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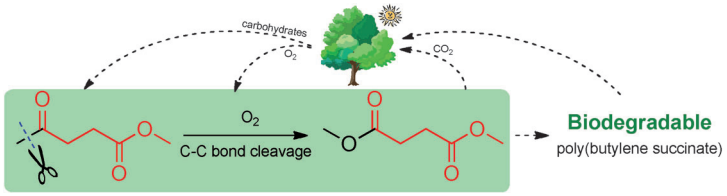

Grand Cleft Oxo: Levulinate, available from biomass, is oxidized into succinate through manganese(III)-catalyzed selective cleavage of C–C bonds with molecular oxygen. In addition to levulinate, a wide range of aliphatic methyl ketones also undergo oxidative C–C bond cleavage at the carbonyl group. This procedure offers a route to valuable dicarboxylic acids from biomass resources by nonfermentive approaches.

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Conversion of Levulinate into Succinate through Catalytic Oxidative Carbon–Carbon Bond Cleavage with Dioxygen

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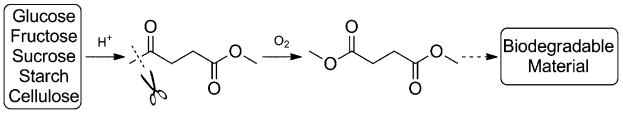
Making full use of oxygen atoms in carbohydrates and its derivatives to produce oxygenated chemicals is an attractive prospect.[1] The well-known biological production of organic acids from carbohydrates usually involves C–C bond cleavage and release of CO_2.[2] Nowadays, chemists are interested in obtaining valuable organic acids from biomass resources by using nonfermentive approaches[1,3] such as catalysis, which has proven effective in the petrochemical industry. For example, lactate can be obtained through selective C–C bond cleavage of sugars.[3a]

Succinic acid is an important chemical for the production of 1,4-butanediol, γ-butyrolactone, tetrahydrofuran, and pyrrolidone. Its derivative poly(butylene succinate) (PBS) is a promising biodegradable polyester.[4] Succinate can be obtained through the fermentation of sugars,[2,4] and through the catalytic conversion of (petroleum-derived) maleic anhydride.[4] Herein, we describe a synthesis of succinate through chemical methods, using carbohydrates as raw material.

Levulinate has been identified as a key platform molecule in biorefineries.[5] It can be easily obtained from carbohydrates such as glucose, fructose, sucrose, starch, and cellulose.[5,6] Levulinate contains both carbonyl and carboxyl functional groups, similar to the structure of succinate. Selective oxidative C–C cleavage of levulinate at the methyl adjacent to the carbonyl group generates succinate (Scheme 1). Although this transformation has been anticipated in several Review articles,[5] only a few research reports describe this reaction, and further development is required using molecular oxygen as oxidant under mild reaction conditions.[7]

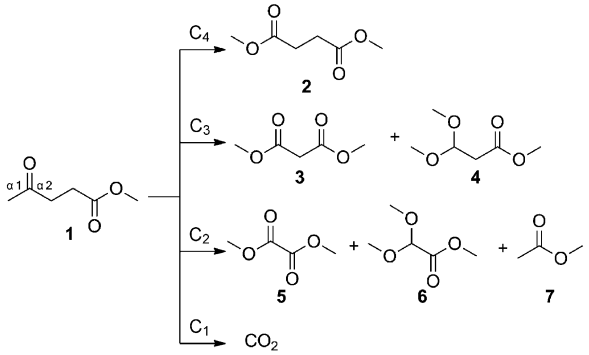


Scheme 1. Selective oxidation of levulinate into succinate.

In essence, the oxidation of levulinate into succinate involves a selective C–C bond cleavage of methyl ketone. Saturated ketones are generally resistant to oxidation, and strong oxidizing agents, such as nitric acid, are still widely used.[8] Catalytic oxidative C–C bond cleavage of ketones, especially unactivated aliphatic ones, with dioxygen is rather challenging. Thus, the oxidation of levulinate with dioxygen would be both an interesting fundamental organic transformation as well as an interesting method of biomass conversion.

