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# Catalytic oxidative C-C bond cleavage route of levulinic acid and methyl levulinate

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Obtaining value-added chemicals from biomass resources has attracted much attention recently. Levulinic acid is one of the most important biomass platform compounds, which could be obtained from carbonhydrate biomass. In this work, levulinic acid was selectively converted into C4 product including succinic anhydride *via* catalytic oxidation with manganese catalyst in acetic anhydride. Besides an unexpected product of maleic anhydride was obtained which differs greatly from that of levulinate ester. The pathway for formation of maleic anhydride was studied by monitoring and confirming intermediates α-angelica lactone and its derivative 2-methyl-5-oxotetrahydro-2-furanyl acetate. Based on obtained mechanistic information the different behaviour between the oxidative cleavage of levulinic acid and levulinate ester was further discussed.

## Introduction

Succinic acid is an versatile platform chemical which can be utilized for the preparation of a variety of value-added downstream products such as succinate ester, succinamide, γ-butyrolactone, 1,4-butanediol, tetrahydrofuran, 2-pyrrolidone and N-methyl-2-pyrrolidone.[1,2] Succinic anhydride is the precursor of succinic acid, both of which are important monomers for biodegradable material poly (butylene succinate).[3-5] Succinic acid and succinic anhydride were traditionally produced from hydrogenation of maleic anhydride[6-12] which was obtained from catalytic oxidation of fossil derived feedstocks such as benzene[13-15] and butane[16-18] However, the raw materials applied in these procedures are short of oxygen atom, therefore extra oxygen resource was needed.

As a renewable oxygen-containing carbon resource, biomass has attracted extensive attention in recent years. Lots of studies have focused on the conversion of saccharides such as cellulose, hemicellulose, glucose, and fructose to value-added chemicals and platform chemicals,[19-27] among which levulinic acid is an important C5 biomass platform compound that can be obtained by hydrolysis of cellulose, glucose and 5-hydroxymethylfurfural.[28-32] Levulinic acid could be converted to various useful chemicals, including levulinate esters,[33] γ-valerolactone[34,35] and 1,4-pentadiol.[36,37]

Levulinic acid contains carbonyl and carboxyl group; structurally similar to that of succinic acid.[38] Therefore production of succinic acid from the oxygenation of levulinic acid is preferable considering the atom economy.[39,40]

To date, there are few reports on catalytic conversion of levulinic acid to succinic acid or succinic anhydride with molecular oxygen. The first example was a patent in 1954 that described $V_2O_5$ catalysed succinic anhydride and succinic acid production from levulinic acid at a high temperature of 200-400 °C.[41] Recently Podolean *et al.* reported the use of noble metal Ruthenium for the conversion of levulinic acid to succinic acid at 150 °C.[42]

However, it is still a challenge to develop a catalytic procedure characterized by using dioxygen under mild conditions. Our group reported in 2013 the first example of manganese-catalysed selective oxidation of levulinate to succinate in 58.6% yield with $O_2$ under mild conditions. Mn(III) acetate was disclosed as an efficient catalyst for the oxidative C-C cleavage of methyl levulinate at the terminal methyl-carbonyl position.[38] The oxidation of substrate methyl levulinate in our previous research was carried out in acetic anhydride. However, the use of methyl levulinate is not arbitrary. When levulinic acid was oxidized under the similar conditions remarkably different results were observed. Succinic anhydride (**1**), as a succinate series C4 product, decreased dramatically compared with that of methyl levulinate; whereas, a certain amount of maleic anhydride (**2**) was detected as a maleate series C4 product. In addition the route for levulinic acid oxidation is vague as well.

Hitherto, no report has been published on oxidation of levulinic acid to succinic anhydride with manganese compounds as catalyst. Nor did any relevant study on the significant difference of the oxidation behaviour between the

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two levulinates been investigated thoroughly. On the basis of previous study, herein we investigated the reaction process and confirmed the possible intermediates, besides the difference between the oxidation of levulinic acid and levulinate ester was also discussed.

