

Transesterification of Dicarboxylic Esters with *Kolakhar* made from *Musa balbisiana* as a Catalyst

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Abstract: These days dicarboxylic esters are believed to be green chemicals containing a large amount of oxygen and many di-esters can be put together with fuels. Di-succinate esters are green solvents that have performance and environmental benefits. Transesterification plays an important role here as it shows a simple path for the synthesis of more complex products from more easily accessible compounds. Here we report the transesterification of diethyl succinate with a series of structurally varied alcohols in presence of a heterogeneous, non-toxic, reusable and inexpensive catalyst derived from the trunk and rhizome of *Musa balbisiana* colla which afforded moderate to low yield of the products. The catalyst is derived from the trunk and rhizome of the post-harvest banana plant waste of the *Musa balbisiana* variety known as *kolakhar* in the Assamese community and available at no cost. The catalytic efficiency is the same for both the catalysts in the transesterification of diethyl succinate.

Keywords - transesterification, diethyl succinate, kolakhar, banana plant, catalysis, heterogeneous.

1. INTRODUCTION

These days dicarboxylic esters are substantially used by an ample number of researchers as a substitute for petroleum-based solvents owing to their bio-degradable nature.[1] Dicarboxylic esters are believed to be green chemicals containing a large amount of oxygen and many di-esters can be put together with fuels. They can play a vital role as intermediates in the synthesis of fine chemicals, drugs, plasticizers, food preservatives, pharmaceuticals and cosmetics.[1] They can act as an added ingredient for the enhancement of the *blended cetane number*, BCN value of the fuel and help to reduce the possibility of particulate matter emissions.[2] Esters of succinic acid are most important as they are utilized in the synthesis of plasticizers, perfumes, fragrance in food and cosmetics, viscosity adjusters diluents in paints and coatings, and intermediates in drugs and dyestuffs.[1], [3], [4] Succinate esters are extensively used in the synthesis of biodegradable copolymer with anti-dripping property.[5] Modern execution of succinate esters have also been proclaimed in the synthesis of a novel *intumescent flame retardant* (IFR) with an anti-dripping property.[6] Di-succinate esters are green solvents that have performance and environmental benefits. Dimethyl succinate is used as a flavouring agent. It also has a wide range of industrial applications such as Functional fluids (open systems), Intermediates, Paint additives and Coating additives, Pigments Solvents, Viscosity adjusters. Dibutyl succinate esters are used as insect repellent especially against biting flies of cattle, household ants and roaches.[7] Diheptyl Succinate is a lightweight, emollient texture enhancer that is sometimes used as a substitute for silicones in cosmetic products.[8] Conventional procedures for the production of dicarboxylic ester involve a stirred batch or continuous reactor in the presence of H₂SO₄ as a homogeneous catalyst. Due to known drawbacks of the traditional liquid acids (corrosiveness, separation problem, slow reaction rates, high temperature and pressure requirement and short life span), much thought has been given on the evolution of effortlessly recoverable, recyclable, non-toxic, inexpensive, environmentally benign solid heterogeneous catalysts with cleaner operations. [9]–[11]

Transesterification reactions catalyzed by homogeneous catalysts have various drawbacks including saponification, difficulty in isolation, purification, and separation of the catalyst as well as immiscibility of the catalyst with the reactants and incomplete transesterification. [12] The use of heterogeneous catalysts can reduce the processing costs associated with the use of homogeneous catalysts and many alkaline catalysts.[13]–[16] Transesterification plays a prominent role here as it shows a simple path for the synthesis of more complex products from more easily accessible compounds.[17] Transesterification has widest applications in academics as well as in industrial research. [10],[11],[18],[19],[22] Transesterification which is a single pot reaction is widely used in the production of biodiesel [23],[24],[25],[26] paint industry and is important in the synthesis of biologically active compounds and drugs. [17],[27]

Here, we report the transesterification of diethyl succinate catalyzed by catalysts derived from the trunk and the rhizome of *Musa balbisiana*. These catalysts are eco-friendly, non-toxic, heterogeneous, economical which comes from biomass available at almost zero cost. The catalyst derived from the trunk of *Musa balbisiana* has been successfully applied for biodiesel production from yellow oleander (*Thevetia peruviana*) seed oil. [22], [28] The same catalyst has also been successfully applied for the transesterification of structurally varied carboxylic esters with methanol, *n*-propanol, *n*-butanol and *n*-heptanol.[22], [29] Here, we observed that the efficacy of the catalysts from the trunk and the rhizome of *Musa balbisiana* was better than that of the catalyst from the trunk of *Musa acuminata* in a series of transesterification reactions involving a variety of monocarboxylic esters. In this paper, we are outlining the applicability of the catalysts in transesterification of diethyl succinate with a string of structurally varied alcohols.

