 5. Based on the study, the catalytic activity can be ordered as follows; carbon catalyst > Amberlyst-15 > ZSM-5 > Kieselguhr G. The yield of isomannide monooleate increased with the increase of reaction period from 4 to 12 h and no significant increase in the yield was observed after 16 h. Among these catalysts, the carbon acid catalyst displayed excellent activity for the formation of isomannide monooleate in ~85% yield in 12 h. In contrast, Amberlyst-15 showed higher conversion (~38%) during initial 4 h of reaction period and a maximum of ~57% yield was observed in 12 h. Whereas, ZSM-5 and Kieselguhr G resulted lower yields of isomannide monooleate in 25 and 10% respectively.

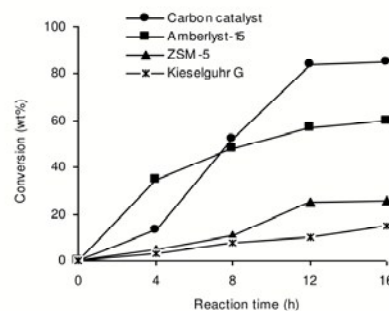


Fig. 5 Comparative study of SO₃H-carbon catalyst against other solid acid catalysts. Reaction conditions: oleic acid (1 g), mannitol (0.97 g), catalyst (0.19 g), temperature (180 °C).

The differences in the catalytic activity of any catalysts could be explained by their acidity and surface area. Total acidity of these catalysts was measured by using temperature-programmed desorption (TPD) of ammonia and data is given in Table 2. From the data, it is clear that the superior catalytic activity exhibited by the carbon acid catalyst is due to its higher acidity (8.19 mmol/g) when compared to other catalysts. Even though ZSM-5 possesses high surface area (400 m²/g), its lower activity may be due to its lower acidity (1.6 mmol/g).

Table 2 Surface area and acidity data of the catalysts

Catalyst	Surface area (m ² /g)	Acidity ^a (mmol/g)
Kieselguhr G	39.4 ^b	0.05
ZSM-5	400 ^b	1.6
Amberlyst-15	45 ^b	4.7
Carbon catalyst	0.21 ^c	8.19

^aEstimated from NH₃-TPD. ^bData obtained from supplier. ^cData from Ref. [46].

Based on the above study, the optimized reaction parameters for the condensation of mannitol with oleic acid for the selective preparation of isomannide monooleate in maximum yield of 84% are: mannitol: oleic acid (1.5:1 mmol), catalyst (20 wt% of mannitol), temperature 180 °C and time 12 h. Employing the optimized reaction conditions, a series of isomannide-based monoesters were synthesized with different fatty acids namely decanoic, lauric, myristic, palmitic and stearic acids in very good yields (Scheme 1). All synthesized compounds **3(a-f)** were further evaluated for their surfactant properties.

2.8 Surfactant properties of isomannide-based fatty acid monoesters (3a-f)

Aqueous solutions of all the synthesized isomannide monoesters **3(a-f)** were prepared by dissolving appropriate amounts in Milli-Q water. These solutions were used for evaluation of surfactant properties, such as surface tension (γ_{CMC}), critical micelle concentration (CMC), surfactant concentration required to reduce the surface tension of the solvent by 20 mN/m (pC_{20}), surface excess (τ_{max}), minimum surface area per molecule (A_{min}) at 27 °C. The surfactant properties were measured by Kruss K100 tensiometer using standard method and the results are summarized in Table 3.

