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Straightforward synthesis of calcium levulinate from biomass-derived levulinic acid and calcium carbonate in egg-shells

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Abstract

Calcium levulinate (CL) is a nutritional supplement for calcium and a chemical intermediate in synthesizing levulinic biofuels. The reported synthesis of CL involve reaction between cellulose-derived levulinic acid (LA) and calcium hydroxide in an aqueous medium. In this work, we report the production of CL using CaCO₃ from poultry egg shells. The scalable production uses biomass-derived LA and egg-shell derived CaCO₃ under conventional heating and mechanical stirring. The reaction was optimized on temperature, duration of reaction, and equivalent of CaCO₃. Using 1.5 equivalent of CaCO₃, the reaction completed within 2h at 50°C and afforded up to 97% isolated yield of CL as a crystalline solid. The reaction was also successfully carried out under mechanical grinding and scaled up to 20 g. The purity of the product was confirmed by melting point, FTIR, ¹H-NMR and ¹³C-NMR spectroscopy.

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Keywords: Calcium levulinate; Levulinic acid; Calcium carbonate, Egg-shells; Renewable Chemistry.

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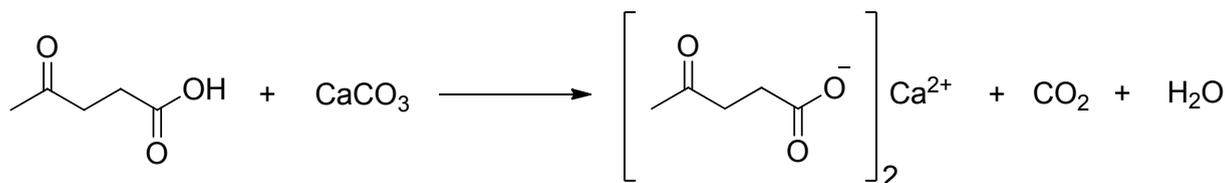
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1. Introduction

In a bio-refinery concept, a handful of small organic compounds are initially produced from biomass feedstock. The compounds are then used as renewable chemical building blocks for the synthesis of fine chemicals and value-added products [1]. Levulinic acid (LA, **1**) is one of the well-recognized biomass-derived chemical building block obtained by acid-catalysed hydrolysis/dehydration of biomass-derived sugars and carbohydrates [2]. LA has been recognized as one of the top-ten biomass-derived renewable chemicals by NREL, USA [3]. LA has been exploited as a biomass-derived renewable chemical building block for the synthesis of a wide range of products such as fuels and fuel additives, solvents, monomer for polymers, plasticizers, agrochemicals, nutritional supplements and pharmaceuticals [4,5]. Various alkali- and alkaline earth metal salts of LA have been synthesized and studied. For example, sodium levulinate has shown promising anti-freeze properties [6]. In this regard, calcium levulinate (CL, **2**) is known for more than 80 years [7].

CL has been studied as a nutritional supplement for calcium [8,9]. Pyrolytic liquefaction of CL into levulinic biofuels via decarboxylative ketonization has recently been reported [10]. Synthesis of γ -valerolactone, a renewable chemical intermediate of much interests, has also been synthesized from CL [11]. The synthesis of CL generally involves reacting LA with excess of calcium hydroxide. The unreacted base is then precipitated as calcium carbonate by passing CO_2 through the reaction mixture [12]. The evaporation of excess water affords CL as a dihydrate [13]. The purity of CL is crucial for its use as a nutritional supplement. However, use of CL in generating fuels and fuel oxygenates, the expensiveness and availability of the reactants are of most importance. In principle, CL can also be produced by reacting LA with CaCO_3 (**Scheme 1**).



Scheme 1. Production of CL from LA.

Since CaCO_3 is nearly insoluble in water, the unreacted CaCO_3 can easily be separated by filtration. In addition, CaCO_3 is naturally available in various mineral deposits as well as various food wastes. Recently, synthesis of CL has been attempted from sea-shells [14]. However, removal of chitin from the calcium carbonate in sea shells require demanding reaction conditions and not be commercially viable for the synthesis of CL.

