CHAPTER V

The catalyst in transesterification reaction:
Transesterification from lower to higher esters
CHAPTER V

The catalyst in transesterification reaction: Transesterification from lower to higher esters

V.1 Introduction

Transesterification reactions constitute a powerful method to synthesize a large variety of organic esters. Synthesis of esters is of increasing interest due to their wide usage in flavoring, perfumery, artificial essences and cosmetics.\(^1\) Usually, methyl and ethyl esters are readily available and thus they can be used in transesterification for an easy access to higher homologues which are of much importance for certain applications.\(^2\) Aromatic esters of hydrocinnamic acid have been used in the synthesis of HIV-1 protease inhibitors or as precursors for the synthesis of analgesic, inflammation inhibitor and antipyretic.\(^3,4\) Cinnamic ester derivatives are also reported to possess antitumour activity\(^5\) as well as a wide range of pharmacological activities such as antioxidative, cytotoxic, antimicrobial and antiviral activities.\(^6,7\) Long chain cinnamic esters are widely used in cosmetics as sunblocks because they are non-irritating to skin and ideally suited for cosmetic applications as they provide lubricity to prevent drying effect of wind.\(^5,8\) Aryl benzoate derivatives constitute important functionality for biologically active moieties.\(^9\) Alkyl benzoates often are used as fragrances and antibacterial agents in cosmetic formulations, as plasticizers in the manufacture of key poly(vinyl chloride) (PVC) polymers and as textile dye carriers for the treatment of synthetic fibers.\(^10\) Benzyl esters - especially benzyl benzoate find use in the treatment of cases of excessive peristalsis, or excessive spasm of smooth muscle, with surprisingly gratifying results.\(^11\) Benzyl benzoate, may be used as an antiparasitic insecticide to kill the mites responsible for the
skin condition scabies. Thus, a number of procedures have been developed for this useful reaction to synthesize esters.\textsuperscript{12}

Chatterjee \textit{et al.}\textsuperscript{12} developed an efficient procedure for transesterification in a ball-mill in the absence of solvent, acid/base or metal catalyst. A variety of methyl, ethyl, allyl esters have been transesterified to higher benzyl and other esters in high yields by this procedure.

\[
\begin{array}{c}
\text{R}_1\text{O}\text{R}^2 + \text{R}^3\text{OH} \xrightarrow{\text{Basic Al}_2\text{O}_3 \text{ ball milling}} \text{R}^1\text{O}\text{R}^3 + \text{R}^2\text{OH} \\
\end{array}
\]

Scheme V.1: Transesterification in ball-mill

Use of Mn(II) salts such as sulfate and carbonate\textsuperscript{2} and niobium(V) oxide\textsuperscript{13} as efficient and selective catalysts for the transesterification of lower esters into its higher homologues have been reported. Transesterification of methyl benzoate into its higher homologues catalyzed by natural phosphate with or without solvent in heterogeneous media have been reported by Fathallaah Bazi \textit{et al.}\textsuperscript{14} Imidazol-2-ylidenes, a family of N-heterocyclic carbenes (NHC), have been reported as efficient catalysts in the transesterification involving numerous esters and alcohols.\textsuperscript{15} Aluminosilicates have also been employed for the transesterification of various β-keto esters with different alcohols in toluene under reflux.\textsuperscript{16} Hatano \textit{et al.}\textsuperscript{17} explored the lanthanum(III) nitrate alkoxide complex catalyzed transesterification of carboxylic esters with a variety of primary, secondary and tertiary alcohols in hydrocarbon solvents with high efficiency. But only a few catalysts have been reported which are derived from natural sources for the transesterification of lower to higher esters that come at zero cost.
Chapter V

Moving on from Chapter IV, with the aim of broadening the scope of this catalytic transformation, we focused our interest in esters which have important applications in cosmetics and pharmaceutical industries having longer chain lengths. We report herein catalytic applications of ash derived from banana plant to transesterify lower esters into higher esters.

As a part of a development program, we tried to generate a number of butyl, amyl and benzyl esters from their lower homologues (Scheme V.2).

![Chemical Reaction Diagram]

**Scheme V.2. General scheme of transesterification reaction**

We have studied the catalytic efficiency of the catalysts from the trunk and the rhizome of *Musa balbisiana* and the trunk of *Musa acuminata* for the transesterification of a large number of ethyl and methyl esters into higher homologues. The beautiful feature of the catalysts is that they are derived from post-harvest banana plant which comes at zero cost and can be used without further processing.