Table 3 CMC and thermodynamic properties of isomannide-based fatty acid monoesters **3(a-f)**^a

Compound	γ_{CMC} (mN/m)	CMC (mM)	$\text{p}C_{20}$	π_{CMC} (mN/m)	$\tau_{\text{max}} \times 10^{12}$ (mol/mm ²)	A_{min} (nm ² /molecule)	$\Delta G_{\text{ads}}^{\circ}$ (kJ/mol)	$\Delta G_{\text{mic}}^{\circ}$ (kJ/mol)
3a	28.64	3.07×10^{-2}	5.09	42.76	6.87	0.24	-32.14	-25.91
3b	26.83	0.53×10^{-2}	5.57	44.43	14.07	0.12	-33.43	-30.28
3c	25.79	0.47×10^{-2}	5.61	45.49	15.08	0.11	-33.56	-30.55
3d	30.30	1.27×10^{-2}	5.49	40.80	7.54	0.22	-33.50	-28.10
3e	38.90	4.38×10^{-2}	4.82	31.96	4.47	0.37	-32.16	-25.02
3f	44.14	1.38×10^{-2}	5.06	26.55	5.34	0.31	-32.87	-27.91

^aSurface tension measured at 27 °C; γ_{CMC} , surface tension value at CMC; CMC, critical micelle concentration; π_{CMC} , effectiveness of surface tension reduction; τ_{max} , maximum surface excess; A_{min} , minimum surface area per molecule; $\Delta G_{\text{ads}}^{\circ}$, standard free energy of adsorption; $\Delta G_{\text{mic}}^{\circ}$, standard free energy of micellization.

2.8.1 Surface tension and critical micelle concentration

Critical micelle concentration and the related surface tension provide a basic characterization of any surfactant. Fig. 6 represents the surface tension versus concentration (log scale) of the synthesized isomannide monoesters at 27 °C. The surface tension profile represents of two characteristic regions, one region located at low surfactant concentrations and characterized by a continuous depression in the surface tension values by increasing the surfactant concentrations. The second region is located at high surfactant concentrations with almost constant surface tension values when the surfactant concentration increased.

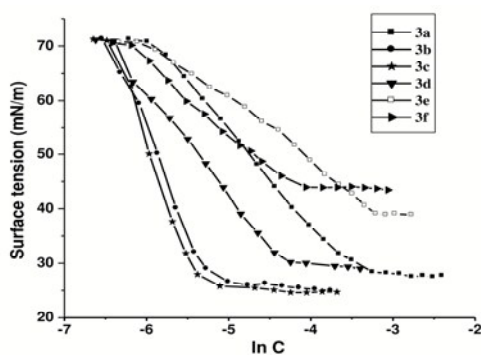


Fig. 6 Variation of surface tension as a function of logarithm of surfactant concentrations of isomannide-based fatty acid monoesters (**3 a-f**).

Generally, an increase in the hydrophobicity decreases the CMC values by increasing length of the hydrophobic chain. This is due to the fact that the increase in hydrophobicity may render the molecule more favorable for aggregation, resulting in lowering of CMC. The similar trend was observed initially for the isomannide-based surfactants on increases of hydrophobicity from C₁₀ to C₁₄ (**3a-c**). However, the deviation in CMC value from regularity was observed with the further increase in the number of carbon atoms in the hydrophobic chain from C₁₆ C₁₈ (**3d-e**), which may be due to the increased intramolecular hydrophobic interaction by the effect of self-coiling.^{53,54} The deviation in CMC was also observed in the case of unsaturation

in the hydrophobic chain. The low CMC value observed in the case of isomannide monooleate (1.38×10^{-2} mM) when compared to isomannide monostearate (4.38×10^{-2} mM). This can be attributed to the presence of the double bond in the hydrophobic chain of the oleate moiety which decreases the CMC value.

The effectiveness of surface tension reduction, π_{CMC} , is another factor which describes the lowering of the surface tension at the interface at surface saturation condition. π_{CMC} value was determined by using the following Eq 1.

