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Tandem thionation of biomass derived levulinic acid with Lawesson Reagent

Received 00th January 20xx, Accepted 00th January 20xx Zheng Li, ^a Xing Tang, ^a Yetao Jiang, ^a Miao Zuo, ^b Yangjun Wang, ^a Wei Chen, ^a Xianhai Zeng*, ^a Yong Sun ^a and Lu Lin* ^a

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Herein we report a tandem thionation of biomass derived levulinic acid (LA) to generate thiophenic compounds. LA is initially converted to several thiophenones then an aromatic di-thionated product, 5-methylthiophene-2-thiol, is obtained with a highest yield of 78%. An overall synthesis of thiophenic products from cellulose is also developed.

Levulinic acid (LA), which can be derived with high yields from acid promoted hydrolysis of lignocellulose via hydroxymethylfurfural (5-HMF) and 5-chloromethylfurfural (5-CMF), is acknowledged as a versatile platform molecule to unlock key renewable market.¹⁻⁸ Many efforts are devoted to the downstream conversion of LA for the production of fuels and value added chemicals via various approaches including hydrogenation, oxidation and ammoniation. LA can be hydrogenated to y-valerolactone (GVL), which is considered to be a potential five-membered heterocycle building block as green solvent and hydrocarbon fuel precursor,⁹⁻¹¹ with a rather high yield in the presence of numerous homogeneous and heterogeneous catalysts with external H₂, formic acid (FA) and alcohols as H-donors.^{9, 12-23} The Baeyer-Villiger oxidation of LA has also been reported for the production of 3hydroxypropanoic acid and succinic acid.24-26 By reductive amination-cyclization, LA can be effectively converted to pyrrole compounds, such as N-substituted pyrrolidones over metal dotted oxides 27-29 or even without catalyst. 30, 31 Otherwise, some N-substituted furan products, such as 3acetamido-5-acetylfuran, have also been reported by Kerton and co-workers.32,33

To our best knowledge, there are no reports yet focusing on the thionation of biomass derived molecules to S-containing products, such as thiophenic compounds. It is acknowledged that thiophene and its derivates, as another important class of

five-membered heterocyclic compounds, have significant applications in natural products, 34, 35 pharmaceuticals 36, 37 and advanced solar cell materials ^{38, 39} due to their distinct electronic and biological activities. Traditional approaches for the construction of thiophene ring in industrial scales are based on the reaction of hydrocarbons, such as n-butane and acetylene, with S or H₂S at a rather high reaction temperature. To obtain thiophene compounds under milder conditions, P₄S₁₀ and its derivate Lawesson reagent (LR) are adopted as S-donors for converting a 1,4-dicarbonyl molecule into 1,4-dithiocarbonyl molecule, which then cyclizes to form thiophene ring by the elimination of H₂S.^{40, 41} The reaction is typically conducted in aprotic solvents, such as toluene that has the potential to be employed as a renewable solvent as it can be produced from biomass derived sugars and its furan derivates by pyrolysis or aqueous phase reforming.42-45

In this study, we demonstrated that LA can be effectively thionated to generate a new family of thiophenic compounds in the presence of Lawesson Reagent (LR). The tandem thionation of LA is shown in Scheme 1, and the thiophenic product distribution is strongly depended on the LR:LA mole ratio. Several thiophenone compounds were detected as monothionated products. By tuning LR:LA mole ratio, an aromatic thiophenic compound, 5-methylthiophene-2-thiol, was obtained as a di-thionated product which is considered of potential significant for functional materials and pharmaceutical industry.46-48

Carbohydrates



Scheme 1 Tandem thionation of biomass derived LA to 5methylthiophene-2-thiol in presence of LR.

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The thionation of LA was conducted in toluene, which is a widely used aprotic solvent for LR promoted thionation reactions.^{40, 41} Table 1 provides a condition control over the thiophenic product distribution. Theoretically, one LR molecule would decompose into two fragments and each of them could react with a carbonyl (Scheme S1),⁴⁰ therefore at the outset, we studied the thionation of LA at an LR:LA ratio of 0.5:1. As expected, a mono-thionation process was observed, as shown in Scheme 2. Primarily, it was verified that the $\gamma\text{-carbonyl}$ of LA was initially thionated to form y-thiocarbonyl pentanoic acid, which was detected as an intermediate under low reaction temperatures (e.g. 70 °C) or at an LR:LA ratio of less than 0.5 (Table 1, Entries 1-2 and Figure S1). An m/z loss of 33 was observed in the mass spectra of this intermediate, proving the existence of thiol group (Figure S2) in this intermediate. Given that the enol form of thiocarbonyl is more stable than its thiocarbonyl,49, 50 the intermediate was deduced to be compound 1 in Scheme 2. Under 90 °C at an LR:LA ratio of 0.5, intermediate 1 was not detected in the product (Table 1, Entry 3), which was assumed to form positional isomers 2 and 3 as mono-thionation products via intramolecular dehydration (Figures S3-4), implying that the reaction was strongly affected by temperature. A higher reaction temperature of 110 °C led to a slight increase of the yield of 2 and 3, plausibly by promoting the H₂S elimination of intermediate 4b. It should be emphasized that the conversion of LA to 2 and 3 via the intramolecular dehydration of 1 forms di-hydrothiophene ring at LR:LA ratio of 0.5:1 (Table 1, Entries 1-3), differently with previous reports that 1,4-dicarbonyl compounds, such as methyl levulinate (ML) and ethyl levulinate (EL), are typically transformed to 1,4thiones followed by the elimination of H_2S to give thiophene rings at an LR:substrate ratio of no less than 1:1 and a much