## Experimental

### Materials and methods

Levulinic acid, dimethyl malonate and dimethyl oxalate were obtained from Aladdin chemistry Co. Ltd.. Methyl levulinate, α-angelica lactone were obtained from TCI (Shanghai) Development Co. Ltd.. Succinic acid was purchased from Sigma-Aldrich. Dimethyl succinate, dimethyl maleate were supplied by Alfa Aesar. Maleic anhydride was purchased from Shenyang chemical reagent Co. Ltd.. Succinic anhydride was obtained from Sinopharm chemical reagent Co. Ltd.. 2-Methyl-5-oxotetrahydro-2-furanyl acetate was separated from the experiments by column chromatography and characterized on a Bruker 400 MHz spectrometer. Methanol, acetic acid, ethyl acetate, DMF, DMSO, dichloromethane, acetonitrile and cyclohexane were purchased from Tianjin Kermel chemical reagent Co. Ltd.. Methanol, acetic acid, ethyl acetate, DMF, DMSO, dichloromethane, acetonitrile and cyclohexane were analytical grade and dried by activated 3A molecular sieve before used. $Mn(OAc)_3{\cdot}2H_2O$ and $Mn(acac)_3$ were purchased from Alfa Aesar. $Mn(OAc)_2{\cdot}4H_2O$ was obtained from aladdin chemistry Co. Ltd.. Deionized water was purified by Milli-Q system (Millipore). All the other reagents were commercially available and used as received.

### Typical Procedure for Catalytic Oxidation

In a typical experiment, Levulinate (2.5 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (5 mol%) and 2 mL solvent were added into a 25 mL teflon-lined stainless steel autoclave equipped with magnetic stirrer, pressure gauge and automatic temperature control apparatus. After purged for 6 times to exclude air, $O_2$ was charged to 0.5 MPa. The autoclave was heated to 90 °C and kept for the desired reaction time.

### Product analysis

The autoclave was cooled to room temperature after the reaction. The liquid products were transferred into a volumetric flask followed by addition of internal standard for analysis. The liquid reaction mixture was analysed by GC calibration curve.

As for the substrate of methyl levulinate, all the liquid reaction mixture was transferred into a 50 mL round-bottomed flask, then $BF_3{\cdot}Et_2O$ (150 mg) and absolute methanol (20 mL) were added and reflux for 6 h. This method is verified experimentally and similar methods are also employed for analysis of carboxylic acid in the previous reports.[38,43] GC measurements were conducted on an Agilent 7890A GC equipped with an auto sampler and a flame ionization detector. DB-225 (30m × 250μm × 0.25μm) and DB-17 (30m × 320μm × 0.25μm) capillary columns were employed for analysis of reaction mixtures of levulinic acid and methyl levuinate respectively. Identification of main products was based on GC-MS (Agilent 7890A/5975C) system equipped with an Agilent HP-5ms (30m × 250μm × 0.25μm) as well as by comparison with authentic samples. 1,2,4,5-Tetramethylbenzene (TMB) was used as the internal standard. The product distribution was shown on the molar basis.

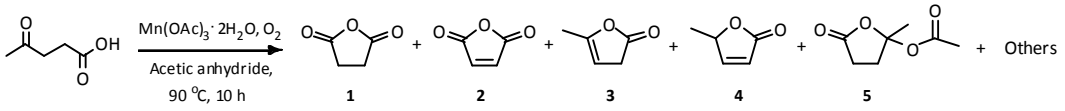
The conversion (mol%) of levulinates and yield (mol%) of main products were calculated as follows:

$$\text{Conversion of levulinate} = \left(1-\frac{\text{Moles of levulinate in product}}{\text{Moles of levulinate loaded initially}}\right)\times 100\%$$

$$\text{Yield of Pi} = \frac{\text{Moles of Pi in product}}{\text{Moles of Pi formed theoratically}}\times 100\%$$

Pi: Succinic anhydride, maleic anhydride, angelica lactones, 2-methyl-5-oxotetrahydro-2-furanyl acetate, dimethyl succinate, dimethyl malonate, dimethyl oxalate and dimethyl maleate.