Hereby, we report a scalable production of CL from biomass-derived LA and CaCO_3 under conventional heating and mechanical stirring (**Scheme 1**). The reaction was optimized on temperature, duration of reaction, and equivalence of CaCO_3 used. The purity of the product was checked by melting point, FTIR, and $^1\text{H-NMR}$ spectroscopy.

2. Experimental

2.1 Materials

Levulinic acid (98%) was purchased from Avra Synthesis Pvt. Limited, Calcium carbonate (98-100%) was purchased from Loba Chemie. The compounds used as received without any further purification. Melting point was recorded on Stuart Melting point. The poultry egg shells were boiled in water and dried in oven at 110°C for 24h. Then, the shells were powdered in a mortar.

2.2 Method

2.2.1 Solution method

In a 50 mL round-bottomed flask, calcium carbonate (2.58 g, 25.8 mmol, 1.5 eq.) was suspended in 3 mL of water. Levulinic acid (2.00 g, 17.24 mmol) was dissolved in 2 mL of water and added drop-wise over 5 min into the CaCO₃ suspension while stirring. The suspension was stirred at room temperature on a magnetic stirrer for 2h. After 2h, the reaction mixture was filtered through a Whatmann filter paper. Then the filter paper was washed with warm water (5 mL, 60 °C) and combined the washed layer with the filtrate. The clear, colourless filtrate was evaporated in a rotary evaporator at 50°C and under vacuum. The pH of the solution was slightly basic (pH 7.6). Calcium levulinate dehydrate crystallized as white needles (5.02g, 95%).

2.2.2 Grinding method

In a mortar, levulinic acid (2.00 g, 17.24 mmol) calcium carbonate (1.73 g, 17.24 mmol) were taken and water (0.4 g) was added. The paste was grinded for 3h at RT. The ¹H-NMR and FRIT spectra of the crude product were comparable to those obtained from reactions using mechanical stirring condition. This process excludes the use of excess water and the obligation to use any energy intensive process to evaporate it later.

2.3 Identification and Characterization of the synthesized molecules

CL was characterized by FTIR and NMR spectroscopy and the purity was confirmed by melting point analysis. Fourier Transform Infrared (FTIR) spectra was recorded on a Bruker Alpha 400 FTIR spectrometer, which is equipped with silicon carbide as IR source. All sample spectra were recorded using ATR technique. The samples under study were recorded with 24 scans having sample resolution of 4 cm⁻¹. ¹H-NMR spectra were recorded on 400 MHz spectrometer using deuterated water as solvent and TMS as an internal standard.

3. Result and Discussion

Initially, the synthesis of CL was attempted using commercial CaCO₃. The reaction between LA, 1 and 1.5 equivalent of CaCO₃ was tried at various reaction temperatures keeping the duration of reaction fixed at 2h as shown in **Table 1**.

Table 1. Effect of temperature on the isolated yield of CL, 2. Reaction conditions: LA (2.00g), CaCO₃ (2.59 g, 1.5 eq.), water (5 mL).

S/N	Temperature (°C)	Yield of CL (%)
1	25	93
2	50	95
3	65	94
4	80	95

The reaction completed within 2h and the isolated yields of CL is nearly same at all temperatures. Interestingly, even room temperature works well for the reaction. At temperatures above 50°C (entry3&4), a small amount of coloured impurity also formed as the colourless solution transformed into light yellow. However, the impurity did not appear on the ¹H-NMR spectrum. The reaction remains essentially colourless at lower temperatures. The reaction mixture produced effervescence as CO₂ was coming out. The reaction at room temperature (entry 1), although afforded CL in high isolated yield, was difficult to stir initially. Reaction at 50°C was found optimum that works smoothly and afforded CL in excellent yield. The reaction was studied by ¹H-NMR spectroscopy but analysing an aliquot of the reaction mixture. After reaction, the unreacted CaCO₃ was filtered under vacuum and washed with water. The pH of the solution in water was found to be 7.47. The clear aqueous filtrate was evaporated under vacuum in a rotary evaporator not allowing the temperature to rise above 50°C. The calcium levulinate dehydrate was obtained as a white crystalline solid. The melting point of CL was found to be 122 °C that closely matches with the literature value of 123 °C. The reaction was then performed at 50C varying the equivalence of CaCO₃ and the duration of reaction. The outcome of the reactions is shown in **Table 2**.

