Synthesis of ester components of spermaceti and a jojoba oil analogue catalyzed by acid activated Indian bentonite under microwave irradiation

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Acid activated Indian bentonite (AAIB) is an excellent catalyst for the esterification of long chain fatty acids with long chain alcohols. The ester constituents of spermaceti (whale wax) and an analogue of jojoba oil are obtained when the reactants with catalyst are exposed to microwave irradiation under solvent-free conditions. The Indian bentonite is used for such a reaction for the first time. The procedure is essentially pollution-free as virtually no waste material is produced. Esters can also be synthesized by solvent-free alkylations of carboxylic anions under microwave irradiation. A few solvent-free alkylations of carboxylic anions have been reported using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst under microwave irradiation.

Keywords: Sperm whale, Jojoba oil, Esters, Acid activated Indian bentonite, Catalyst

Esters have many applications as intermediates in the synthesis of fine chemicals, drugs, plasticizers, perfumes, food preservatives, cosmetics, pharmaceuticals, solvents, and chiral auxiliaries. Particularly, esters derived from sperm whale oil are used as special lubricants1, in pharmaceuticals2, cosmetics3, and food industry4. Spermaceti (or white of whale or cetaceum or spermaceti wax) is a wax extracted either from a large cavity located in the head of sperm-whale Physeter macrocephalus, or from its adipose tissues. Horiguchi et al.4 have determined the composition of wax esters of spermaceti by GC-MS. Cetyl palmitate, cetyl myristate and cetyl laurate are the major constituent esters present in untreated spermaceti isolated from the head cavities of sperm whale. Presently, the whale is an endangered animal and the ban on whale hunting has made researchers to develop chemical methods for the synthesis of these esters.

Jojoba oil is very similar to that of spermaceti for which it is an excellent substitute. Jojoba oil is a liquid wax present in a very high proportion (45 to 60%) in the seeds of the Simmondsia chinensis bush which grows naturally in the semi-desert areas of North Mexico, South Arizona and California. Jojoba oil is clear and doesn't become rancid easily, even under harsh conditions. Because of its softening qualities, it is very popular as a raw material for a wide range of cosmetics, from tanning lotions to shampoos. An analogue of jojoba oil might be obtained by preparing ester of oleic acid and oleyl alcohol5,6.

A common method of preparing esters is to react the required carboxylic acid and alcohol in presence of an acid catalyst, such as conc. H2SO4, HCl, etc. The present tendency is to replace these catalysts by heterogeneous catalysts. Several heterogeneous catalysts have been reported to synthesize industrially important esters7. Hirose et al.8 have employed imidazole as a promoter for microwave assisted esterification of carboxylic acid anhydrides with alcohols. Bautista et al.9 have carried out the development and optimization of a process for the synthesis of an analogue of sperm whale oil. Mantri et al.10 have reported esterification of long chain aliphatic carboxylic acids over ZrOCl2.8H2O. Habib et al.11 have studied direct esterification reactions on trichlorotitanium(IV) trifluoromethane sulfonate.

The modified clays are versatile heterogeneous catalysts for a wide variety of organic reactions12. The usefulness of microwave radiation in activating a wide range of organic reactions is well

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established\textsuperscript{13}. In addition, the importance of heterogeneous catalysts is becoming more significant, because of their enhanced selectivity and use of milder reaction conditions compared to conventional ones\textsuperscript{14}.

Here the microwave-assisted synthesis of the ester components of spermaceti and an analogue of jojoba oil using acid activated Indian bentonite (AAIB) as an acid catalyst has been reported for the first time.

A few solvent-free alkylations of carboxylic anions have been performed using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst under microwave irradiation.

**Experimental Procedure**

**Materials and methods**

Acid activated Indian bentonite was prepared and characterized by following the methods reported in literature\textsuperscript{15}.