Table 1 Thionation of LA with different LR:LA mole ratio,reaction temperature and time. Typical reaction conditions: 15mL toluene, 4 mmol LA, 40 min.

slower reaction rate (Scheme S2).40, 41, 51

Entry	LR:LA mole ratio	т (°С)	C _{LA} ^[a] (%)	Yield ^[b] (%)						
				AL	1	2	3	4b	5	6
1	0.25	90	65	11	13	12	21	12	0	0
2	0.5	70	87	15	23	16	18	19	0	0
3	0.5	90	100	0	0	24	52	21	1	0
4	0.5	110	100	0	0	26	55	16	2	0
5	1	90	100	0	0	16	35	24	17	0
6	1	110	100	0	0	6	8	5	46	3
7 ^[c]	1	110	100	0	0	5	4	3	66	6
8 ^[c, d]	1	110	100	0	0	6	6	2	63	4
9	1.25	110	100	0	0	2	3	0	78	2
10 ^[c]	1.25	110	100	0	0	0	0	0	61	6
11	1.5	110	100	0	0	1	1	0	77	2

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12 ^[c] 1.5 110 100 0 0 0 Vi@v Art& OnTre DOI: 10.1039/C6GC00566G [a]: percentage conversion of LA. [b]: the yield of **1** was measured using the standard curve of LA. The yields of **2**, **3** and **4b** were measured using the standard curve of AL, as illustrated in section 1.3 of ESI. AL, **5** and **6** were quantified by external standard method. [c]: 3 h. [d]: 13 mmol LA and 13 mmol LR.



Scheme 2 First step thionation of LA to 2 and 3.

On the other hand, the carboxyl in 1 might be further thionated to compound 4a with a molecular weight of 148 in the presence of partial excessive LR (Scheme 2) as we found that the hydroxyl in carboxyl of pentanoic acid was completely thionated to form pentanethioic acid by LR as well, which was in accordance with Rao's report.⁵² Compound 4a could be isomerized to its cycle form 4b that has a similar structure as pseudo-levulinic acid, which can be formed by the direct cyclization of LA and has the nearly equal free energy with LA.53 However, only one compound with a molecular weight of 148 was detected in the product (Figures S3 and S5), indicating that only 4a or 4b existed stably in the product. We assumed that 4b was more likely as there was probably an equilibrium between 2, 3 and 4b by the addition/elimination of H₂S (Table 1, Entries 3 and 4), which was also confirmed by Brunet and co-workers.⁵⁴ Moreover, 4b could generate a much more stable tertiary carbocation (m/z=115) by the elimination of thiol group, as indicated by the mass spectrum in Figure S5. The above conclusion suggests that the isomerization of 4a to 4b is fast under the applied conditions. Unfortunately, it is quite difficult to separate and purify compounds 2, 3 and 4b from the product because that 2, 3 and 4b were easy to polymerize and quite unstable against H₂O and H₂S during the separation process due to the equilibrium among them (Scheme 2). Moreover, to our best knowledge, no commercial standards for the quantification of these compounds are available yet. Thus, the amounts of 1, 2, 3 and 4b were semi-quantified as illustrated in ESI. When the mole ratio of LR to LA was 0.25, the conversion of LA (CLA) was higher than the theoretical conversion of 50% (Table 1, Entry 1), probably due to the dynamic equilibrium between LA and angelica lactone (AL) which contributed partially to the consumption of LA (Table 1, Entries 1-2). However, AL could be

probably due to the dynamic equilibrium between LA and angelica lactone (AL) which contributed partially to the consumption of LA (Table 1, Entries 1-2). However, AL could be reversibly hydrated to LA and then further thionated under higher temperature, LR dosage (Table S1) and prolonged reaction time (Figure S6), thus no AL was detected under these reaction conditions (Table 1, Entries 3-12).^{53, 55} Published on 08 April 2016. Downloaded by New York University on 11/04/2016 04:06:50.