All the reactions afforded excellent isolated yield of CL. Using only 1.1 equivalent of CaCO₃, the isolated yield of CL reached 95% after 6h. The same reaction produced slightly lower yield (91%) after 2h. The reaction produced 95% isolated yield of CL after 2h using 1.5 eq. of CaCO₃ (entry 2). Additional reaction time did not improve the yield of CL. Using higher equivalent of CaCO₃ (entry 3) did not have observable impact on the yield of CL.

Finally, poultry egg-shells were used as the source of CaCO₃ and the reaction was carried out under optimized conditions. When the reaction was carried out at 50 °C for 2h using 2 g of LA and 1.5 eq. of egg-shells (assuming it to be pure CaCO₃), CL was obtained in 96% isolated yield as shown in **Figure 1**.

The loss in mass is attributed to physical loss during filtration. In fact, when the reaction scaled up using 20 g of LA, the isolated yield of CL reached 97%.

3.1 FTIR Spectroscopy

The product was characterized by FTIR spectroscopy (figure 2). The corresponding peaks are obtained for C=O stretch (1689 cm⁻¹) of keto group and C=O stretch (1548 cm⁻¹) of carboxylate ion.

Table 2. Influence of reaction time and the equivalence of CaCO_3 on CL yield. Reaction conditions: LA (2.00g), CaCO_3 (1.1-2 eq.), water (5 mL), 50°C .

S/N	CaCO_3 (eq.)	Reaction Time (h)	Yield of CL (%)
1	1.1	2	91
		4	92
		6	95
2	1.5	2	95
		4	94
		6	93
3	2	2	93
		4	92
		6	95



Figure 1. Synthesis of CL from poultry egg-shells.

3.2 NMR (^1H , ^{13}C) analysis of CL

CL was identified and its purity was analysed by ^1H -NMR and ^{13}C -NMR spectra. ^1H -NMR (D_2O , 300MHz, ppm): 2.73 (t, 2H, $J = 6.8$ Hz), 2.36 (t, 2H, $J = 6.8$ Hz), 2.18 (s, 3H). ^{13}C -NMR (D_2O , 100MHz, ppm): 29.2, 31.1, 39.4, 181.8, 215.2 as shown in fig. 3 and 4.

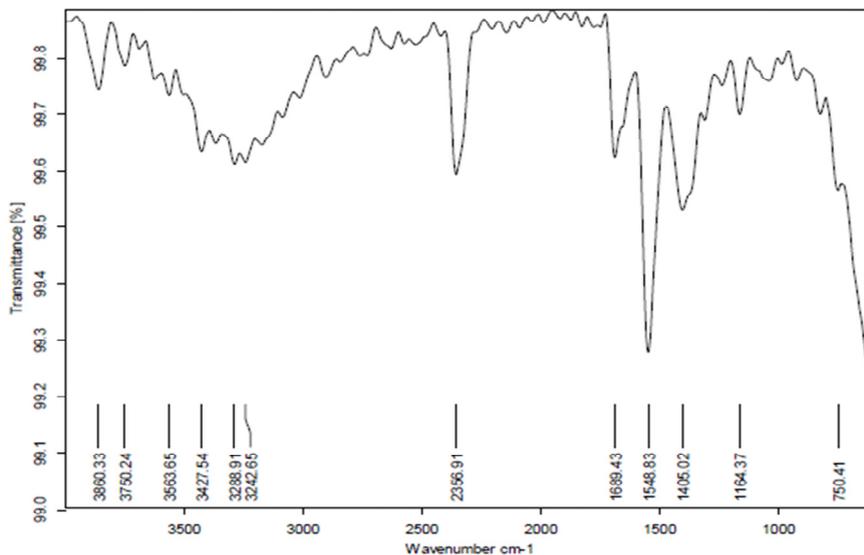


Figure 2. FT-IR spectrum of calcium levulinate.