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \quad (1)$$

where γ_0 is the surface tension of the pure water and γ_{CMC} is the surface tension of the surfactant solution at CMC. The most efficient surfactant was the one that lowered the surface tension value at the CMC. All the synthesized surfactant solutions have π_{CMC} values range from 26-45 mN/m and the data shown that the compounds **3c** (45.5 mN/m) and **3b** (44.4 mN/m) were exhibited as efficient surfactants. The efficiency and effectiveness of a surfactant can also be assessed by the $\text{p}C_{20}$ value, which is the negative logarithm of concentration of the surfactant required to reduce the surface tension of water by 20 units. A higher $\text{p}C_{20}$ value indicates higher hydrophobic character of the surfactant, resulting in higher efficiency of reduction of surface tension. Isomannide monomyristate (**3c**) and monolaurate (**3b**) showed significantly higher $\text{p}C_{20}$ values, indicates their tendency to be adsorbed at the air-water interface and also to form micelle much greater than the other synthesized surfactants.

The surface excess, τ_{max} (mol/mm²), can be calculated according to Eq 2.

$$\tau_{\text{max}} = (\partial\gamma / \partial \ln C) / RT \quad (2)$$

where R is the gas constant (8.314) and T is the absolute temperature (K). The maximum surface excess (τ_{max}) values decreases by increasing the hydrophobic chain length from C₁₄-C₁₈ (**3 c-e**) and the trend was reversed in the case of shorter hydrophobic chains from C₁₀-C₁₂ (**3 a-b**).

The minimum surface area (A_{min}) can be calculated using Eq 3.

$$A_{\min} = 1/N \cdot \tau_{\max} \quad (3)$$

where N is the Avogadro number (6.023×10^{23} molecule mol⁻¹) and A_{\min} is given in nm² molecule⁻¹. The surface area per molecule (A_{\min}) values increases gradually by the increase of hydrophobic chain length as mentioned in Table 3. The A_{\min} values of isomannide monomyristate (**3c**), monopalmitate (**3d**), and monostearate (**3e**) surfactants, viz. 0.11, 0.22 and 0.37 nm² molecule⁻¹ respectively. On the contrary, the trend was reversed in the case of shorter chain lengths of isomannide monoesters (**3a-b**).

2.8.2 Thermodynamic aspects

The thermodynamic characteristics of the synthesized isomannide based fatty acid esters were studied using calculated values of micellization and adsorption free energies, $\Delta G_{\text{mic}}^{\circ}$, $\Delta G_{\text{ads}}^{\circ}$ respectively (Table 3), according to Eq 4 and 5.

$$\Delta G_{\text{mic}}^{\circ} = RT \ln \text{CMC} \quad (4)$$

where R is the gas constant and T is the absolute temperature.

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{mic}}^{\circ} - (\pi_{\text{CMC}} / \tau_{\max}) \quad (5)$$

The micellization ($\Delta G_{\text{mic}}^{\circ}$) free energies of the synthesized surfactants in their aqueous media showed a negative value, indicating that micellization is a spontaneous process at a constant temperature. The driving force of micelle formation is the repulsion occurring between the hydrophobic chains and the polar medium. The negativity of both $\Delta G_{\text{mic}}^{\circ}$ and $\Delta G_{\text{ads}}^{\circ}$ indicates that the two processes occurred spontaneously. $\Delta G_{\text{ads}}^{\circ}$ is more negative than $\Delta G_{\text{mic}}^{\circ}$ indicated that adsorption is more spontaneous due to lesser repulsion between water and hydrophobic group interactions than for micellization at air-water interface. The increase of $\Delta G_{\text{ads}}^{\circ}$ values may be ascribed to the tendency of the molecules to adsorb at the air-water interface until there is complete surface coverage. Beyond this, the surfactant molecules diffuse to the bulk of their solution to form micelles. Hence, the micellization and adsorption processes are governed by the thermodynamic aspects.

3. Experimental

3.1 Chemical reagents

Amberlyst-15 (Dow Chemicals, India), ZSM-5 zeolite with a SiO₂/Al₂O₃ mole ratio of 30 (Zeolyst, Netherlands), Kieselguhr G (Alfa aesar, India) and all other chemicals were purchased from M/s. SD Fine Chemicals Pvt. Ltd., Mumbai, India. All solvents used were of analytical grade. Reaction was monitored on silica gel TLC plates (coated with TLC grade silica gel, obtained from Merck) employing iodine vapors for detection of spots. Column chromatography was performed over silica gel (100-200 mesh) procured from Qualigens (India) using freshly distilled solvents.