**V.2 Results and Discussion**

We examined the efficacy of the catalysts derived from the trunk and the rhizome of *Musa balbisiana* and the trunk of *Musa acuminata* for the transesterification of a variety of methyl and ethyl esters to corresponding higher esters like *n*-butyl, *n*-amyl and benzyl esters under reflux in nitrogen atmosphere. In total 45 transesterification reactions, 15 with each of the catalysts, have been examined. Results are recorded in Tables V.1 to V.3.
Transesterification of aromatic esters with a variety of primary alcohols in presence of the three varieties of banana plant derived catalysts have been carried out efficiently by simply refluxing with continuous stirring. Most of the reactions proceed smoothly with all the varieties of the catalysts mentioned here. Reactions with ethyl benzoate, methyl benzoate and methyl cinnamate exhibit higher reactivity in presence of \( n \)-butanol and \( n \)-pentanol than aromatic alcohol. However, the catalyst from the trunk of \textit{Musa acuminata} seems to be less efficient than the other two with a decrease in the yields of the products as compared to the corresponding yields with the catalysts derived from the trunk and the rhizome of \textit{Musa balbisiana}. 
### Table V.1: Transesterification with the catalyst from the trunk of *Musa balbisiana* under reflux

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<th>Time (h)</th>
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Table V.2: Transesterification with the catalyst from the rhizome of *Musa balbisiana* under reflux

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### Table V.3: Transesterification with the catalyst from the trunk of *Musa acuminata* under reflux

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### Chapter V

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Reactions with benzyl alcohol are visibly sluggish with both methyl and ethyl benzoate. One of the factors for this may be due to steric hindrance between the substrate and the bulky alcohol. Almost no conversion was observed in the transesterification reaction of cinnamic acid esters with benzyl alcohol [Table V.(1-3), entry 9]. The reactions are highly favourable in case of aromatic esters with an electron withdrawing substituent such as nitro group at para position with both aliphatic as well as aromatic alcohols [Table V.(1-3), entry 10-12]. Esters with electron donating substituent such as hydroxy group at meta position show less reactivity with n-butanol and n-pentanol [Table V.(1-3), entry 13,14] and no reactivity with benzyl alcohol [Table V.(1-3), entry 15]. Reactivity of m-hydroxybenzoate with benzyl alcohol is less than that of p-nitrobenzoate. NO₂ group is an electron withdrawing group and it decreases the electron density in the ring, thereby decreasing the repulsive π-π interaction in the key steps of the reaction (cf. Mechanism in section I.3.2). Electron donating substituent like OH, increases the electron density in the ring and hence increases the π-π repulsion, thereby destabilizing the intermediate. Probably, for this reason, benzyl alcohol does not form any product with methyl m-hydroxybenzoate. Reactions with n-butanol and n-amyl alcohol is also moderate.

Spectral data were extensively used to identify the products of transesterification reactions. In methyl esters, we can see characteristic ¹H NMR signals in the range δ 3.4 to 3.9 ppm. In ¹H NMR spectra of the transesterified products, disappearance of the signal due to the methoxy protons indicates the successful transesterification of the ester. In ¹³C NMR spectra, characteristic signal due to methoxy carbon at around δ 52 ppm is also found to be absent. We can see some additional signals in ¹³C NMR spectra due to carbons present in the transesterified products in the range δ 13-167 ppm. This indicates the successful completion of the transesterification process. IR stretching frequencies are also in the characteristic range.
3.1 Experimental Section

3.1.1 Materials

Esters used were prepared in the laboratory and they are described in Chapter II. Following alcohols were procured from commercial sources, and were dried over anhydrous Na$_2$SO$_4$ prior to use.

(i) $n$-Butanol (Merck Ltd.)

(ii) $n$-Amyl alcohol (Loba Chemie)

(iii) Benzyl alcohol (Merck)

3.1.2 Typical procedure for transesterification

A mixture of the ester (1.5 mmol) and alcohol (30 mmol) together with the catalyst (20% wt. of ester) was stirred with a magnetic stirrer in a two neck round bottom flask in nitrogen atmosphere. Reactions (Scheme V. 2) were carried out under reflux condition. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was partitioned between petroleum ether and water. The organic layer was washed with brine solution (10%, 10 ml×2) and dried over anhydrous Na$_2$SO$_4$. Solvent was removed under vacuum and 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. $^1$H 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 Shimadzu IR Affinity-1 IR spectrometer.
V.3.3 Spectral data