**Table 1.** Catalytic oxidation of levulinic acid[a]




| Entry | Catalyst | Conv. [mol%] | Yield of main products [mol%] | | | | | Others |
|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3+4 | 5 | C4-C5 products | |
| 1 | $Mn(OAc)_3{\cdot}2H_2O$ | 97.6 | 6.8 | 14.8 | 5.8 | 38.3 | 65.7 | 31.9 |
| 2 | $Mn(acac)_3$ | 97.7 | 6.6 | 15.3 | 6.5 | 31.5 | 59.9 | 37.8 |
| 3 | None | 96.1 | 0.9 | 2.0 | 3.5 | 83.7 | 90.1 | 6.0 |
| 4 | $Mn(OAc)_2{\cdot}4H_2O$ | 96.8 | 4.9 | 12.7 | 1.4 | 44.2 | 63.2 | 33.6 |
| 5[b] | $Mn(OAc)_3{\cdot}2H_2O$ | 97.8 | 5.3 | 8.8 | 3.9 | 61.7 | 79.7 | 18.1 |
| 6[c] | $Mn(OAc)_3{\cdot}2H_2O$ | 97.9 | 9.4 | 26.0 | 1.2 | 1.0 | 37.6 | 60.3 |
| 7[d] | $Mn(OAc)_3{\cdot}2H_2O$ | 61.8 | 7.1 | 17.0 | 4.7 | - | 28.8 | 33.0 |

[a] Reaction conditions: Levulinic acid (2.5 mmol), catalyst (5 mol% Mn), acetic anhydride (2 mL), 90 °C, 0.5 MPa $O_2$, 10 h. Data were analysed by GC. [b] 10 mol% Mn. [c] 20 h. [d] Substrate: **5** (2-methyl-5-oxotetrahydro-2-furanyl acetate). Others refer to those cannot be quantified through calibration curve but conformed by GC-MS, including 1,2,3,5-tetra-O-acetylpentofuranose, acetoxy acetic acid, 1,3-cyclopentanedione, 1,1-ethanediol diacetate, 4-hydroxy-2-pentenoic acid and 1,1,2-ethanetriol triacetate.

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## Results and discussion

### Comparison of oxidation of levulinic acid and methyl levulinate

Our group previous study focused on the manganese (III) catalysed aerobic oxidation of methyl levulinate to dimethyl succinate in acetic anhydride, and 95.3% conversion with 58.6% yield of succinate was obtained.[38] In this study, when levulinic acid was oxidised under the same reaction conditions, 97.6% of levulinic acid was converted whereas the yield of **1** decreased dramatically to 6.8% (Table 1, entry 1). In addition, reaction catalysed by $Mn(acac)_3$ showed the similar results: 97.7% conversion with negligible yield of **1** (6.6%) were detected compared with 92.4% conversion and 49.8% yield of succinate from that of methyl levulinate. **2** was observed in both systems. Based on these results, it was suggested that there might exists a different conversion pathway between the two substrates while methyl levulinate may be more preferable for the production of succinate through catalytic oxidation compared with levulinic acid.