3.2 General methods and analysis

Melting points of the products were recorded using Barnstead Electro thermal 9200 instrument. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX. Mass spectra were recorded using electron spray ionization-mass spectrometry (ESI-MS). ¹H NMR and ¹³C NMR spectra were recorded on Bruker UXNMR (operating at 300 MHz, 500 MHz for ¹H and 75 MHz for ¹³C NMR) spectrometer using CDCl₃. Chemical shifts δ are reported relative to TMS ($\delta = 0.0$) as an internal standard. All spectra were recorded at 25 °C. Conversion percentages were studied using Agilent 6850 Gas Chromatograph unit equipped with FID. A fused silica capillary column HP-1 (30 m \times 0.25 mm i.d \times 0.25 μ m film of 100% methyl polysiloxane) was used for the conversion percentage. The oven temperature was programmed at 80 °C for 2 min and increased to 300 °C at 10 °C/min, held for 20 min. The flow rate of carrier gas (N₂) was 1 mL/min. The inlet and detector temperatures were maintained at 280 and 300 °C, respectively. The area percentage was recorded with a standard HP chemstation data system.

The acidity of the catalysts was measured by using temperature-programmed desorption (TPD) of ammonia⁵⁵ on a BELCAT II instrument (Japan BEL Inc.). Sample was loaded (100 mg) and analyzed as per program given to the instrument. The sample was preheated at 500 °C for 1 h by passing pure helium (99.9%, 50 mL/min). After pretreatment, sample was saturated with anhydrous ammonia (10% NH₃) at 100 °C at a flow rate of 30 mL/min for 1 h and subsequently flushed with helium at the same temperature to remove physisorbed ammonia. The TPD analysis was carried out from 100 °C to 800 °C at a ramping rate of 10 °C/min. The amount of ammonia evolved was calculated from the peak area of the calibrated TCD signal.

The surface tension was measured using Kruss K100 tensiometer (Kruss, GmbH, Hamburg, Germany) equipped with platinum ring having radius of 9.545 mm and wire diameter of 0.37 mm. Before measurement, the platinum ring was burned in an oxidizing flame by use of a Bunsen burner and thoroughly cleaned with methanol followed by distilled water. The surface tension was (γ) measured at different concentrations by adding a subsequent volume of stock solution with a 765 Dosimat (Metrohm) which was connected to a Kruss bowl (120 mL) containing a known volume of water (50 mL) until the value almost reached saturation. For each concentration, the solution was stirred for 60 s and equilibrated for 60 s, and the average of five readings was taken.

3.3 Preparation of glycerol-based SO₃H-carbon catalyst

A mixture of glycerol (10 g) and concentrated sulfuric acid (30 g) were taken in a 500 ml glass beaker and gently heated on hotplate from ambient temperature to 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 was ceased. The resultant black crystalline product was washed with hot water under agitation till the wash water becomes neutral to pH. The partially crystalline product was filtered and dried in an oven at 120 °C for 2 h in order to ensure free of moisture to obtain glycerol-based carbon acid catalyst (4.67 g). The complete characterization of the carbon catalyst was carried out to establish

its physico-chemical characteristics.⁴⁶ The surface area of the catalyst was estimated as 0.21 m²/g by BET method. The acidity of the catalyst was found to be 8.19 mmol/g by NH₃-TPD method.

3.4 General procedure for the synthesis of isomannide-based fatty acid monoesters (3a-f)

A mixture of fatty acid (1 mmol), D-mannitol (1.5 mmol), and carbon acid catalyst (20 wt% of mannitol) taken in an ACE pressure tube was heated to 180 °C by immersing in an oil bath with electrical heating under magnetic stirring for 12 h. The progress of the reaction was monitored by TLC and Gas Chromatography using HP-1 capillary column. The catalyst was separated by filtration and washed with chloroform (10 mL). The filtrate was dried over anhydrous sodium sulphate and removed the solvent under reduced pressure. The resulted crude product was subjected to silica gel column chromatography using hexane/ethyl acetate (80:20 v/v) as eluent to obtain pure isomannide fatty acid monoester (yield 70-85%).