**Compound V.1 n-Butyl benzoate (Table V.1, V.2, V.3, entry 1,4)**

\[
\begin{align*}
1^\text{H} \text{NMR (300 MHz, CDCl}_3\text{): } & \delta 0.977 \text{ (t, } J = 7.2 \text{ Hz, 3H, CH}_3), \\
& 1.440-1.516 \text{ (m, 2H), 1.654-1.776 (m, 2H), 4.322 (t, } J = 6.6 \text{ Hz, 2H, OCH}_2\text{), 7.408-7.458 (m, 2H, aromatic), 7.525-7.550 (m, 1H, aromatic), 8.03 (d, } J = 6.9 \text{ Hz, 2H, aromatic). } \\
13^\text{C} \text{NMR (75 MHz, CDCl}_3\text{): } & \delta 13.73, 19.24, 30.73, 64.80, 128.27, 129.48, 130.48, 132.75, 166.67. \\
\text{FT-IR (thin film/cm}^{-1}\text{): } & 1026, 1111, 1176, 1384, 1450, 1600, 1716, 2873, 2958, 3062 \text{ (Fig. V.1 to V.3). }
\end{align*}
\]

**Compound V.2 n-Amyl benzoate (Table V.1, V.2, V.3, entry 2,5)**

\[
\begin{align*}
1^\text{H} \text{NMR (300 MHz, CDCl}_3\text{): } & \delta 0.936 \text{ (t, } J = 6.9 \text{ Hz, 3H, CH}_3), \\
& 1.409-1.419 \text{ (m, 4H), 1.681-1.800 (m, 2H, CH}_2\text{), 4.322 (t, } J = 6.6 \text{ Hz, 2H, OCH}_2\text{), 7.418-7.467 (m, 2H, aromatic), 7.534-7.582 (m, 1H, aromatic), 8.05 (d, } J = 7.8 \text{ Hz, 2H, aromatic). } \\
13^\text{C} \text{NMR (75 MHz, CDCl}_3\text{): } & \delta 13.97, 22.34, 28.17, 28.39, 65.10, 128.28, 129.49, 130.48, 132.76, 166.68. \\
\text{FT-IR (thin film/cm}^{-1}\text{): } & 1018, 1273, 1427, 1712, 2943, 3078 \text{ (Fig. V.4 to V.6). }
\end{align*}
\]

**Compound V. 3 Benzyl benzoate (Table V.1, V.2, V.3, entry 3,6)**

\[
\begin{align*}
1^\text{H} \text{NMR (300 MHz, CDCl}_3\text{): } & \delta 5.385 \text{ (s, 2H), 7.336-8.114 (m, 10H, aromatic). } \\
13^\text{C} \text{NMR (75 MHz, CDCl}_3\text{): } & \delta 66.63, 128.11, 128.19, 128.32, 128.54, 129.64, 130.03, 132.99, 135.97, 166.39. \\
\text{FT-IR (thin film/cm}^{-1}\text{): } & 1107, 1450, 1716, 2947, 3035 \text{ (Fig. V.7 to V.9). }
\end{align*}
\]
Chapter V

Compound V.4 n-Butyl cinnamate (Table V.1, V.2, V.3, entry 7)

\[
\text{\begin{tikzpicture}
\begin{scope}
\draw[thick,black] (0,0) -- (0.5,0) -- (0.5,0.5) -- (1,0.5) -- (1,1) -- (0.5,1) -- (0.5,1.5) -- (0,1.5) -- cycle;
\end{scope}
\end{tikzpicture}}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.0 (t, \(^3\)J = 6.6 Hz, 3H, CH\(_3\)), 1.259-1.504 (m, 2H, CH\(_2\)), 1.649-1.742 (m, 2H, CH\(_2\)), 4.215 (t, \(^3\)J = 6.6 Hz, OCH\(_2\)), 6.45 (d, \(^3\)J = 15.9 Hz, 1H, olefinic), 7.381-7.532 (m, 5H, aromatic), 7.69 (d, \(^3\)J = 15.9 Hz, 1H, olefinic). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 13.69, 19.13, 30.69, 64.37, 118.17, 127.97, 128.79, 130.14, 134.36, 144.50, 167.07. FT-IR (thin film/cm\(^{-1}\)): 1172, 1454, 1635, 1712, 2870, 2958, 3062 (Fig. V.10 to V.12).

