

A Green Approach for Synthesis of Alkyl Levulinates as a Biofuel component from Biomass derived Levulinic Acid by Mineral Acid

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ABSTRACT: Levulinic acid as a versatile and important promising biomass derived platform chemical can be converted into value added chemicals (VAC). As the presence of attractive functionalities in Levulinic acid (LA) i.e., Carbonyl (-CO-) group and (-COOH) group so synthetically it will be useful for the organic transformations process like esterification of levulinic acid to formed alkyl levulinates hydrogenation followed by cyclization to formed GVL. These products can be utilized as a biofuel additive. So, in present work we have synthesized various alkyl levulinates from Levulinic acid via. mineral acid (H₂SO₄) from lower aliphatic alcohol to higher alcohols like (methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, n-pentyl alcohol, n-hexyl alcohol, n-heptyl alcohol and n-octyl alcohol). The structural analysis of levulinates were confirmed by ¹H NMR and molecular weight of these derivatives was confirmed by GCMS analysis.

Keywords: Esterification, alkyl levulinates, Value added compounds, biofuel additives, extraction method, higher alcohols.

INTRODUCTION

Biomass derived levulinic acid and its alkyl levulinates has recognized a remarkable contract of devotion in last few years due to chances of attractive a substitute resource for the sustainable production of value-added chemicals. (Pileidis *et al.*, 2014; Dharne and Bokade 2011) Levulinic acid can be generated by hydrolysis of cellulose in presence of acid as the structure of levulinic acid possess the presence of active functional moieties like ketone and carboxylic group, (Pileidis and Titirici 2016; Di Bucchianico *et al.*, 2022;) which can be utilized for the synthesis of various organic compounds (Huang *et al.*, 2016; Liu *et al.*, 2019) such as gamma-Valero lactone (GVL) formed by hydrogenation of LA followed by cyclization and its good additive in jet fuel, (Sajid *et al.*, 2021; Tiong *et al.*, 2018) then esterification of LA with higher alcohols to formed higher alkyl levulinates can be utilized as biofuel (Rackemann and Doherty 2013; Tian *et al.*, 2021) component and many more organic chemicals can be synthesized like acrylic acid, angelica lactone and 1,4-pentane diol (Girisuta and Heeres 2017; Yan *et al.*, 2015; Ramli and Amin 2017; Nandiwale and Bokade 2015).

Alkyl levulinates are very important compounds that are using as flavouring agent, as fuel additives, as solvent. In specially the (Peixoto *et al.*, 2020; Kong *et al.*, 2016) ethyl levulinate (EL) is successfully blended with diesel (7%) with high miscibility in both the components (Appaturi *et al.*, 2022; Onkarappa *et al.*, 2019). So, we can utilize the levulinic acid is platform chemical which can be converted into value added

compounds. Subsequently LA can be easily extracted from the different biomass (Raut *et al.*, 2022; Bhuse *et al.*, 2022). And its green approach will be esterification of biomass derived LA with bioethanol for synthesis of ethyl levulinates (Mthembu *et al.*, 2021).

The esterification reaction generally carried out in presence of mineral acid (H₂SO₄, HCl or H₃PO₄) via liquid phase system (Raut *et al.*, 2022; Raut and Bhagat 2021). But in past few decades the replacement of homogeneous by heterogeneous catalyst is necessary because solid heterogeneous catalyst is easily soluble and separable from the reaction mixture. Esterification reaction can be possible with levulinic acid and primary alcohols at room temperature (without catalyst) but the rate of reaction will be slow. If it is in presence of catalyst at high temperature then the reaction will be in fast rate (Raut *et al.*, 2022; Maheria *et al.*, 2021).

To achieve the successful transformation in rational period of time. Many more acid catalysts have been utilized for the different esterification reaction protocols with different alcohols (Ramli *et al.*, 2018; Ogino *et al.*, 2018). But to the superlative about our information in recently for the esterification of levulinic acid with primary alcohols (Nandiwale *et al.*, 2014). The main objective of this work is to synthesize the different alkyl levulinates by esterification of levulinic acid by very simple and easy work up method as a green approach to separate out the alkyl levulinates (Badgujar *et al.*, 2020).