2. EXPERIMENTAL SECTION

2.1 Materials

Following chemicals were procured from commercial sources. While esters were used without further treatment, alcohols were dried over anhydrous Na_2SO_4 prior to use: Diethyl succinate (Loba Chemie), Methanol (Merck Ltd), *n*-Propanol (Merck Ltd), *n*-Butanol (Merck Ltd), *n*-Amyl alcohol (Loba Chemie), *n*-Heptanol (Merck Ltd).

2.2 Preparation of the Catalyst

The traditional method was followed for the preparation of the catalyst. The trunk of the banana plant was sliced into thin pieces and air dried under the sun for several days. The dry material was ignited and allowed to burn and cool down to ambient temperature in its own. The ashes were then preserved in an airtight plastic container for use as and when necessary. The time required for burning and natural cooling down process depends on the quantity of material taken. Burning is usually expected to complete within half an hour but cooling down process may take hours. The Brunauer Emmet Teller, BET surface area, pore volume, and pore size of the catalysts were measured, and the results are shown in Table 1

Table 1: Textural properties of the catalysts

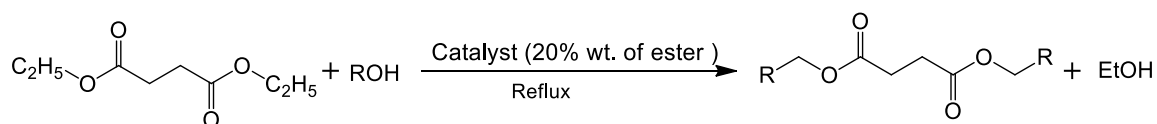
Catalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Catalyst from the trunk of <i>Musa balbisiana</i>	1.4870	0.019329	51.99612
Catalyst from the rhizome of <i>Musa balbisiana</i>	0.5790	0.010196	70.44064

2.3 Typical procedure for transesterification

A mixture of 1:20 molar ratio of dicarboxylic ester (1.5 mmol) and alcohol (30 mmol) together with the catalyst (20% wt. of ester) derived from the banana plant was stirred with a magnetic stirrer in a two neck round bottom flask. Reactions were carried out under reflux in a nitrogen atmosphere. The advancement of the reaction was monitored on TLC. After completion of the reaction, the reaction mixture was partitioned between ethyl acetate and water. The organic layer was washed with brine solution (10%, 10 ml \times 2) and dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel (60-120 mesh size) using light petroleum ether (bp. 40-60 °C) and ethyl acetate as the eluent. Products were identified by IR and NMR. ^1H and ^{13}C NMR were recorded in CDCl_3 at 300 and 75 MHz, respectively using Bruker Advance III 300MHz/54mm NMR spectrometer. FT-IR spectra were obtained on a Perkin Elmer RX I FT-IR spectrometer.

2.4 Transesterification of diethyl succinate with catalysts derived from the trunk and the rhizome of *Musa balbisiana* under reflux

Transesterifications of diethyl succinate to corresponding esters with higher and lower alcohols are carried out with the catalysts derived from the trunk and the rhizome of *M. balbisiana* (Scheme 1).



Ester : alcohol = 1:20 Molar ratio

R = Methyl, *n*-Propyl, *n*-Butyl, *n*-Amyl, *n*-heptyl.

Scheme 1: Transesterification of diethyl succinate

3. RESULTS AND DISCUSSIONS

Transesterification reactions with a series of alcohols like methanol, *n*-propanol, *n*-butanol, *n*-amyl alcohol and *n*-heptanol afforded moderate to low yields. Results are reported in Table 2 and 3.

Table 2: Transesterification of diethyl succinate with the catalyst from the trunk of *Musa balbisiana* under reflux

Entry	Ester	Alcohol	Time (h)	Product	Isolated yield (mol%)
1		CH ₃ OH	48		35
2		n-C ₃ H ₇ OH	58		29
3		n-C ₄ H ₉ OH	50		55
4		n-C ₅ H ₁₁ OH	46		52
5		n-C ₇ H ₁₅ OH	51		33

Table 3: Transesterification of diethyl succinate with the catalyst from the rhizome of *Musa balbisiana* under reflux

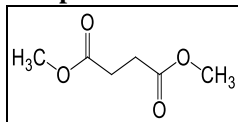
Entry	Ester	Alcohol	Time (h)	Product	Isolated yield (mol%)
1		CH ₃ OH	48		33
2		n-C ₃ H ₇ OH	58		28
3		n-C ₄ H ₉ OH	50		53
4		n-C ₅ H ₁₁ OH	46		49
5		n-C ₇ H ₁₅ OH	51		30

¹H NMR spectrum of dimethyl succinate shows a singlet signal at δ 3.676 due to the methoxy protons. In ¹H NMR and ¹³C NMR spectra of transesterified esters, we can see all the signals within the characteristic range expected for the protons and carbons present in the products. IR stretching frequencies expected for the products are also observed in the characteristic range which confirms the existence of the transesterified product.

