Supporting Information

Highly selective one-step dehydration, decarboxylation and hydrogenation of citric acid to methylsuccinic acid

Jasper Verduyckt[a] and Dirk E. De Vos*[a]

[a] Centre for Surface Chemistry and Catalysis, Department of Microbial and Molecular Systems, KU Leuven - University of Leuven, Leuven Chem&Tech, Celestijnenlaan 200F, Post Box 2461, 3001 Heverlee, Belgium

* E-mail: dirk.devos@kuleuven.be

1. Experimental details

1.1. Materials

All chemicals were used as received: citric acid monohydrate (Sigma-Aldrich, ≥99.5%), citric acid-2,4-^{13}C (Sigma-Aldrich, 99% ^{13}C), methylsuccinic acid (Sigma-Aldrich, 99%), trans-aconitic acid (Sigma-Aldrich, 98%), mesaconic acid (Sigma-Aldrich, 99%), itaconic acid (TCI, >99.0%), methacrylic acid (Acros Organics, 99.5%), tricarballylic acid (Sigma-Aldrich, ≥99%), isobutyric acid (Fluka, ≥99.5%), NaOH (Fischer Scientific, 99.1%), cerium(IV)sulphate tetrahydrate (abcr, 97%), *p*-methoxyphenol (Sigma-Aldrich, 99%), N_2 (Air Liquide, α1), H_2 (Air Liquide, N40), O_2 (Air Liquide, N25), Pt/C (5 wt%, Johnson Matthey), Pd/C (5 wt%, Johnson Matthey), Pd/Al_2O_3 (5 wt%, Alfa Aesar), Pd/$BaSO_4$ (5 wt%, Sigma-Aldrich), $MgAl_2O_4$ (Sigma-Aldrich), ZrO_2 (Alfa Aesar), $BaSO_4$ (Merck), $(NH_3)_4PdCl_2.H_2O$ (Sigma-Aldrich, ≥99.99%), methanol anhydrous (Sigma-Aldrich, 99.8%), acetyl chloride (Janssen Chimica, 98%), benzyl alcohol (Sigma-Aldrich, 99+%) and D_2O (Sigma-Aldrich, 99.9% D).

1.2. Catalyst synthesis

Pd/$MgAl_2O_4$ and Pd/ZrO_2 (5 wt%) were synthesised by incipient wetness impregnation according to De Schouwer *et al.*[1] In a typical procedure 1 g of support was impregnated with a solution of $(NH_3)_4PdCl_2$ in deionised water. Impregnated supports were then dried overnight at 60°C, granulated to particles with sizes between 250 and 500 µm, followed by calcination (35 min, 400°C, 2°C/min, 50 mL/min O_2) and reduction (1 h, 400°C, 2°C/min, 150 mL/min H_2). The synthesised catalysts were stored under N_2 until use.

1.3. Catalytic reaction

In a typical reaction a solution of citric acid in deionised water (2 mL, 0.1 M), a catalyst (4 mol% Pd/$BaSO_4$) and a magnetic stirring bar were loaded into a stainless steel reactor (11 mL). Next, the reactor was sealed and the atmosphere was flushed six times with N_2. Then, after pressurizing the reactor with 2 bar N_2 followed by 4 bar H_2, the mixture was magnetically stirred at 500 rpm and heated to 225°C. After 40 min the reaction was quenched by cooling with water and ice. Afterwards, the catalyst was separated from the solution by centrifugation.

1.4. Product analysis and identification

To determine the conversion of citric acid and the selectivities to the different products, the reaction mixtures were analysed by ^{1}H-NMR. Samples were prepared by adding 300 µL of the reaction mixture to 300 µL of D_2O containing an external standard (benzyl alcohol, 0.1 M). ^{1}H- and ^{13}C-NMR spectra, as well as ^{1}H,^{13}C-HSQC spectra, were recorded on a Bruker Ascend 400 MHz spectrometer equipped with a BBO 5 mm atma probe and a sample case. The broad signal of water in the ^{1}H-NMR spectra was suppressed by applying an adapted zgpr pulse program: p1 9.75 µs; plw1 15W; plw9 5.7-05W; o1P on the resonance signal of water, determined and selected automatically. Besides ^{1}H-, ^{13}C- and 2D-NMR, the products were also identified by gas chromatography coupled to mass spectrometry (GC-MS) with an Agilent 6890

GC, equipped with a HP-5ms column, coupled to a 5973 MSD mass spectrometer. GC-MS was performed after derivatisation of the products with methanol. For this derivatisation first water was removed by evaporation under reduced pressure, after which the products were dissolved in methanol (anhydrous, 1 mL). Then acetyl chloride (100 µL) was added while cooling the solution on ice; the resulting mixture was stirred and heated to 70°C for 2 h. Finally, the produced hydrogen chloride and the remaining acetyl chloride were evaporated at room temperature under a gentle stream of N_2. The identification of gaseous products was done using a Gasmet DX4000 FTIR gas analyser. The IR data were processed with Calcmet Standard software version 12.161.