**Esterification in liquid phase: Ester components of spermaceti**

In a typical experiment (Scheme 1) 1.2 mmol of the carboxylic acid was treated with 1.0 mmol of alcohol dissolved in 25 mL of dry \(\alpha\)-xylene. To this, 300 mg of AAIB was added and the resultant mixture was refluxed, accompanied by azeotropic removal of water using Dean-Stark apparatus. After appropriate reaction time, the mixture was cooled, the catalyst was filtered off, and washed with the solvent (10 mL). The unreacted acid was removed by washing the filtrate with 5\% NaOH (4×10 mL) followed by water (3×10 mL). The organic layer was dried over anhydrous Na\(_2\)SO\(_4\). The solvent was removed under reduced pressure. The resulting residue was purified by passing through a silica gel column (100-200 mesh) using benzene-petroleum ether (1:5) as eluant to obtain the pure ester.

\[
\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{AAIB, reflux}} \text{RCOOCH}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

**Scheme 1**

**Esterification under microwave irradiation: Ester components of spermaceti**

In a typical experiment (Scheme 2) 1.0 - 1.5 mmol of carboxylic acid, 1.0 or 2.0 mmol of oleyl alcohol and 150 or 300 mg of \(p\)-TSA or AAIB were taken into a 10 mL beaker and mixed well. The resultant mixture was microwave irradiated (KenStar MO-9706 A, 2450 MHz, 800 W) for appropriate reaction time in full power. The reaction mixture was cooled, hexane (5 mL) was added, the catalyst was filtered off, and washed with hexane (10 mL). The filtrate was concentrated and the residue was chromatographed on a silica gel (100-200 mesh) column using hexane-ethylacetate (9:8:0:2) as eluant to give the pure ester.

\[
\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{MW, p-TSA or AAIB}} \text{RCOOCH}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

**Scheme 2**

**Esterification under microwave irradiation: Jojoba oil analogue**

In a typical experiment (Scheme 3) 1.5 or 2.4 mmol of oleic acid, 1.0 or 2.0 mmol of oleyl alcohol and 150 or 300 mg of \(p\)-TSA or AAIB were taken into a 10 mL beaker and mixed well. The resultant mixture was microwave irradiated (KenStar MO-9706 A, 2450 MHz, 800 W) for appropriate reaction time in full power. The reaction mixture was cooled, hexane (5 mL) was added, the catalyst was filtered off, and washed with hexane (10 mL). The filtrate was concentrated and the residue was chromatographed on a silica gel column using hexane-ethylacetate (9:8:0:2) as eluant to give the pure ester.

\[
\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{MW, p-TSA or AAIB}} \text{RCOOCH}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

**Scheme 3**

**Carboxylate alkylations under microwave irradiation**

In a 5 mL Borosil\textsuperscript{®} beaker (Scheme 4) 2.0 mmol of carboxylic acid, 2.0 mmol of finely ground K\(_2\)CO\(_3\) and 1.0 mmol of tetrabutylammonium bromide (TBAB) or 0.3 g of tetrabutylammonium clay\textsuperscript{16} (TBA clay) were introduced. After mixing, 2.0 mmol of \(n\)-octyl bromide were added. The resultant mixture was microwave irradiated (KenStar MO-9706 A, 2450 MHz, 800 W) for appropriate reaction time in full power. The reaction mixture was cooled, dissolved in petroleum ether or diethyl ether, and filtered. The filtrate was passed through a silica gel column using benzene-petroleum ether (1:3) as eluant to obtain the pure ester.

\[
\text{RCOO}^- + \text{C}_8\text{H}_{17}\text{Br} \xrightarrow{TBA or TBA Clay} \text{RCOO}_\text{Cl}\text{C}_8\text{H}_{17} + \text{KBr}
\]

**Scheme 4**
The esters were identified by their melting points and $^1$H NMR and IR spectra. Melting points are uncorrected. All acids and alcohols (except myristic acid, which was procured from Merk-Schuchardt, Germany and oleyl alcohol, which was procured from Aldrich Chemical Company, Inc., USA) and solvents were purchased from SD fine-chem Limited, India. All solvents were distilled prior to use. The IR spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer and $^1$H NMR spectra on a Bruker-AMX 400MHz NMR spectrometer.