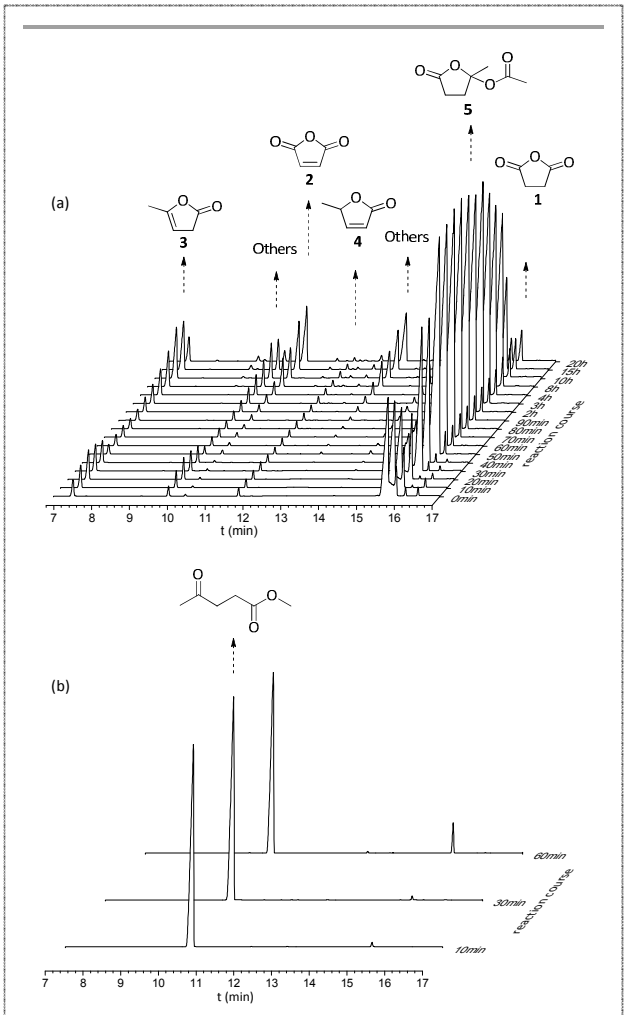
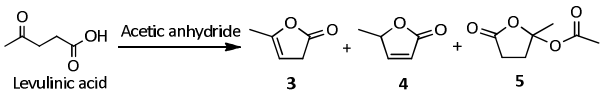



**Fig. 1.** (a) GC trace at different reaction time of the oxidation of levulinic acid. The retention time correspond to the following compounds: 7.37 min (α-angelica lactone), 10.42 min (maleic anhydride), 11.68 min (β-angelica lactone), 15.83 min (2-methyl-5-oxotetrahydro-2-furanyl acetate), 16.06 min (succinic anhydride). (b) GC trace of the first period of the oxidation of methyl levulinate (methyl levulinate retention time: 10.6 min).




**Scheme 1.** Dehydration of levulinic acid to angelica lactones and its derivative.

In order to investigate the differences, controlled experiments were carried out. In the oxidation of levulinic acid catalysed by $Mn(OAc)_3{\cdot}2H_2O$ and $Mn(acac)_3$ respectively, **2** was obtained unexpectedly as one of the main C4 products with yield of 14.8 and 15.3% (Table 1, entries 1 and 2). In contrast, succinate was given as the only C4 product in the oxidation of methyl levulinate,[38] which further confirmed different reaction routes existed for the oxidation of levulinic acid and methyl levulinate. According to the GC-MS results, α-angelica lactone (α-AL, **3**), β-angelica lactone (β-AL, **4**) and its derivative 2-methyl-5-oxotetrahydro-2-furanyl acetate (**5**) were detected during the oxidation (Fig. S1,S3,S13). About 6% of ALs (α,β-AL) with more than 30% of **5** were obtained after 10 h of reaction under the catalysis of Mn(III) (Table 1, entries 1 and 2). To further explore the reaction mechanism, comparative experiments of these two substrates were carried out under the same conditions while samples were taken periodically at different time along the reaction course while possible intermediates and products were monitored and confirmed by GC (Fig. 1) and GC-MS (Fig. S1-S3). The products of oxidation of levulinic acid and methyl levulinate were traced and shown in Fig. 1(a) and (b), suspected intermediates **3** and its isomer **4** as well as its derivative **5** generated during the reaction of levulinic acid. The dramatic difference between the oxidation behaviour of levulinic acid and methyl levulinate illustrated that there exist a "non-oxidative" consumption of levulinic acid (Scheme 1). During that process it generates **3** through dehydration cyclization with the aid of acetic anhydride. This was followed by an addition reaction with acetic acid that derived from the dehydration process of acetic anhydride to form **5**. And the yield of **5** was in relatively large quantity especially without any catalysts (83.7%, Table 1, entry 3). This is in agreement with former researches. Mascal *et al.* reported recently the dehydration of levulinic acid under the catalysis of solid acid to give **3**.[44] The treatment of levulinic acid and methyl levulinate with acetic anhydride under a nitrogen atmosphere respectively (Fig. 2) showed that products **3**, **4** and **5** generated due to the dehydration process of levulinic acid, whereas no such products were obtained for that of methyl levulinate. These indicated that acetic anhydride promoted the dehydration of levulinate substrates while the ester group of methyl levulinate prohibited the process from generating intermediate **3**, **4** and **5**. On the basis of former reports and our results, we can come to the conclusion that the dehydration of levulinic acid generates **3** which undergo isomerization to **4**[45] and further addition reaction with acetic