Transesterification of diethyl succinate went successfully with a series of alcohols with both the catalysts. Transesterification of diethyl succinate is affected by the nature of the alcohol. Diethyl succinate transesterified to methyl and propyl esters shows a very poor yield with both the catalysts (Table 2 & 3, entry 1,2). This may be due to the low boiling point of the alcohols and transesterification of diethyl succinate requires a very high reaction temperature. Substrate conversion reached a good value when the alcohols used are *n*-butanol and *n*-amyl alcohol (Table 2, Table 3, entry 3,4). Again, with the increase in chain length of the alcohol (*n*-heptanol) substrate conversion decreases (Table 2, Table 3, entry 5). Transesterification with methanol and *n*-propanol shows comparatively low yields of the products than those with *n*-butanol and *n*-amyl alcohol. This trend has been observed in the case of both the catalysts.

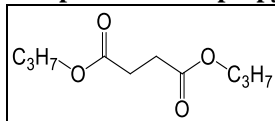
3.1 Spectral data

Compound 1 Dimethyl succinate



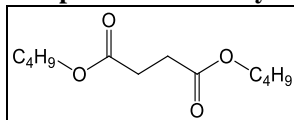
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 2.617 (s, 4H, CH_2CH_2), 3.676 (s, 3H, 2OCH_3). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 29.04, 51.80, 172.72. FT-IR (thin film/ cm^{-1}): 1165, 1442, 1739, 2954, 2997.

Compound 2 Di-*n*-propyl succinate



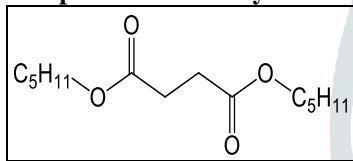
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.938 (t, $^3J = 7.5$ Hz, 6H, 2CH_3), 1.593-1.686 (m, 4H), 2.626 (s, 4H, CH_2CH_2), 4.051 (t, $^3J = 6.9$ Hz, 4H, 2OCH_2). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 10.35, 21.92, 29.18, 66.32, 172.38. FT-IR (thin film/ cm^{-1}): 1111, 1458, 1685, 1739, 2924, 2966.

Compound 3 Di-*n*-butyl succinate



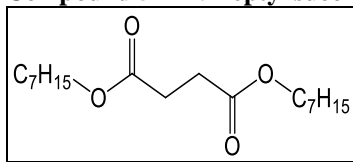
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.901 (t, $^3J = 7.2$ Hz, 6H, 2CH_3), 1.286-1.408 (m, 4H), 1.534-1.627 (m, 4H), 2.594 (s, 4H, CH_2CH_2), 4.085 (t, $^3J = 6.6$ Hz, 4H, 2OCH_2). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 13.67, 19.07, 29.16, 30.57, 64.58, 172.40. FT-IR (thin film/ cm^{-1}): 1165, 1357, 1462, 1735, 2954.

Compound 4 Di-*n*-amyl succinate



$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.898 (t, $^3J = 6.9$ Hz, 6H, 2CH_3), 1.246-1.362 (m, 8H), 1.575-1.667 (m, 4H), 2.619 (s, 4H, CH_2CH_2), 4.075 (t, $^3J = 6.9$ Hz, 4H, 2OCH_2). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 13.97, 22.31, 28.01, 28.26, 29.18, 64.90, 172.43. FT-IR (thin film/ cm^{-1}): 1161, 1354, 1408, 1462, 1631, 1735, 2951.

Compound 5 Di-*n*-heptyl succinate



$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.882 (t, 6H), 1.296 (m, 16H), 1.615-1.638 (m, 4H), 2.619 (s, 2H), 4.078 (t, $^3J = 6.6$ Hz, 4H, 2OCH_2). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 14.04, 22.55, 25.80, 28.61, 29.68, 31.69, 64.90, 172.40. FT-IR (thin film/ cm^{-1}): 1161, 1342, 1411, 1627, 1739, 2858, 2927.

4. CONCLUSION

Transesterification of dicarboxylic esters has been examined with diethyl succinate in the presence of two catalysts. Both the catalysts, one from the trunk and the other from the rhizome of *Musa balbisiana*, are successful catalysts. However, yields are moderate, and the reactivity of a given ester varies from alcohol to alcohol.

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