Results and Discussion

In continuation of the previous work on the use of acid activated Indian bentonite as catalyst for the esterification reactions,$^{17}$ the esterifications of long chain fatty acids with fatty alcohols under thermal condition and under the influence of microwave irradiation using acid activated Indian bentonite as catalyst have been investigated. The ester components of spermaceti and an analogue of jojoba oil are synthesized.

Synthesis of the ester components of spermaceti (sperm whale oil)

It is an established fact that reactions carried out under microwave condition are faster than those carried out conventionally.$^{13}$ The esterification reaction of palmitic acid with cetyl alcohol is studied with various catalysts, with different molar ratios and in different time intervals under microwave irradiation.

The reactions between long chain fatty acids and fatty alcohols to prepare corresponding esters require high temperatures and long reaction times.$^{10}$ The results of the microwave assisted synthesis of cetyl palmitate, the major component of spermaceti, are presented in Table 1. In the present study, the esterification of palmitic acid with cetyl alcohol was carried out in the absence of catalyst, with raw clay, $p$-toluenesulphonic acid and acid activated Indian bentonite. It can be seen from Table 1 that 5% of cetyl palmitate was obtained in the absence of catalyst after 60 min of microwave irradiation (Table 1, entry 1). It is observed that when raw clay or 400 mg of AAIB were used as catalysts, the formation of cetyl palmitate was reduced (Table 1, entries 2 and 4). In general, microwave assisted organic reactions go to completion in less time. However, the reaction between palmitic acid and cetyl alcohol (molar ratio = 1.2:1) in presence of 300 mg of AAIB under the influence of microwave irradiation for 60 min and 120 min yielded cetyl palmitate in 69 and 81% respectively (Table 1, entries 5 and 6). Therefore, for further esterification studies, the acid to alcohol ratio of 1.2:1, amount of AAIB 300 mg and duration of irradiation 60 min were selected.

Table 2 summarizes the results of the synthesis of the ester components of spermaceti. From Table 2, it is clear that palmitic acid, myristic acid and lauric acid react satisfactorily with cetyl alcohol to give esters in 50-70% yield (Table 2, entries 1-3). However, the yields were less than 20% in other five esterification reactions catalysed by AAIB (Table 2, entries 4, 5 and 7-10). This is due to the fact that AAIB settles down in the beaker as the reaction progresses and only a fraction of the reaction mixture is in contact with the catalyst. Although AAIB reduces the energy required for bringing about the reaction between palmitic acid and cetyl alcohol, due to its lesser contact area with reaction mixture, longer reaction times have been observed to get cetyl palmitate in good yield.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molar ratio PA:CA</th>
<th>Catalyst</th>
<th>Catalyst amount (mg)</th>
<th>Time (min)</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>No catalyst</td>
<td>Nil</td>
<td>60</td>
<td>05</td>
</tr>
<tr>
<td>2</td>
<td>1:1</td>
<td>Raw clay</td>
<td>300</td>
<td>60</td>
<td>02</td>
</tr>
<tr>
<td>3</td>
<td>1:1</td>
<td>$p$-TSA</td>
<td>300</td>
<td>01</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>1:1</td>
<td>AAIB</td>
<td>400</td>
<td>60</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>1.2:1</td>
<td>AAIB</td>
<td>300</td>
<td>60</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>1.2:1</td>
<td>AAIB</td>
<td>300</td>
<td>120</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>1.5:1</td>
<td>AAIB</td>
<td>300</td>
<td>45</td>
<td>58</td>
</tr>
</tbody>
</table>

$^a$ Isolated yields based on alcohol; PA= Palmitic acid; CA= Cetyl alcohol; $p$-TSA = $p$-toluenesulphonic acid
The AAIB catalyzed esterification reactions of cetyl alcohol with palmitic acid, myristic acid and lauric acid have also been studied in o-xylene under reflux. The esters are obtained in 82-98% yield after 12 h.