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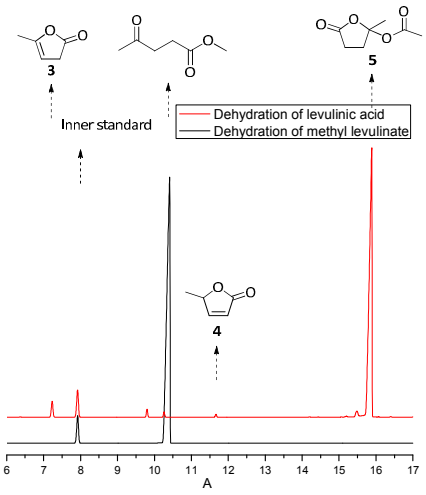
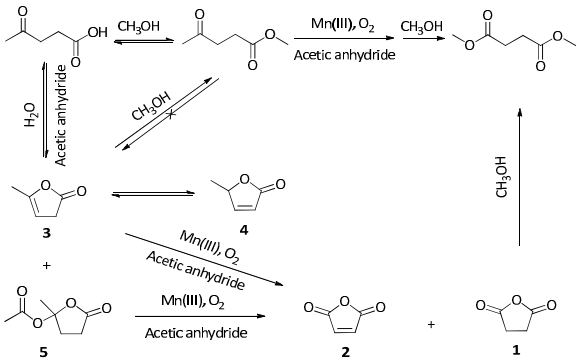



**Fig. 2**. Controlled experiments of dehydration of levulinic acid and methyl levulinate. The retention time correspond to the following compounds: 7.37 min (α-angelica lactone), 7.92 min (inner standard: 1,2,4,5-tetramethylbenzene (TMB)), 10.41 min (methyl levulinate), 11.68 min (β-angelica lactone), 15.83 min (2-methyl-5-oxotetrahydro-2-furanyl acetate).

acid to form **5**. However, the reaction of methyl levulinate does not undergo this route nor does it give any ALs or its derivatives as intermediates under the same conditions (Fig. 1b and 2).

As shown in Fig. 1(a), ALs formed instantly by dehydration of levulinic acid in acetic anhydride during the reaction, thus resulted in the increase of ALs at the first 20 min followed by the decrease of which to a relatively stable level as the reaction went on to 2 h. Meanwhile, the quantity of intermediate **5** rapidly increased to a high level within the first 1 or 2 h. When the reaction time was prolonged to 3 h and longer, an increasing amount of dehydration product **3** was detected after 10 or 15 h while the amount of **5** almost kept in a relative stable level. As for this abnormal phenomenon, it is supposed that this was partially due to the decreasing consumption of which due to the deactivation of the catalyst Mn(III) by trace water formed during the reaction process. This can be demonstrated by the decline in quantity of intermediate **3** and **5** as well as increase of products **1** and **2** when adding fresh catalyst to the system and prolonged the reaction for another 5 h. Whereas doubling the catalyst amount at the beginning of the reaction did not increase any of the main C4 products except by-product **5** (Table 1, entry 5). Besides, prolonging the reaction time showed some positive effects especially on **2** (26.0%) with nearly trace of **5** detected (Table 1, entry 6), which indicated that intermediate **5** could be further convert to **1**, **2** and **3**. This was also evidenced by oxidation of **5** as the substrate under our reaction system (Table 1, entry 7) in which a similar products distribution was obtained; other side products can be confirmed by GC-MS (Fig. S3-S12).