The different selectivities mentioned in the paper were calculated as follows:

$$S_{MSA} = \frac{Y_{MSA}}{X}$$

$$S_{PTA} = \frac{Y_{PTA}}{X}$$

$$S_{2^{nd}\ deca} = \frac{Y_{MAA} + Y_{BA} + Y_{IBA}}{X}$$

$$S_{Fragmentation} = \frac{Y_{Ac} + Y_{AA}}{X}$$

$$S_{Itaconic\ isomers} = \frac{Y_{IA} + Y_{MA} + Y_{CA}}{X}$$

Where MSA, PTA, MAA, BA, IBA, Ac, AA, IA, MA and CA stands for methylsuccinic acid, propane-1,2,3-tricarboxylic acid, methacrylic acid, butyric acid, isobutyric acid, acetone, acetic acid, itaconic acid, mesaconic acid and citraconic acid, respectively. Pyruvic and lactic acid were not considered in the calculation of the selectivity for fragmentation products, since these compounds originate from the same citric acid molecule as acetic acid. Y = yield and X = conversion, always on a molar basis.

2. Catalyst characterisation

2.1 Pd dispersion

Table S1. Dispersion of Pd based catalysts.

	Pd/C	Pd/Al_2O_3	Pd/$MgAl_2O_4$	Pd/$BaSO_4$	Pd/ZrO_2
Pd dispersion [%]	32 [a]	14 [a]	28 [bc]	6 [a]	8 [b]

[a] Commercial catalysts; characterised in literature.[2,3] [b] Self-prepared catalysts; characterised in previous work of our group.[1,4] [c] The dispersion was calculated based on the particle size distribution determined by De Schouwer *et al.*, using the method of Mallat and Petró.[1,5]

2.2 Texture

Table S2. BET surface area of Pd based catalysts.

	Pd/C	Pd/Al_2O_3	Pd/$MgAl_2O_4$	Pd/$BaSO_4$	Pd/ZrO_2
S [m^2/g]	425[a]	148[a]	175[b]	5[a]	49[b]

[a] Commercial catalysts; characterised in literature.[2,6] [b] Self-prepared catalysts; characterised in previous work of our group.[1]

3. Time course

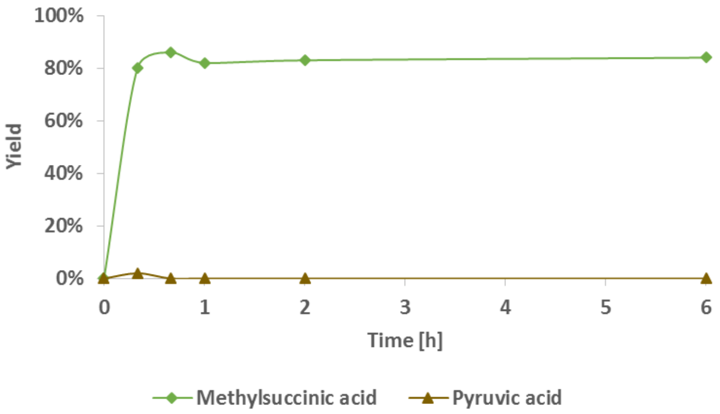


Figure S1. Time course of the decarboxylation of citric acid in the presence of H_2. Reaction conditions: citric acid (0.2 mmol), 4 mol% Pd/$BaSO_4$, water (2 mL), 2 bar N_2 and 4 bar H_2, 225°C. Other side products, besides pyruvic acid, were omitted for clarity.