Synthesis of an analogue of jojoba oil

Table 3 shows the microwave assisted synthesis of oleyl oleate. The reaction between oleic acid and oleyl alcohol yielded 5% of the ester in presence of 300 mg of AAIB after 60 min of microwave irradiation (Table 3, entry 2), whereas the ester was obtained in 44% yield in presence of 150 mg of p-toluenesulphonic acid after 2 min of microwave irradiation. This is because both the reactants are liquids and the AAIB settles down in the beaker. Hence only a fraction of the reaction mixture will be in contact with the catalyst.

The reaction between oleic acid and 2-ethoxyethanol with 500 mg of AAIB gave 87% yield of the corresponding ester after 8 h of reflux in toluene. The reaction between oleic acid (1 mmol) and oleyl alcohol (2 mmol) with 500 mg of AAIB in toluene failed to give the ester even after 12 h of reflux. However, the dimerization of polyunsaturated fatty acids or their esters using acid activated clays was first reported by Johnston and De Groote. Barrett et al. have described the clay catalyzed dimerization of monounsaturated fatty acids. Investigations are in progress to synthesize long chain unsaturated esters in good yields. In this direction, the partial success achieved with microwaves is significant.

Carboxylate alkylations

Solvent-free alkylations (Scheme 4) of carboxylic anions under microwave irradiation have been studied using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst and n-octyl bromide as an alkylating agent. The potassium salts in situ were prepared by reacting the carboxylic acids in the presence of K$_2$CO$_3$. The potassium salt of stearic acid (5.0 mmol) with 0.5 mg of AAIB gave 61% yield of the corresponding ester after 2 min of microwave irradiation in toluene.

| Entry | Acid or its Potassium salt (mmol) | Base (mmol) | Amount of catalyst (mmol) | Amount of alkylation agent (mmol) | Time (min) | Yield (%)$^a$
|-------|----------------------------------|------------|--------------------------|-------------------------------|-----------|---------------
| 1     | Oleic acid (2.0)                 | 2.0        | 1.0                      | 2.0                           | 02        | 91            |
| 2     | Palmitic acid (2.0)              | 2.0        | 1.0                      | 2.0                           | 02        | 87            |
| 3     | Stearic acid (2.0)               | 2.0        | 1.0                      | 2.0                           | 01        | 93            |
| 4     | C$_7$H$_{13}$COOK (5.0)          | ---        | 0.5                      | 5.0                           | 02        | 61            |
| 5     | Oleic acid (2.0)                 | 2.0        | 0.3 g                    | 2.0                           | 02        | 30$^b$        |

$^a$Isolated yields (unoptimized). $^b$Tetrabutylammonium clay catalyst.
acid was prepared from carboxylic acid and a stoichiometric amount of KOH in ethyl alcohol and subsequent evaporation of ethanol. The results are presented in Table 4. The yields are 87-93% within 2 min or less of microwave irradiation (Table 4, entries 1-3). The preparation of \( n \)-octyl palmitate in presence of AAIB needs 60 min to yield 16% while 87% of the ester was obtained in 2 min under phase transfer conditions. TBAB, when adsorbed on Indian clay (tetrabutylammonium clay\(^{16} \)) was less efficient in the \( n \)-octylation of olate anion and gave a lower yield than did neat TBAB (Table 4, entry 5). Loupy et al.\(^{22} \) had also reported the negative effect of the presence of a support in solvent-free esterifications.

**Conclusions**

The process of synthesizing the major ester components of spermaceti presented here has at least two important advantages considering environmental aspects - (i) the whales are spared as they are not required for producing the valuable spermaceti wax, and (ii) the esterification (which would otherwise use hazardous chemicals) employs the reusable, inexpensive and totally eco-friendly Indian bentonite as catalyst. The catalyst is easily regenerated and the regenerated catalyst is found to retain the same activity even after three experimental cycles. This is the first observation of the use of the acid activated Indian bentonite as catalyst for direct esterification of long chain carboxylic acids with high molecular weight fatty alcohols. Although solvent-free alkylation of carboxylic anions under microwave irradiation yield quantitative amounts of esters, the method is not eco-friendly and catalyst cannot be reused. In addition, all alkylation agents are toxic and potential carcinogens because they can react with physiological nucleophiles in the body.

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**References**