The studies of oxidation behaviour of levulinic acid and methyl levulinate proved that **3** and its derivatives were key intermediates during the reaction in the presence of acetic anhydride. However, it is still vague on the formation route of




**Scheme 2**. Plausible protocol of oxidation of levulinic acid and methyl levulinate.

**2**. In order to figure out the relationship between the formation of **2** and the generation of the intermediate **3**, extra controlled experiments were needed. When **3** was subjected to the similar conditions; about 13.1% of **2** and less than 1% **1** and **5** were detected within 1 h, which was in quite resemblance as the oxidation of levulinic acid. Neither of which could be associated with the oxidation of methyl levulinate where succinate (58.6%) consisted exclusively the majority of the final products without any maleate or other detectable C4 products.[38] As for the oxidation of **3**, the conversion reached more than 99%. We assumed that these results may due to its high activity and instability, especially under the specific conditions with a high concentration. As shown in Fig. 1(a), during the oxidation of levulinic acid, quite small amount of ALs were formed through the dehydration process and the concentration of which kept at a relatively low level during the whole reaction course. The concentration difference of ALs between the two systems and the high activity and instability of **3** might account for the low selectivity of target C4 product. Some of the products were confirmed and shown in Fig. S14-S18.

Consequently, a plausible reaction route for the Mn(III)-catalysed oxidation of levulinic acid and methyl levulinate in acetic anhydride was proposed as summarized in scheme 2. The dehydration of levulinic acid with the aid of solvent acetic anhydride played an important role, in which the substrate was dehydrated to ALs followed by the subsequent oxidation ring opening to give **2**. The controlled experiments of **3** further supported the hypothesis that **3** and its isomer **4** as well as derivative **5** were the specific intermediates in the catalytic oxidation of levulinic acid which differed from that of methyl levulinate.

### The solvent effect on the oxidation of levulinate

Since the generation of intermediates and **2** were closely related to the dehydration role of acetic anhydride solvent, therefore solvent effect on the manganese catalytic oxidation of levulinic acid and methyl levulinate should be considered. The results in different solvents are summarized in Table 2 in which products were analysed after esterification with excess of methanol in order to facilitate detection and comparison.

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**Table 2.** Solvent effect on the oxidation of levulinic acid and methyl levulinate.[a]

| Entry | Solvent | Subatrate | Conv. [mol%] | Yield of important products [mol%][b] | | | |
|---|---|---|---|---|---|---|---|
| | | | | Succinate | Maleate | Malonate | Oxaliate |
| 1 | Acetic acid | **levulinic acid** | **82.1** | **Trace** | **2.5** | **-** | **-** |
| | | methyl levulinate | 26.9 | 5.2 | - | 3.9 | 8.5 |
| 2 | DMF | **levulinic acid** | **75.9** | **-** | **7.2** | **0.5** | **-** |
| | | methyl levulinate | 29.8 | 0.4 | - | - | 1.4 |
| 3 | Ethyl acetate | **levulinic acid** | **24.1** | **2.5** | **1.4** | **-** | **1.2** |
| | | methyl levulinate | 11.4 | 0.1 | 1.9 | - | - |
| 4[c] | Methanol | **levulinic acid** | **46.3** | **2.1** | **-** | **-** | **7.9** |
| | | methyl levulinate | 17.9 | 3.5 | - | - | 14.0 |
| 5 | Acetonitrile | **levulinic acid** | **19.6** | **2.0** | **-** | **-** | **1.8** |
| | | methyl levulinate | Trace | - | - | - | - |
| 6 | Cyclohexane | **levulinic acid** | **31.4** | **2.2** | **-** | **-** | **6.4** |
| | | methyl levulinate | 5.7 | 1.7 | - | 0.6 | 2.0 |
| 7 | DMSO | **levulinic acid** | **18.0** | **0.2** | **-** | **-** | **-** |
| | | methyl levulinate | 7.9 | 1.0 | - | - | - |
| 8 | Dichloromethane | **levulinic acid** | **19.5** | **2.5** | **-** | **-** | **3.5** |
| | | methyl levulinate | 3.8 | 1.3 | - | - | - |

[a] Reaction conditions: Levulinate (2.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5 mol% Mn), slolvent (2 mL), 90 °C, 0.5 Pa $O_2$, 10 h. [b] Data detected by GC after esterification. [c] Data in second row of entry 4 was from reference [38].