4. Optimisation of H_2 pressure using 0.5 mol% Pd

Table S3. Optimisation of H_2 pressure using 0.5 mol% Pd for the conversion of citric acid to methylsuccinic acid.[a]

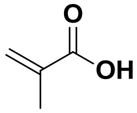
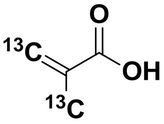
	Catalyst	P_{H2} [bar]	Conversion [%]	Selectivity [%]				
				MSA [b]	PTA [c]	2nd deca [d]	Fragmentation [e]	Itaconic isomers [f]
1	Pd/C	4	>99	82	4	5	6	<1
2	Pd/C	8	>99	84	5	2	7	<1
3	Pd/C	12	>99	74	6	2	8	<1
4	Pd/C	16	>99	76	5	2	9	<1
5	Pd/C	20	>99	77	5	2	9	<1
6	Pd/$BaSO_4$	20	>99	36	0	11	29	17

[a] Reaction conditions: citric acid (0.2 mmol), 0.5 mol% Pd, water (2 mL), 2 bar N_2, 225°C, 40 min. [b] Methylsuccinic acid. [c] Propane-1,2,3-tricarboxylic acid. [d] '2nd deca' represents isobutyric acid, butyric acid and methacrylic acid. [e] 'Fragmentation' represents acetone, acetic acid, pyruvic acid and lactic acid. [f] 'Itaconic isomers' represents itaconic acid, mesaconic acid and citraconic acid.

5. Isotopic labelling experiment

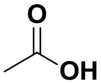
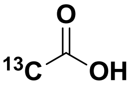
Citric acid and citric acid-2,4-^{13}C were reacted under following reaction conditions: substrate (0.2 mmol), water (2 mL), 2 bar N_2 + 4 bar H_2, 225°C, 6 h. The fate of the carbon in the products was tracked by analysing the aqueous reaction mixture with ^{13}C-NMR (**Figure S2-S3**). The ^{13}C-NMR signals were attributed to the right compounds by using ^{1}H-^{13}C HSQC. For the abundant products, *i.e.* methacrylic acid, acetic acid and β-carboxy-γ-butyrolactone, the carbon signals are (almost) all visible in the 'non-isotope enriched' reaction mixture. Therefore a comparison can be made between the ^{13}C-NMR spectrum of the 'isotope enriched' reaction mixture and that of the 'non-isotope enriched' mixture (**Table S4-S6**). Signals originating from a non-labelled carbon position in citric acid-2,4-^{13}C indeed disappear in the spectrum of the 'isotope enriched' solution, confirming the right positions of ^{13}C and thus the reaction mechanisms. For the products that are less abundant, *i.e.* acetone, pyruvic acid, itaconic acid, mesaconic acid and citraconic acid, there are not many carbon signals visible in the 'non-isotope enriched' mixture. For these molecules, we can therefore at most confirm that the ^{13}C-labelled positions give the only visible signals in the spectrum of the 'isotope enriched' solution, which supports the proposed reaction mechanisms (**Table S7-S11**).

Table S4. ^{13}C-NMR signals of methacrylic acid in the isotopic labelling experiment starting from either citric acid or citric acid-2,4-^{13}C.

Signals [ppm]		172.0	136.2	126.9	17.5
Citric acid		🟢	🟢	🟢	🟢
Citric acid-2,4-^{13}C		🔴	🔴	🟢	🟢

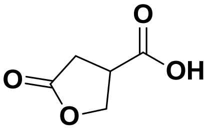
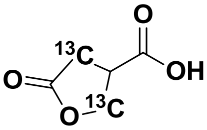
🟢 = observed. 🔴 = not observed.

Table S5. ^{13}C-NMR signals of acetic acid in the isotopic labelling experiment starting from either citric acid or citric acid-2,4-^{13}C.

Signals [ppm]		176.9	20.6
Citric acid		🟢	🟢
Citric acid-2,4-^{13}C		🔴	🟢

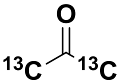
🟢 = observed. 🔴 = not observed.

Table S6. ^{13}C-NMR signals of β-carboxy-γ-butyrolactone in the isotopic labelling experiment starting from either citric acid or citric acid-2,4-^{13}C.

Signals [ppm]		180.2	176[a]	70.6	40.4	31.5
Citric acid		🟢	🔴	🟢	🔴	🟢
Citric acid-2,4-^{13}C		🔴	🔴	🟢	🔴	🟢

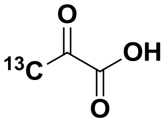
[a] Predicted value. 🟢 = observed. 🔴 = not observed.

Table S7. ^{13}C-NMR signals of acetone in the isotopic labelling experiment starting from citric acid-2,4-^{13}C.

Signals [ppm]		207[a]	30.2
Citric acid-2,4-^{13}C		🔴	🟢

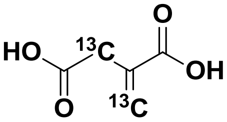
[a] Predicted value. 🟢 = observed. 🔴 = not observed.