Oxidative C–C cleavage of levulinate at the carbonyl group requires C–C bond fission and C–O bond formation. Inspired by previous reports on C–C bond cleavage of oxygen-containing compounds such as α-hydroxy ketones and vicinal diols,[9] we envisioned that oxygenation of the C–H bond adjacent to the carbonyl group would facilitate C–C bond fission. Owing to its electronic structure, there have been several reports on hydrogen abstraction reactions by stoichiometric and catalytic amounts of Mn^{III} species.[10] On the basis of these reports, we describe herein Mn^{III}-catalyzed oxidative C–C bond cleavage of levulinate into succinate with dioxygen under mild conditions.

Methyl levulinate was selected as substrate and the oxidation products were determined after catalytic esterification, which was convenient for analysis (Scheme 2). When the reaction was performed with 5 mol% $Mn(OAc)_3{\cdot}2H_2O$ under



Scheme 2. Oxidation products of levulinate after esterification. The C_1–C_4 labels refer to the number of carbon atoms, excluding the methoxy group.

0.5 MPa oxygen in acetic anhydride, about 95.3% methyl levulinate (**1**) was converted within 10 h at 90 °C (Table 1, entry 2). Oxidation products ranging from C_1 to C_4 were detected, indicating that both C–C bonds adjacent to the carbonyl group (α1 and α2) were cleaved (Scheme 2). Ideally, the total amounts of succinate/CO_2 and malonate/acetate should be approximately equal, if the oxidative cleavage occurs at the α1 and α2 positions with comparable probability. However, succinate (**2**) was detected as the main product with a yield of 58.6%; much higher than the yield of C_3 (**3**+**4**) products

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Table 1. Catalytic oxidation of levulinate with dioxygen as oxidant.[a]

Entry	Catalyst	Conv. [mol%]	Yield of important diesters[b] [mol%]		
			2	**3+4**	**5+6**
1	none	trace	n.d.	n.d.	n.d.
2	$Mn(OAc)_3{\cdot}2H_2O$	95.3	58.6	2.5	10.6
3[c]	$Mn(OAc)_3{\cdot}2H_2O$	2.4	0.1	2.3	n.d.
4	$Mn(acac)_3$	92.4	49.8	2.9	14.1
5	$Mn(OAc)_2{\cdot}4H_2O$	12.9	7.7	0.7	4.4
6[d]	$Mn(OAc)_2{\cdot}4H_2O$	88.8	52.4	3.2	16.6
7	MnO_2	1.1	0.3	0.4	0.4
8	Mn_2O_3	2.7	0.6	0.8	0.6
9	Mn_3O_4	1.9	0.3	1.0	0.4

[a] Reaction conditions: methyl levulinate (2.5 mmol), catalyst (5 mol% Mn), acetic anhydride (2 mL), $T=90\,^{\circ}C$, $P=0.5$ MPa O_2, $t=10$ h; n.d. = no detection. [b] Yield of important diesters after esterification, others products were mainly acetate and CO_2. [c] N_2 atmosphere. [d] Reaction time 20 h.

(2.5%). Moreover, the yield of C_2 diesters, including dimethyl oxalate and methyl dimethoxyacetate (**5+6**), was about 10.6%. Methyl acetate was also generated through catalytic oxidation. This was confirmed by using another solvent (methanol) instead of acetic anhydride (Scheme S2). In addition to the esters in the liquid phase, CO_2 was also detected in the gas phase. The amount of CO_2 was higher than that of succinate (87%, based on the amount of levulinate). On the other hand, no oxidation product was observed when the reaction was performed without catalyst (entry 1). A control experiment under N_2 revealed that most of methyl levulinate remained intact (entry 3). Hence, manganese(III) acetate proved effective for the catalytic oxidative C–C cleavage of methyl levulinate into succinate with molecular oxygen as oxidant, and selective cleavage of the C–C bond mainly occurred at the α1-position. To the best of our knowledge, this is the first report on the conversion of levulinate into succinate, catalyzed by manganese compounds, with molecular oxygen as oxidant under mild conditions. Although the yield of succinate should be improved further, this is the best result achieved so far for this challenging transformation.