Compound V.5 n-Amyl cinnamate (Table V.1, V.2, V.3, entry 8)

\[
\text{\begin{tikzpicture}
\begin{scope}
\draw[thick,black] (0,0) -- (0.5,0) -- (0.5,0.5) -- (1,0.5) -- (1,1) -- (0.5,1) -- (0.5,1.5) -- (0,1.5) -- cycle;
\end{scope}
\end{tikzpicture}}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 0.931 (t, \(^3\)J = 6.6 Hz, 3H, CH\(_3\)), 1.259-1.438 (m, 4H), 1.670-1.737 (m, 2H), 4.206 (t, \(^3\)J = 6.6 Hz, 2H, OCH\(_2\)), 6.45 (d, \(^3\)J = 16.2 Hz, 1H, olefinic), 7.38-7.39 (m, 3H, aromatic), 7.52-7.54 (m, 2H, aromatic), 7.69 (d, \(^3\)J = 15.9 Hz, 1H, olefinic). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 13.94, 22.31, 28.07, 28.36, 64.68, 118.20, 127.99, 128.81, 130.16, 134.39, 144.52, 167.08. FT-IR (thin film/cm\(^{-1}\)): 1176, 1458, 1635, 1712, 2873, 2943, 3055 (Fig. V.13 to V.15).

Compound V.6 n-Butyl \(p\)-nitrobenzoate (Table V.1, V.2, V.3, entry 10)

\[
\text{\begin{tikzpicture}
\begin{scope}
\draw[thick,black] (0,0) -- (0.5,0) -- (0.5,0.5) -- (1,0.5) -- (1,1) -- (0.5,1) -- (0.5,1.5) -- (0,1.5) -- cycle;
\end{scope}
\end{tikzpicture}}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 1.015 (t, \(^3\)J = 6.6 Hz, 3H, CH\(_3\)), 1.422-1.546 (m, 2H), 1.731-1.825 (m, 2H), 4.375 (t, \(^3\)J = 6.6 Hz, 2H, OCH\(_2\)), 8.189-8.298 (m, 4H, aromatic). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 13.69, 19.17, 30.57, 65.79, 123.47, 130.61, 135.81,
150.40, 164.74. FT-IR (thin film/cm$^{-1}$): 871, 1107, 1346, 1523, 1732, 2866, 2954, 3062 (Fig. V.16 to V.18).

**Compound V.7 n-Amyl p-nitrobenzoate (Table V.1, V.2, V.3, entry 11)**

![](image1)

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.929 (t, $^3$J = 6.9 Hz, 3H, CH$_3$), 1.405-1.412 (m, 4H), 1.709-1.814 (m, 2H), 4.362 (t, $^3$J = 6.6 Hz, 2H, OCH$_2$), 8.189-8.298 (m, 4H, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 13.93, 22.29, 28.07, 28.25, 66.07, 123.47, 130.61, 135.82, 150.40, 164.72. FT-IR (thin film/cm$^{-1}$): 867, 1107, 1354, 1527, 1724, 2862, 2954, 3113 (Fig. V.19 to V.21).

**Compound V.8 Benzyl p-nitrobenzoate (Table V.1, V.2, V.3, entry 12)**

![](image2)

$^1$H NMR (300 MHz, CDCl$_3$): δ 5.410 (s, 2H, CH$_2$), 7.263-7.450 (m, 5H, aromatic), 8.222-8.299 (m, 4H, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 67.61, 123.50, 126.92, 127.59, 128.40, 130.78, 135.16, 135.42, 150.50, 164.49. FT-IR (thin film/cm$^{-1}$): 848, 1107, 1346, 1523, 1716, 2862, 2935, 3066 (Fig. V.22 to V.24).

**Compound V.9 n-Butyl m-hydroxybenzoate (Table V.1, V.2, V.3, entry 13)**

![](image3)

$^1$H NMR (300 MHz, CDCl$_3$): δ 1.266 (t, $^3$J = 7.2 Hz, 3H, CH$_3$), 1.431-1.528 (m, 2H), 1.698-1.787 (m, 2H), 4.322 (t, $^3$J = 6.6 Hz, 2H, OCH$_2$), 6.643 (bs, 1H, OH), 7.064-7.33 (m, 3H, aromatic), 7.509 (s, 1H, aromatic). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 13.71, 19.20,
30.63, 65.20, 116.29, 120.26, 121.65, 129.64, 131.55, 156.01, 167.05. FT-IR (thin film/cm\textsuperscript{-1}): 756, 1107, 1296, 1392, 1708, 2866, 2958, 3414 (Fig. V.25 to 27).