3.5 Spectral data

All the synthesized isomannide-based fatty acid monoester compounds **3(a-f)** were thoroughly characterized by using different spectral techniques like IR, NMR ESI-MS, and HRMS. The spectral data of all the compounds are given as follows.

3.5.1 Isomannide monodecanoate (3a)

Yield 70.3%. [α]_D²⁴ +108.2 (*c* 0.65 in CHCl₃). $\nu_{\max}/\text{cm}^{-1}$: 3441 (OH), 2926 and 2857 (CH), 1739 (C=O), 1169 (C-O). ¹H NMR (300 MHz, CDCl₃): δ 0.87 (3H, t, *J* = 6.7 Hz, 10-H), 1.23-1.35 (12H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H), 1.58-1.67 (2H, m, 3-H), 1.69 (1H, br s, OH), 2.36 (2H, t, *J* = 7.5 Hz, 2-H), 3.57 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, *J*¹ = 6.0 Hz, *J*² = 9.0 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, *J*¹ = 6.0 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOCO, H_a), 4.23-4.37 (1H, m, CH₂CHOH), 4.48 (1H, t, *J* = 5.2 Hz, CHCHOH), 4.69 (1H, t, *J* = 5.2 Hz, CHCHOCO), 5.12-5.18 (1H, q, CHOCO). ¹³C NMR (75 MHz, CDCl₃): δ 14.01, 22.58, 24.79, 28.99, 29.17, 29.33, 31.78, 33.86, 34.10, 70.78, 72.19, 73.75, 73.82, 80.41, 81.51, 173.21. HRMS (ESI⁺): calcd for C₁₆H₂₉O₅ [M+H]⁺, 301.2009; found, 301.2012.

3.5.2 Isomannide monolaurate (3b)

Yield 75.6%. White solid; mp 66-68 °C. [α]_D²⁴ +26.2 (*c* 1.0 in CHCl₃). $\nu_{\max}/\text{cm}^{-1}$: 3443 (OH), 2925 and 2855 (CH), 1739 (C=O), 1173 (C-O). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (3H, t, *J* = 6.7 Hz, 12-H), 1.23-1.37 (16H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H), 1.57-1.69 (2H, m, 3-H), 2.38 (2H, t, *J* = 7.5 Hz, 2-H), 3.57 (1H, dd, *J*¹ = 7.5 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, *J*¹ = 6.0 Hz, *J*² = 9.0 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, *J*¹ = 6.0 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOCO, H_a), 4.24-4.36 (1H, m, CH₂CHOH), 4.49 (1H, t, *J* = 5.2 Hz, CHCHOH), 4.69 (1H, t, *J* = 5.2 Hz, CHCHOCO), 5.12-5.18 (1H, q, CHOCO). ¹³C NMR

(75 MHz, CDCl₃): δ 14.03, 22.61, 24.81, 29.07, 29.19, 29.27, 29.39, 29.54, 31.84, 33.88, 34.12, 70.79, 72.20, 73.78, 73.82, 80.43, 81.51, 173.22. HRMS (ESI⁺): calcd for C₁₈H₃₃O₅ [M+H]⁺, 329.2322; found, 329.2323.