We continued our study by focusing on the yields of the important diesters, including the succinate, malonate, and oxalate ones (Table 1). Similar results were obtained when $Mn(acac)_3$ was used (entry 4). However, when $Mn(OAc)_2{\cdot}4H_2O$ was used, the conversion of methyl levulinate was only 12.9% within 10 h after an induction period of ca. 300 min (entry 5). Nevertheless, when the reaction time was extended to 20 h, the conversion of methyl levulinate reached 88.8% (entry 6). In contrast, manganese oxide (entries 7–9) exhibited a rather low activity, indicating that homogenous Mn^{III} catalysts are preferred for this transformation. In previous reports, vanadium compounds have proved effective for catalytic C–C bond cleavage of α-hydroxy ketones and vicinal diols,[9] however, dimethyl succinate yields of only 1.0% and 10.2% were reported over $H_5PV_2Mo_{10}O_{40}$ and $VO(acac)_2$, respectively. Moreover, the use of ferric nitrate, copper acetate, and cobalt(II) acetate resulted in much lower conversions under similar reaction conditions (see Figure 1). Thus, the homogenous Mn^{III} compounds offer a unique advantage in the catalytic selective oxidative C–C cleavage of levulinate at the α1-position.

Important issues in this transformation are the formation

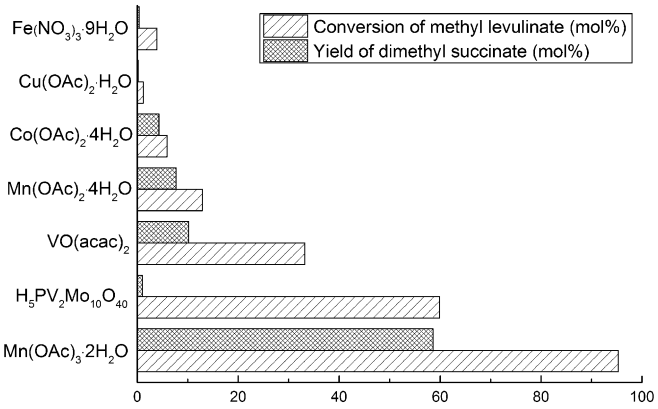
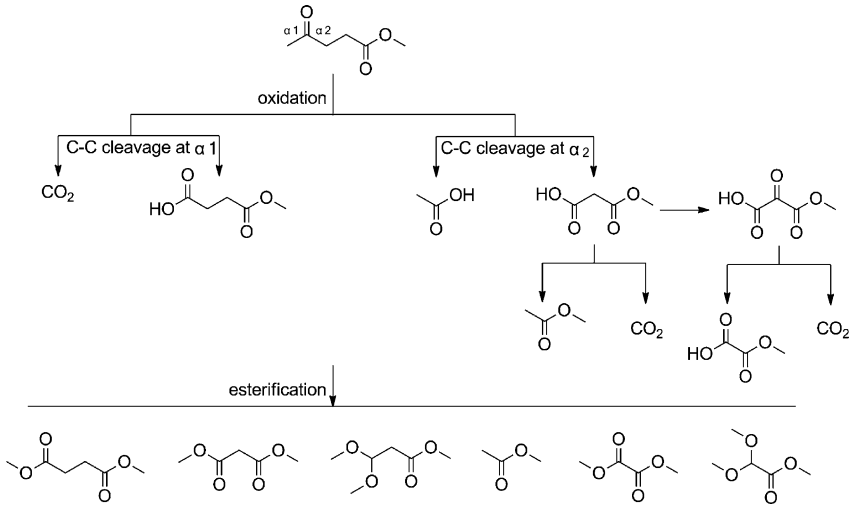


Figure 1. Oxidation of methyl levulinate with different transition-metal compounds. Reaction conditions: methyl levulinate (2.5 mmol), 5 mol% catalyst ($H_5PV_2Mo_{10}O_{40}$ based on vanadium), acetic anhydride (2 mL), $T=90\,^{\circ}C$, $P=0.5$ MPa O_2, $t=10$ h.

pathway of the oxidation products and the amount of carbon dioxide released; more than the theoretical value. Cleavage of the C–C bond could occur inevitably at both sides adjacent to the carbonyl group (Scheme 3, α1 and α2 position). C–C bond cleavage at the α1-position gives carbon dioxide and a C_4 product. At the same time, C–C cleavage at the α2 position leads to the formation of acetic acid and C_3 compounds such as malonate in the beginning. Malonate is known to easily de-