In present work, we have used levulinic acid and primary alcohols by adding few drops of sulphuric acid (H₂SO₄) under reaction conditions. After completion of reaction the product separation was done by simple

extraction method. Here we have used the extracting solvent as ethyl acetate with the similar ratio with water. If excess mineral acid is present in reaction mixture will removed easily while extracting with water and brine solution. So in this work, we have explore the simple reaction pathway for the synthesis of alkyl levulinates as a biofuel component.

MATERIAL AND METHODS

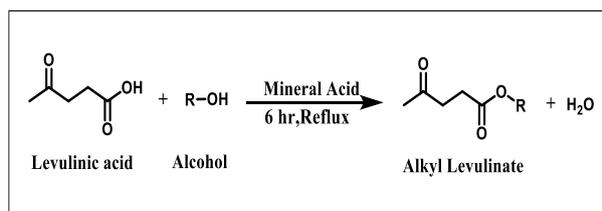
Methanol (99.5 %), Ethanol (99.9%), 1-propanol (98%), 1-butanol (97%), 1-pentanol (98%), 1-hexanol (97%), 1-heptanol (99.9%), 1-octanol (97%) and levulinic acid (98%) were purchased from SD Fine-Chem Ltd. ethyl acetate (98%) were procured from Avra chemical Pvt. Ltd. Sodium chloride Were acquired from Sisco Research Laboratories Pvt. Ltd.

Characterization Technique. The Chemical structure of synthesized compounds was confirmed by spectral data. ¹H-NMR spectra were recorded on BRUKER AVANCE NEO 500 MHz spectrometer using DMSO and CDCl₃ solvent and TMS as internal standards at SAIF, Punjab University, Chandigarh (India). Chemical shifts are expressed in ppm. Mass spectrums were recorded on Thermo Scientific TSQ 8000 Gas Chromatograph

GENERAL REACTION OF ESTERIFICATION

The synthesis of various alkyl levulinates from levulinic acid was developed by adapting from the literature (Wang *et al.*, 2022). To a 50 mL round bottom flask levulinic acid was added with few drops of H₂SO₄ and stirred for 5 minutes and addition of primary alcohol (1:1) ratio of (mmol) and refluxed for 6 hr. Then after completion of reaction, the reaction mixture was taken in separating funnel and added the equimolar quantity of extracting solvent (ethyl acetate) and water with brine solution. And shake the separating funnel with 2-3 times properly for which the products can be easily separable.

And then allow to stand the separating funnel for few minutes. We can saw the two layers one is organic layer (the product with ethyl acetate) and other later with water (if excess sulphuric acid is present). Drained out the water layer and collect the organic layer and kept it with 12 hr. with sodium sulphate for the absorption of excess moisture or water in organic layer lastly evaporate the organic layer by rotatory evaporator to get desired product alkyl levulinates. And its structural analysis was confirmed by ¹H NMR and molecular weight was confirmed by GCMS analysis.



Scheme 1. Synthesis of Alkyl Levulinates.

Plausible mechanism of acetylation of naphthol

The stepwise mechanism of esterification of LA from the literature (Raut, *et al.*, 2022) (Fig. 1).

Step 1. Protonation: The donation of proton from mineral acid to carbonyl oxygen of levulinic acid. Via protonation the electrophilic nature of LA enhances. This protonated form of aromatic LA can resonate in other canonical forms which can act as a electrophile.

Step 2. Nucleophilic attack: The loan pair present over the oxygen of naphthol attack over the carbonyl carbon of protonated LA. And generation of unstable tetrahedral intermediate.

Step 3. Rearrangement of tetrahedral intermediate: As the generation of tetrahedral intermediate (unstable di-hydroxy compound) in previous step. Which is highly unstable and highly energetic is susceptible to become stable via eliminating the water molecule.

Step 4. Deprotonation: The generation intermediate in step 3. Which undergoes deprotonation to from the desired product.