3.5.3 Isomannide monomyristate (3c)

Yield 73.5%. White solid; mp 38-40 °C. [α]_D²⁴ +92.2 (*c* 0.55 in CHCl₃). $\nu_{\max}/\text{cm}^{-1}$: 3442 (OH), 2924 and 2855 (CH), 1740 (C=O), 1171 (C-O). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (3H, t, *J* = 6.0 Hz, 14-H), 1.21-1.35 (20H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H), 1.55-1.70 (2H, m, 3-H), 2.36 (2H, t, *J* = 7.5 Hz, 2-H), 3.57 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOCO, H_a), 4.26-4.38 (1H, m, CH₂CHOH), 4.48 (1H, t, *J* = 5.2 Hz, CHCHOH), 4.69 (1H, t, *J* = 5.2 Hz, CHCHOCO), 5.12-5.18 (1H, q, CHOCO). ¹³C NMR (75 MHz, CDCl₃): δ 14.07, 22.63, 24.79, 29.00, 29.19, 29.29, 29.59 (4 × C), 31.85, 33.85, 34.04, 70.75, 72.16, 73.75, 73.79, 80.40, 81.47, 173.22. HRMS (ESI⁺): calcd for C₂₀H₃₇O₅ [M+H]⁺, 357.2635; found, 357.2637.

3.5.4 Isomannide monopalmitate (3d)

Yield 77.2%. White solid; mp 77-79 °C. [α]_D²⁴ +22.2 (*c* 1.0 in CHCl₃). $\nu_{\max}/\text{cm}^{-1}$: 3443 (OH), 2920 and 2852 (CH), 1740 (C=O), 1175 (C-O). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (3H, t, *J* = 6.7 Hz, 16-H), 1.21-1.35 (24H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H), 1.56-1.70 (2H, m, 3-H), 2.36 (2H, t, *J* = 7.5 Hz, 2-H), 3.57 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, *J*¹ = 6.0 Hz, *J*² = 9.0 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, *J*¹ = 6.7 Hz, *J*² = 9.8 Hz, OCH₂CHOCO, H_a), 4.24-4.36 (1H, m, CH₂CHOH), 4.48 (1H, t, *J* = 5.2 Hz, CHCHOH), 4.69 (1H, t, *J* = 5.2 Hz, CHCHOCO), 5.12-5.18 (1H, q, CHOCO). ¹³C NMR (75 MHz, CDCl₃): δ 14.09, 22.66, 24.81, 29.03, 29.21, 29.32, 29.42, 29.64 (5 × C), 31.88, 33.87, 34.12, 70.77, 72.18, 73.81 (2 × C), 80.42, 81.49, 173.24. HRMS (ESI⁺): calcd for C₂₂H₄₁O₅ [M+H]⁺, 385.2948; found, 385.2952.

3.5.5 Isomannide monostearate (3e)

Yield 85.1%. White solid; mp 42-44 °C. [α]_D²⁴ +45.5 (*c* 0.65 in CHCl₃). $\nu_{\max}/\text{cm}^{-1}$: 3434 (OH), 2919 and 2851 (CH), 1740 (C=O), 1173 (C-O). ¹H NMR (500 MHz, CDCl₃): δ 0.88 (3H, t, *J* = 7.0 Hz, 18-H), 1.21-1.35 (28H, m, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, 10-H, 11-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H), 1.58-1.67 (2H, m, 3-H), 1.73 (1H, br s, -OH), 2.38 (2H, t, *J* = 7.5 Hz, 2-H), 3.57 (1H, dd, *J*¹ = 7.1 Hz, *J*² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, *J*¹ = 6.5 Hz, *J*² = 9.3 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, *J*¹ = 6.2 Hz, *J*² = 9.1 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, *J*¹ = 6.4 Hz, *J*² = 9.3 Hz, OCH₂CHOCO, H_a), 4.23-4.32 (1H, m, CH₂CHOH), 4.48 (1H, t, *J* = 5.1 Hz, CHCHOH), 4.69 (1H, t, *J* = 5.1 Hz, CHCHOCO), 5.13-5.18 (1H, q, CHOCO). ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.67, 24.82, 29.04, 29.23, 29.34, 29.43,

29.66 (8 × C), 31.90, 33.89, 70.77, 72.20, 73.81, 73.87, 80.43, 81.50, 173.21. HRMS (ESI⁺): calcd for C₂₄H₄₄O₅Na [M+Na]⁺, 435.3081; found, 435.3083.