Scheme 3. Formation pathways for the main products of methyl levulinate oxidation.

compose into acetic acid and CO_2. We tested the stability of different diesters under the reaction conditions (Table S2). When dimethyl succinate and dimethyl oxalate were tested, about 95.6% and 98.8% was recovered, respectively. In contrast, when dimethyl malonate was tested less than 5% was recovered, and oxalate, dimethoxyacetate, oxomalonate, and CO_2 were detected. These results are in good agreement with the inherent properties of malonate, and the observed low yield of malonate as well as the increase of CO_2. Meanwhile, oxidation of the active methylene group gave oxomalonate, which led to the formation of C_2 products such as oxalate. The complete proposed reaction pathway is shown in Scheme 3. The loss of C_3 products, the formation of oxalate, and increased amount of carbon dioxide are closely related to the unique structure of levulinate, and this is why selective oxidation of levulinate into succinate is rather challenging.

Generating carboxyl groups through oxidative C–C bond cleavage is useful from both academic and industrial perspectives, especially when using dioxygen as oxidant.[11] Besides methyl levulinate, the substrate scope was investigated with manganese(III) acetate as catalyst (Table 2). When 2-pentanone, 2-hexanone, 2-octanone, and 2-nonanone were oxidized, the main products were also derived from cleavage of the C–C bond between methyl and carbonyl. The ratio of C–C bond fissions at the corresponding methyl and methylene position was approximately 3–4 (entries 1–4). 5-Chloro-2-pentanone could also be transformed smoothly, with 99% conversion and a similar product ratio, and the halide substituent was still present after the reaction (entry 5). Moreover, branched-chain aliphatic ketones could also be converted under the same reaction conditions (entries 6 and 7). The oxidative cleavage occurred on only one side, with 100% selectivity to 2,2-dimethyl propionate + propionate when 2,2-dimethyl-3-hexanone was oxidized. In contrast, when 4-nonanone was used as substrate, the ratio of hexanoate + propionate was roughly that of pentanoate + butyrate (entry 8). Hence, a wide range of unactivated linear aliphatic ketones could smoothly undergo Mn^{III}-catalyzed oxidative C–C bond cleavage at the carbonyl group with molecular oxygen as oxidant. The C–C cleavage occurs preferentially between the carbonyl and methyl groups when methyl ketones are used.

Table 2. Oxidative C–C bond cleavage of aliphatic ketones with dioxygen.[a]

Entry	Substrate	Conv. [%]	Main products
1	2-pentanone	97	butyrate (79%), propionate (21%)
2	2-hexanone	>99	pentanoate (72%), butyrate (20%)
3	2-octanone	>99	heptanoate(69%), hexanoate (20%)
4	2-nonanone	>99	octanoate (67%), heptanoate (21%)
5	5-chloro-2-pentanone	>99	4-chlorobutyrate (76%), 3-chloropropionate (14%)
6	4-methyl-2-pentanone	>99	3-methylbutyrate (85%), 2-methylpropionate (15%)
7	2,2-dimethyl-3-hexanone	45	2,2-dimethylpropionate + propionate (100%)
8	4-nonanone	84	hexanoate + propionate(46%) pentanoate + butyrate (54%)

[a] Reaction conditions: ketones (2.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5 mol%), acetic anhydride (2 mL), $T = 90\,^{\circ}C$, $P = 0.5$ MPa O_2, $t = 10$ h; [b] Corresponding methyl esters after esterification. The other products are mainly CO_2 and acetate.

Another key issue is transfer of the oxygen atom, from O–O to C–O during the oxidative C–C bond cleavage. Previous studies on Mn^{III}-catalyzed reactions proposed that hydrogen abstraction occurs by enolization of the ketone.[10] This interpretation is in agreement with our experimental observations. For example, in the oxidation of 2,2-dimethyl-3-hexanone (entry 7), the are hydrogen atoms at only one side adjacent to the carbonyl group. Thus, enolization can occur at only one side, as can the subsequent C–C cleavage.