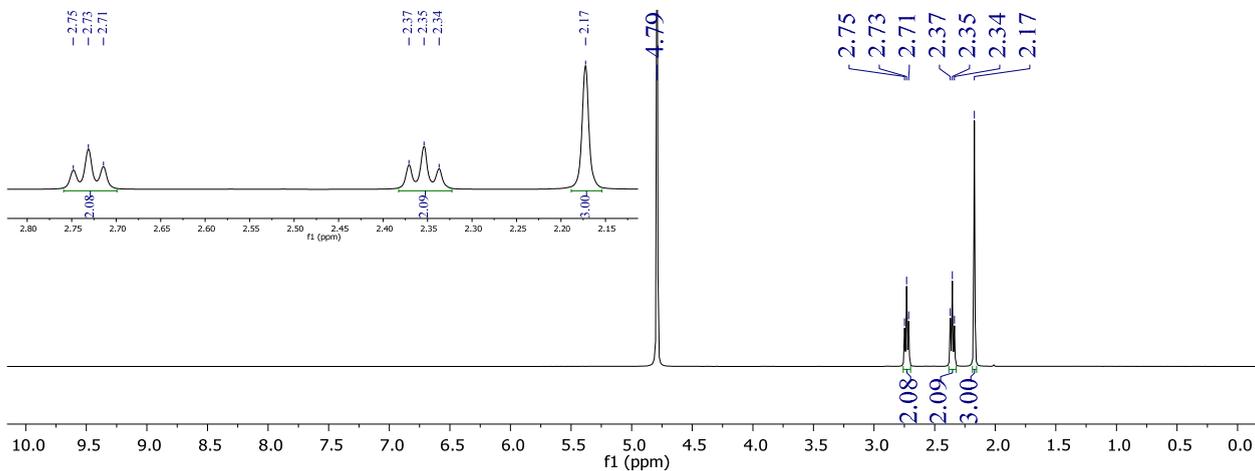


Figure 3. ¹H-NMR spectrum of calcium levulinate and its splitting pattern (inset).

3. Conclusion

Calcium levulinate was produced from biomass-derived levulinic acid and calcium carbonate in poultry egg-shells. The reaction was optimized on temperature, duration, and equivalence of calcium carbonate used. The straightforward reaction was carried out up to 20g scale of levulinic acid and afforded 97% isolated yield of calcium levulinate at 50°C within 2h.

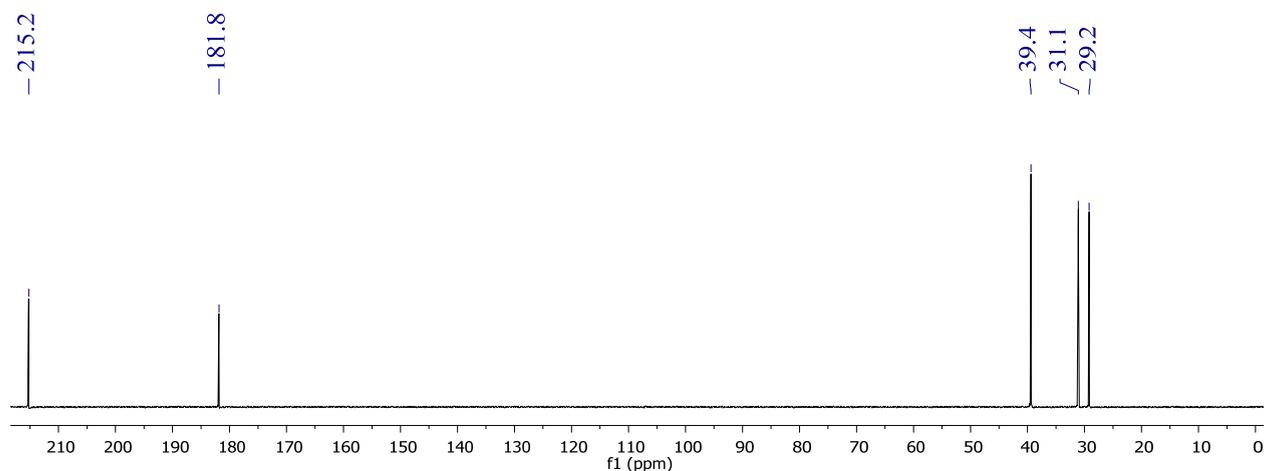


Figure 4. ^{13}C -NMR spectrum of calcium levulinate.

CL was also successfully synthesized in high purity by grinding using only minimal water. The identity and purity of the compound was analysed by melting point, FTIR spectroscopy and NMR spectroscopy.

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