Confirmation of compounds by ¹H NMR and GCMS

1) Methyl Levulinate

¹HNMR(500MHz,CDCl₃):δ3.61(s,3H),2.84(t,2H),2.62(t,2H),2.10(s,3H) GCMS: Cal m/z: 130.06, Found m/z : 130.14

2) Ethyl levulinate

¹HNMR(500MHz,CDCl₃):δ4.01(q,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.07(t,3H) GCMS:Cal.m/z: 144.17, Found m/z: 144.09

3)n-Propyl levulinate

¹HNMR(500MHz,CDCl₃):δ4.13(q,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.73(m,2H),1.01(t,3H) GCMS: Cal.m/z: 158.09 Found m/z: 158.10

4) n-Butyl levulinate

¹HNMR(500MHz,CDCl₃):δ4.14(q,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.54(m,2H),1.40(m,2H),0.90(t,3H) GCMS: Cal.m/z: 171.11 Found m/z: 172.19

5) n-Pentyl Levulinate

¹HNMR(500MHz,CDCl₃):δ4.14(t,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.60(m,2H),1.39(m,2H),1.38(m,2H),0.90(t,3H) GCMS: Cal.m/z:186.13, Found m/z: 185.90

6) n-Hexyl levulinate

¹HNMR(500MHz,CDCl₃):δ4.14(t,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.60(m,2H),1.39(m,2H),1.38(m,2H),1.37(m,2H),0.90(t,3H)GCMS:Cal.m/z:200.14, Found m/z: 200.21

7) n-Heptyl levulinate

¹HNMR(500MHz,CDCl₃):δ4.11(t,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.60(m,2H),1.43(m,2H),1.26(m,6H),0.88(t,3H) GCMS:Cal.m/z: 214.16, Found m/z: 214.19

8) n-Octyl Levulinate

¹HNMR(500MHz,CDCl₃):δ4.11(t,2H),2.84(t,2H),2.62(t,2H),2.10(s,3H),1.60(m,2H),1.43(m,2H),1.30(m,4H),1.26(m,4H),0.88(t,3H)GCMS:Cal.m/z: 228.17, Found m/z: 227.21.

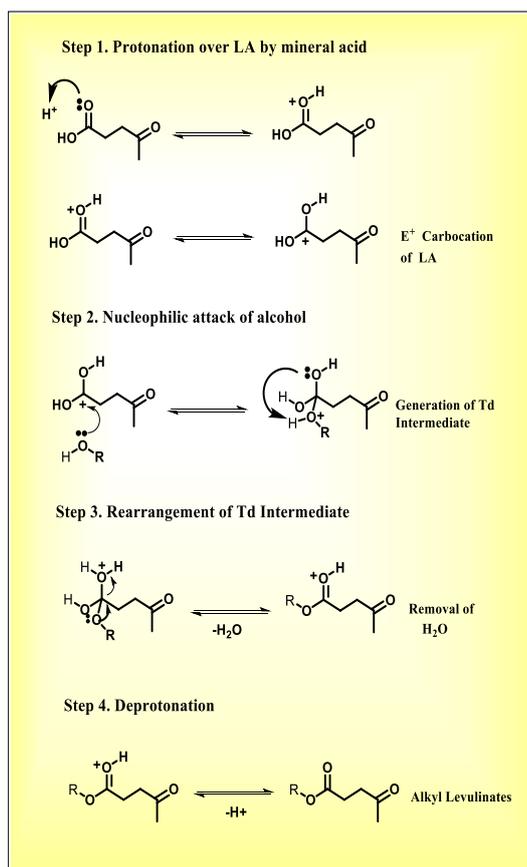


Fig. 1. Plausible mechanism of esterification of Levulinic acid.

Sr. No.	LA	Alcohols	Alkyl Levulinates	Time (h)	Yield%
1.				6	81
2.				6	89
3.				6	83
4.				6	86
5.				6	88

6.				6	80
7.				6	82
8.				6	87

CONCLUSIONS

In summary, we have confirmed the esterification of levulinic acid to methyl-, ethyl-, n-propyl- and n-butyl levulinates by reaction with methyl alcohol, ethyl alcohol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-octanol the levulinates can be used as biofuel component and its miscible in neat diesel with (5-7%). In synthetic path the separation of product was done by simple extraction process with two solvent and brine solutions. Here we have used ethyl acetate (Ester extracting solvent) and water to remove the excess mineral acid. This esterification reaction of biomass derived levulinic acid is promising and efficient protocol to synthesize the different alkyl levulinates from higher to lower alcohols. Which is having wide application in many other fields.

FUTURE SCOPE

From the previous protocol literature, the esterification of biomass derived levulinic acid is a green, important and promising protocol for the generation of fuel additives and biofuel components.

In future, this protocol will be the renewable resource as it can be substitute and compatible like the ethanol; instead of ethanol we can blend fuel additives and biofuel components to petrol and diesel.

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Conflict of Interest. None.

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