Valence variation of manganese was also studied by UV/Vis spectroscopy. When chelated with H_3PO_4, the Mn^{III} complex showed a maximum absorption at approximately $\lambda = 510$ nm, while the Mn^{II} species did not show this peak (Figure S10).[12] After $Mn(OAc)_3 \cdot 2H_2O$ was stirred with methyl levulinate under an atmosphere of N_2 at 90 °C, the Mn^{III}absorption band disappeared. This result is consistent with the above-mentioned hydrogen abstraction. Moreover, when 5 mol% 2,6-di-*tert*-butyl-*p*-cresol (BHT) was added during the oxidation of methyl levulinate, the reaction was completely impeded. This indicates that a free radical process is involved at the beginning.

After hydrogen abstraction by Mn^{III} from the C–H bond adjacent to the carbonyl group, reaction of monoketones with Mn^{III} gave acetoxy ketones in the absence of oxygen.[13] In contrast, the formation of organic peroxide would be inevitable in the presence of oxygen (Figure S6). We terminated the oxidation halfway by destroying the catalyst with water. The colorless solution obtained was able to change the color of an aqueous KI/starch solution. Furthermore, it could oxygenate Ph_3P into triphenylphosphine oxide at room temperature. When $^{18}O_2$ was used instead of ordinary oxygen, ^{18}O-enriched triphenylphosphine oxide was formed (Figures S7 and S8). This suggests that peroxides are formed during the oxidation. The preparation of stable peroxides by Mn^{III} catalysts at low temperature also agrees with this result.[14] These results indicate that oxygen atoms are transferred from dioxygen to the substrate via a peroxide.

Decomposition of peroxide is known to occur in the presence of manganese ions. This decomposition may generate oxygen-functionalized ketones, such as α-dicarbonyls. To test this hypothesis, we selected 2,3-heptanedione as a model compound (Table S3 and Figure S9). 2,3-Heptanedione could be converted into pentanoate and butyrate smoothly through catalytic oxidation with dioxygen. Reaction of 2,3-heptanedione with 1.0 equiv $Mn(OAc)_3 \cdot 2H_2O$ under nitrogen atmosphere also gave pentanoate (53% conversion, 100% selectivity). In the same reaction conditions, 1.0 equiv $Mn(OAc)_2 \cdot 4H_2O$ failed to convert 2,3-heptanedione. These results suggest α-dicarbonyl C–C bond cleavage by Mn^{III}, even in the absence of oxygen.[15] Based on these results, we propose that peroxide

and α-dicarbonyl are two key intermediates in catalytic oxidative C–C bond cleavage (Scheme S4). Although it is difficult to isolate these intermediates in large quantities under the reaction conditions we used, the proposed reaction pathway is a logical explanation of the experimental results.

Finally, we further examined the catalytic transformation of biomass carbohydrates into levulinate. By using methylsulfonic acid as catalyst, glucose, fructose, sucrose starch, and microcrystalline cellulose could be easily converted in water at 170 °C (Table S4). After removal of insoluble solids by filtration, levulinic acid could be extracted from the aqueous mixture in yields of 20–59%, and then methyl levulinate could be generated through catalytic esterification in methanol. Moreover, a number of reports also described the preparation of levulinate from various biomass resources.[5,6] Based on these studies and this work, succinate could be prepared from biomass by using catalytic approaches. This work would also expand levulinate-based chemistry.[16]

In summary, we report an approach to obtain succinate via Mn^{III}-catalyzed oxidation of levulinate with molecular oxygen under mild conditions. Besides levulinate, a wide range of aliphatic methyl ketones undergo catalytic selective oxidative C–C bond cleavage at the carbonyl group. C–C cleavage occurs preferentially between the carbonyl and methyl groups. This work provides an example of obtaining valuable dicarboxylic acids from biomass resources through nonfermentive routes.

Experimental Section

Methyl levulinate (2.5 mmol) and $Mn(OAc)_3 \cdot 2H_2O$ (5 mol%) were loaded into a 30 mL stainless steel autoclaves equipped with a magnetic stirrer, pressure gauge, and automatic temperature-control apparatus. After purging to exclude air, O_2 was charged to 0.5 MPa. The autoclave was heated to 90 °C and kept at that temperature for the desired reaction time. After reaction, the autoclave was cooled to room temperature. The residual gas was released carefully and collected for subsequent analysis. All of the liquid reaction mixture was transferred and refluxed in excess methanol before analysis.

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Keywords: C–C bond cleavage · levulinate · oxidation · succinate · sustainable chemistry

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