Table S8. ^{13}C-NMR signals of pyruvic acid in the isotopic labelling experiment starting from citric acid-2,4-^{13}C.

Signals [ppm]		197[a]	168[a]	29.1
Citric acid-2,4-^{13}C		🔴	🔴	🟢

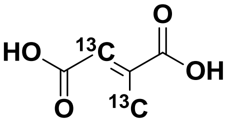
[a] Predicted value. 🟢 = observed. 🔴 = not observed.

Table S9. ^{13}C-NMR signals of itaconic acid in the isotopic labelling experiment starting from citric acid-2,4-^{13}C.

Signals [ppm]		174[a]	169[a]	137[a]	130.1	38.1
Citric acid-2,4-^{13}C		🔴	🔴	🔴	🟢	🟢

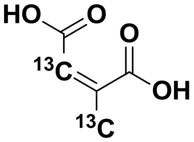
[a] Predicted value. 🟢 = observed. 🔴 = not observed.

Table S10. ^{13}C-NMR signals of mesaconic acid in the isotopic labelling experiment starting from citric acid-2,4-^{13}C.

Signals [ppm]		168[a]	167[a]	141[a]	128.9	14.2
Citric acid-2,4-^{13}C		🔴	🔴	🔴	🟢	🟢

[a] Predicted value. 🟢 = observed. 🔴 = not observed.

Table S11. ^{13}C-NMR signals of citraconic acid in the isotopic labelling experiment starting from citric acid-2,4-^{13}C.

Signals [ppm]		176[a]	167[a]	147[a]	121.3	21.1
Citric acid-2,4-^{13}C		🔴	🔴	🔴	🟢	🟢

[a] Predicted value. 🟢 = observed. 🔴 = not observed.

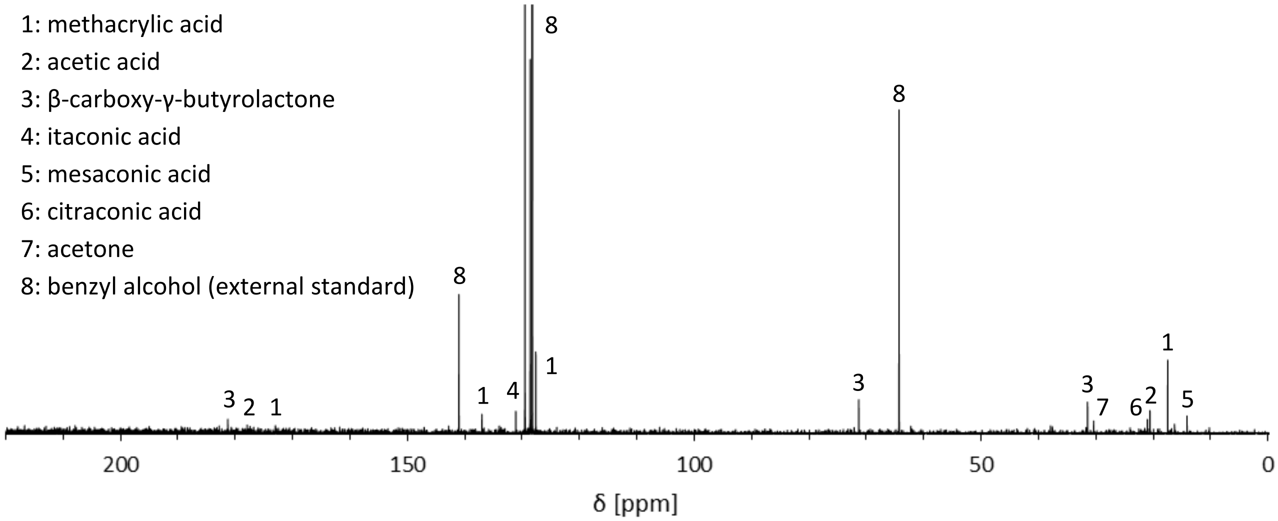


Figure S2. ^{13}C-NMR spectrum of the ‘non-isotope enriched’ reaction mixture in the isotopic labelling experiment.