3.5.6 Isomannide monooleate (3f)

Yield 81.3%. [α]_D²⁴ +65.6 (c 1.0 in CHCl₃). ν_{max}/cm⁻¹: 3446 (OH), 2926 and 2856 (CH), 1737 (C=O), 1650 (C=C), 1175 (C-O). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (3H, t, J = 6.7 Hz, 18-H), 1.23-1.40 (m, 20H, 4-H, 5-H, 6-H, 7-H, 12-H, 13-H, 14-H, 15-H, 16-H, 17-H), 1.57-1.71 (2H, m, 3-H), 1.96-2.07 (4H, m, 8-H, 11-H), 2.38 (2H, t, J = 7.5 Hz, 2-H), 3.57 (1H, dd, J¹ = 6.9 Hz, J² = 9.0 Hz, OCH₂CHOH, H_b), 3.84 (1H, dd, J¹ = 6.7 Hz, J² = 9.6 Hz, OCH₂CHOCO, H_b), 3.97 (1H, dd, J¹ = 6.2 Hz, J² = 9.0 Hz, OCH₂CHOH, H_a), 4.11 (1H, dd, J¹ = 6.4 Hz, J² = 9.4 Hz, OCH₂CHOCO, H_a), 4.22-4.38 (1H, m, CH₂CHOH), 4.48 (1H, t, J = 5.2 Hz, CHCHOH), 4.69 (1H, t, J = 5.0 Hz, CHCHOH), 5.12-5.18 (1H, q, CHOCO), 5.30-5.41 (2H, m, 9-H, 10-H). ¹³C NMR (75 MHz, CDCl₃): δ 14.11, 22.66, 24.80, 27.13, 27.18, 29.01, 29.07, 29.12, 29.29 (2 × C), 29.50, 29.65, 29.73, 31.88, 33.87, 70.76, 72.18, 73.81, 73.87, 80.41, 81.49, 129.69, 129.97, 173.19. HRMS (ESI⁺): calcd for C₂₄H₄₃O₅ [M+H]⁺, 411.3105; found, 411.3110.

3.6 Surfactant properties

All the synthesized compounds of isomannide monoesters were evaluated for surfactant properties. Aqueous solutions of non-ionic isomannide monoesters were prepared by dissolving appropriate amounts in Milli-Q water. A total of five tension measurements for each surfactant were determined using Kruss K100 tensiometre and the results presented are mean of such independent measurements.

4 Conclusions

In conclusion, we have developed a simple, smooth, an efficient and environmental benign protocol for the synthesis of novel isomannide-based fatty acid monoesters employing a novel, highly efficient and reusable SO₃H-carbon catalyst as a heterogeneous green catalyst in good yields. The catalyst exhibited a remarkable efficiency for the selective formation of isomannide fatty acid monoesters under solvent free conditions at 180 °C. The merits of this protocol are operationally simple, cleaner reaction profile, ease of product isolation, and reusability of the catalyst. Synthesized compounds were evaluated for their surface active properties. Decrease in CMC value with the increase in hydrophobicity was observed for C₁₀, C₁₂ and C₁₄ fatty acid esters of isomannide (3a-c). Whereas, deviation in CMC value from regularity was observed in case of C₁₆ and C₁₈ fatty acid esters of isomannide (3d-e). Among all the synthesized compounds, isomannide monomyristate (3c) and monolaurate (3b) exhibited superior surface active properties followed by isomannide monopalmitate (3d).

Acknowledgements

One of the authors T.V.K. Reddy is greatly acknowledge to the financial support from Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the award of Senior Research Fellowship (SRF).

Notes and references

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† Electronic Supplementary Information (ESI) available: [Gas chromatogram of isomannide monooleate, ¹H and ¹³C NMR spectra for all compounds]. See DOI: 10.1039/b000000x/

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