When oxidation of levulinic acid was carried out in acetic acid and DMF separately, only 2.5 and 7.2% of dimethyl maleate with trace amount of dimethyl succinate were obtained though the conversion did not vary significantly (82.1 and 74.8% respectively) (Table 2, entries 1 and 2). In other solvents like ethyl acetate, methanol, acetonitrile, cyclohexane, DMSO and dichloromethane, the conversion of levulinic acid range from 18.0 to 46.3% while the yield of succinate was less than 3% with trace or even no amount of maleate. As for methyl levulinate, when the oxidation was carried out in solvents like acetic acid, DMF and methanol,[38] the conversion dramatically reduced to 26.9, 29.8 and 17.9 from 95.3% that obtained in acetic anhydride respectively and the yield of succinate was less than 6.0% (Table 2, entries 1,2,4). Results in other solvents like ethyl acetate, acetonitrile, cyclohexane, DMSO and dichloromethane (Table 2, entries 3-8) indicated that the majority of methyl levulinate maintained unconverted and negligible succinate and even no maleate were detected as the C4 products. Both levulinic acid and methyl levulinate yielded some portion of oxaliate or malonate as by-products in these solvents.

Compared with other solvents, therefore, acetic anhydride played a key role in the oxidation of levulinic acid for the generation of dehydration products **3** which further oxidized to **2**. In addition, acetic anhydride was the appropriate solvent for the Mn(III)-catalytic oxidation of methyl levulinate to succinate, since small amount of water produced during the oxidation process could be absorbed by acetic anhydride thus keeping the Mn(III) catalyst effective by avoiding it from disproportionation.[46] This was confirmed by the results of replacing $Mn(OAc)_3 \cdot 2H_2O$ with $Mn(OAc)_2 \cdot 4H_2O$, which the conversion of methyl levulinate dropped to 12.9 from 95.3% and yield of succinate decreased from 58.6 to 7.7%.[38] To the best of our knowledge, this is the first report on insights of the mechanism comparison of the Mn(III)-catalysed aerobic oxidation of levulinic acid and methyl levulinate under mild conditions.

## Conclusions

In summary, catalytic oxidative cleavage of the biomass derived platform compound levulinic acid was carried out using manganese (III) as catalyst with molecular oxygen to give succinic anhydride. Moreover maleic anhydride was obtained. This process differs greatly from the oxidation of methyl levulinate under the same reaction conditions, which afforded the only C4 product succinate. The pathway for levulinic acid oxidation was disclosed by confirming the intermediates α and β-angelica lactone and 2-methyl-5-oxotetrahydro-2-furanyl acetate for the generation of maleic anhydride and low selectivity of succinic anhydride. Acetic anhydride was proved to be a key solvent in the oxidation conversion reaction for dehydration of levulinic acid and maintaining the activity of Mn(III) catalyst. This study provides an insight into the comparison in catalytic oxidation of levulinic acid and methyl levulinate thus indicated the protection of ester group of methyl levulinate in its oxidative conversion to succinate. Further study on the transformation of levulinic acid is currently underway.

## Acknowledgements

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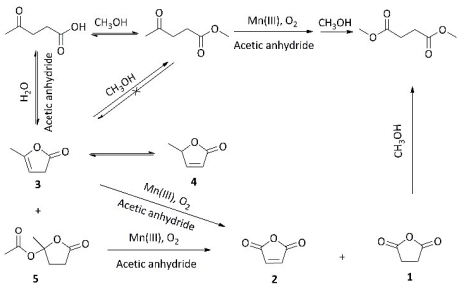


The difference of catalytic oxidative cleavage route between levulinic acid and methyl levulinate were intensively investigated.