**Compound V.10 n-Amyl m-hydroxybenzoate (Table V.1, V.2, V.3, entry 14)**

![Compound Structure](image)

\(^1\text{H} \text{NMR} (300 \text{ MHz, CDCl}_3):\)  δ 0.927 (t, \(^3\text{J} = 6.9 \text{ Hz, } 3\text{H, CH}_3),\) 1.397-1.407 (m, 4H), 1.721-1.788 (m, 2H), 4.313 (t, \(^3\text{J} = 6.6 \text{ Hz, } 2\text{H, CH}_3),\) 5.946 (bs, 1H, OH), 7.054-7.342 (m, 3H, aromatic), 7.594 (s, 1H, aromatic). \(^1\text{C} \text{NMR} (75 \text{ MHz, CDCl}_3):\)  δ 13.97, 22.33, 28.14, 28.33, 65.41, 116.25, 120.12, 121.81, 129.66, 131.74, 155.81, 166.75. FT-IR (thin film/cm\textsuperscript{-1}): 756, 1103, 1222, 1292, 1454, 1597, 1689, 2873, 2954, 3402 (Fig. V.28 to V.30).
Fig. V.1: $^1$H NMR spectrum of n-butyl benzoate (Table V.1, V.2, V.3, entry 1,4)

Fig. V.2: $^{13}$C NMR spectrum of n-butyl benzoate (Table V.1, V.2, V.3, entry 1,4)
Fig. V.3: IR spectrum of n-butyl benzoate (Table V.1, V.2, V.3, entry 1.4)

Fig. V.4: $^1$H NMR spectrum of n-amyl benzoate (Table V.1, V.2, V.3, entry 2.5)
Fig. V.5: $^{13}$C NMR spectrum of $n$-amyl benzoate (Table V.1, V.2, V.3, entry 2.5)

Fig. V.6: IR spectrum of $n$-amyl benzoate (Table V.1, V.2, V.3, entry 2.5)
Fig. V.7: $^1$H NMR spectrum of benzyl benzoate (Table V.1, V.2, V.3, entry 3,6)

Fig. V.8: $^{13}$C NMR spectrum of benzyl benzoate: (Table V.1, V.2, V.3, entry 3,6)
Fig. V.9: IR spectrum of benzyl benzoate (Table V.1, V.2, V.3, entry 3,6)

Fig. V.10: $^1$H NMR spectrum of $n$-butyl cinnamate (Table V.1, V.2, V.3, entry 7)
Fig. V.11: $^{13}$C NMR spectrum of $n$-butyl cinnamate (Table V.1, V.2, V.3, entry 7)

Fig. V.12: IR spectrum of $n$-butyl cinnamate (Table V.1, V.2, V.3, entry 7)
Fig. V.13: $^1$H NMR spectrum of $n$-amyl cinnamate (Table V.1, V.2, V.3, entry 8)

Fig. V.14: $^{13}$C NMR spectrum of $n$-amyl cinnamate (Table V.1, V.2, V.3, entry 8)
Fig. V.15: IR spectrum of n-amyl cinnamate (Table V.1, V.2, V.3, entry 8)

Fig. V.16: $^1$H NMR spectrum of n-butyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 10)
Fig. V.17: $^{13}$C NMR spectrum of $n$-butyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 10)

Fig. V.18: IR spectrum of $n$-butyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 10)
Fig. V.19: $^1$H NMR spectrum of $n$-amyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 11)

Fig. V.20: $^{13}$C NMR spectrum of $n$-amyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 11)
Fig. V.21: IR spectrum of *n*-amyl *p*-nitrobenzoate (Table V.1, V.2, V.3, entry 11)

Fig. V.22: $^1$H NMR spectrum of benzyl *p*-nitrobenzoate (Table V.1, V.2, V.3, entry 12)
Fig. V.23: $^{13}$C NMR spectrum of benzyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 12)

Fig. V.24: IR spectrum of benzyl $p$-nitrobenzoate (Table V.1, V.2, V.3, entry 12)
Fig. V.25: \(^1\)H NMR spectrum of \(n\)-butyl \(m\)-hydroxybenzoate: (Table V.1, V.2, V.3, entry 13)

Fig. V.26: \(^{13}\)C NMR spectrum of \(n\)-butyl \(m\)-hydroxybenzoate (Table V.1, V.2, V.3, entry 13)
Fig. V.27: IR spectrum of n-butyl m-hydroxybenzoate (Table V.1, V.2, V.3, entry 13)

Fig. V.28: $^1$H NMR spectrum of n-amyl m-hydroxybenzoate (Table V.1, V.2, V.3, entry 14)
Fig. V.29: $^{13}$C NMR spectrum of $n$-amyl $m$-hydroxybenzoate (Table V.1, V.2, V.3, entry 14)

Fig. V.30: IR spectrum of $n$-amyl $m$-hydroxybenzoate (Table V.1, V.2, V.3, entry 14)
Chapter V

V.4 Conclusion

The ashes derived from the trunk and the rhizome of *Musa balbisiana*, and the trunk of *Musa acuminata* are efficient catalysts for transesterification of esters of lower alcohols to esters of higher alcohols. However, their efficiency depends on the size and structure of the alcohols as well as those of the esters.

V.5 References