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As shown in Table 1, LA was completely converted if LR:LA ratio was 0.5 and the main products were 2, 3 and 4b, while small amount of compound 5, known as 5-methylthiophene-2-thiol, was also detected at 90 °C (Scheme 3 and Table 1, Entry 3). With a rise of temperature up to 110 °C, only 2% of LA was converted to 5 at a LR:LA ratio of 0.5 (Table 1, Entry 4), whereas a 17% yield of 5 was obtained if the LR:LA ratio was doubled at 90 °C (Table 1, Entry 5), which clearly suggests that the degree of thionation of LA is mainly dominated by the LR:LA ratio. Interestingly, the yield of compound 5 was increased to 46% at 110 °C in 40 min, and the yield further increased to 66% with a reaction time extension to 3 h (Table 1, Entries 6-7). A slightly lower yield of 63% was obtained when the dosage of LA and LR were tripled (Table 1, Entry 8). The generation of 5 was significantly accelerated under a higher LR:LA ratio of 1.25 as the yield reached 78% within 40 min (Table 1, Entry 9). However, with a further increase of LR:LA to 1.5, no more pronounced increase in the yield of 5 was observed in 40 min (Table 1, Entry 11). As the reaction time prolonged, a small amount of 2methylthiophene (compound 6) was detected, which was derived from 5 by the elimination of H₂S (Table 1, Entries 6-12). The mass balance of the reaction was not 100% probably due to the different signal response of the compounds in the products and/or undetectable minor-products formed by the polymerization among products and LR residues.⁴⁰ It was assumed that 2, 3 and 4b were precursors of 5 because their yields declined as the reaction proceeded along with the formation of 5 (Figures S7-8). As Scheme 3 showed, the carbonyl groups in the ring of 2 and 3 would be further thionated under excessive LR followed by keto-enol isomerization to form 5, which was a quite stable enol form due to its conjugated structure (MS and NMR spectra see Figures S9-11).49,50



Scheme 3 Tandem thionation of LA to 5 through 2 and 3.

In our previous research, toluene has been proved quite effective for the extraction of EL against humins, which were intractable by-products formed during the EL production by the alcoholysis of cellulose.⁵⁶ Considering that the reaction in this research is also performed in toluene, we proposed an integrated process by the combination of extraction and thionation of LA (Scheme 4). A crude LA solution, which was derived from H_2SO_4 promoted hydrolysis of cellulose and contained considerable amounts of humins (Scheme 4A), was

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adopted instead of off-the-shelf pure LA. The cruderted owns partially neutralized, concentrated and the extracted by toluefie, as described in ESI in details. A yellowish solution with a LA mass concentration of 2 wt% was then obtained, and about 85% LA was extracted by toluene from the concentrated hydrolysate (Scheme 4B). The thionation reaction was *in-situ* conducted in the extract under identical LR dosage and conditions as shown in Table 1, Entry 9. The yield of **5** was up to 77% even in the presence of trace humins and no coking was observed, which memorably ensures the successive extraction and tandem thionation of crude LA for the production of **5**.



Scheme 4 Integrated conversion of cellulose to 5 via successive extraction and thionation of crude LA. Photos: A) cellulose derived crude LA; B) separation of LA and humins by toluene; C) *in-situ* thionation of LA to 5 in extractant.

After thionation, LR was converted to a phenylthioxophosphine oxide,40 which is soluble in toluene at room temperature and may lead to undesired issues, such as polymerization during and H_2S generation further aftertreatments. Thereby, the beforehand elimination of LR residue is quite necessary. Herein, a concise aftertreatment process was developed to remove LR residue before further purification process. First, LR residue was converted to its hydrolysate, P-(4-methoxyphenyl)-phosphonic acid (MPPA), by adding 4 mmol water into the liquid product followed by heating at 90 °C for 10 min (Scheme S3). Crystalline MPPA was observed during cooling stage (Figure S12). We have demonstrated that the acidity of 5 is weaker than carbonic acid but stronger than water, resulting in the chemistry of 5 guite similar with phenol. Thus, 5 can be easily separated from LR residue and MPPA by mild alkali washing using NaHCO₃ or Na₂CO₃ solution, during which LR residue is nearly completely neutralized and then removed into aqueous phase.

Conclusions

In conclusion, we have described here a tandem thionation reaction of biomass derived LA to thiophenic compounds under mild conditions. 5-Methylthiophene-2-thiol, an aromatic versatile platform compound, was effectively produced under mild conditions. We also managed to develop a successive

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extraction and thionation process using biomass derived crude LA solution as substrate which provided a quite satisfying yield of **5**. Moreover, LR residue can be removed by simply washing by NaHCO₃ solution, which facilitates further purification and application of the desired products. Notably, the aromatic structure and thiol group of **5** ensures its versatility for downstream conversion into various peculiar building blocks for functional materials, pharmaceutical intermediates and solvent applications, which include that a) thiophene, sulfoxide and sulphone compounds by the hydrogenation/oxidization of thiophene ring or thiol group; b) thiophene aldehyde, thiophene carboxylic acid and halothiophene by substitution reactions on the aromatic thiophene ring; c) thienothiophene compounds, which is proposed to be synthesized from **5** by alkylating the thiol group followed by annulation.

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Tandem thionation of biomass derived levulinic acid with

Lawesson Reagent

Zheng Li,^a Xing Tang, ^a Yetao Jiang, ^a Miao Zuo,^b Yangjun Wang, ^a Wei Chen, ^a Xianhai Zeng*, ^a Yong Sun ^a and Lu Lin*^a

Graphical Abstract



Tandem thionation of off-the-shelf and crude levulinic acid is performed with Lawesson Reagent (LR) to generate biomass derived thiophenic compounds.