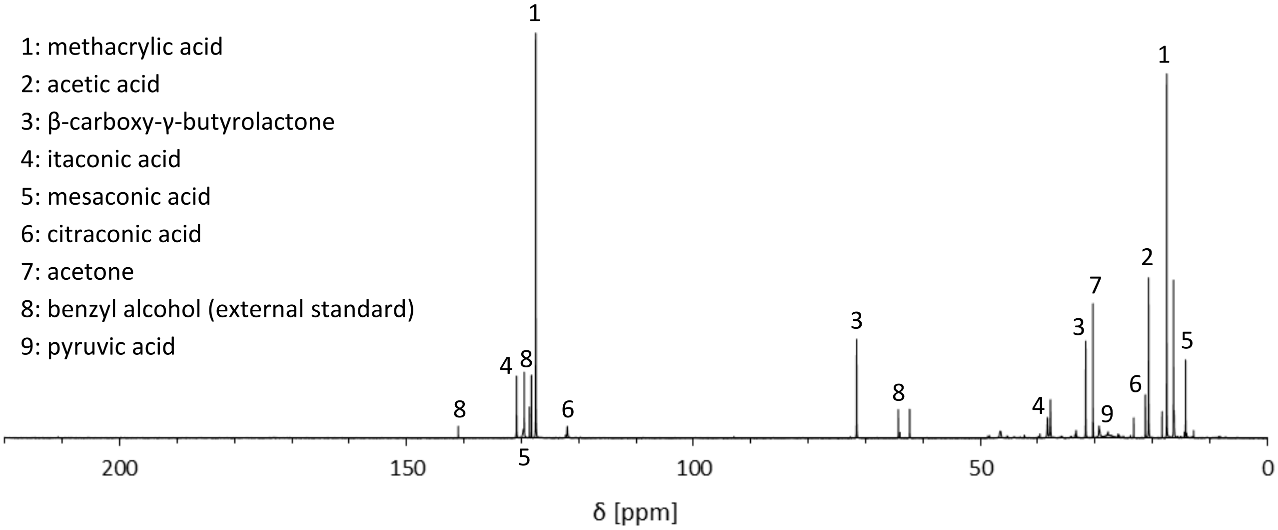
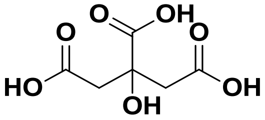


Figure S3. ^{13}C-NMR spectrum of the ‘isotope enriched’ reaction mixture in the isotopic labelling experiment. The signals that are not assigned, correspond to compounds the yield of which is lower than 3% (based on ^{1}H-^{13}C HSQC and quantitative ^{1}H-NMR) and can therefore be neglected.

6. Product identification

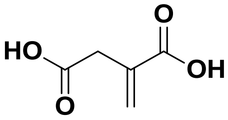
General information: ^{1}H-NMR spectra were calibrated by setting the singlet signal of the external standard (benzyl alcohol) to 4.65 ppm.[7]

Citric acid (1, MW = 192 g/mol)



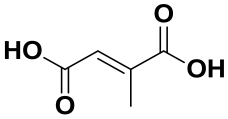
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 3.02 (d, 2H, -C**<u>H</u>**$_2$-COOH), 2.85 (d, 2H, -C**<u>H</u>**$_2$-COOH).

Itaconic acid (2, MW = 130 g/mol)



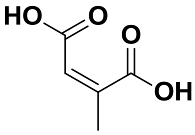
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 6.32 (s, 1H, C**<u>H</u>**$_2$=C(COOH)-), 5.85 (s, 1H, C**<u>H</u>**$_2$=C(COOH)-), 3.42 (s, 2H, -C**<u>H$_2$</u>**-COOH).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 130.1 (1C, **<u>C</u>**H$_2$=C<), 38.1 (1C, COOH-**<u>C</u>**H$_2$-). Carbons that do not couple with a proton, were not observed via HSQC.

Mesaconic acid (3, MW = 130 g/mol)



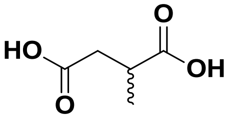
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 6.76 (s, 1H, =C**<u>H</u>**-COOH), 2.19 (s, 3H, C**<u>H$_3$</u>**-C(COOH)=).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 128.9 (1C, -**<u>C</u>**H=C<), 14.2 (1C, ≥C-**<u>C</u>**H$_3$). Carbons that do not couple with a proton, were not observed via HSQC.

Citraconic acid (4, MW = 130 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 5.97 (s, 1H, =C**<u>H</u>**-COOH), 2.04 (s, 3H, C**<u>H$_3$</u>**-C(COOH)=).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 121.3 (1C, -**<u>C</u>**H=C<), 21.1 (1C, ≥C-**<u>C</u>**H$_3$). Carbons that do not couple with a proton, were not observed via HSQC.

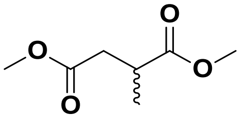
Methylsuccinic acid (5, MW = 132 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.97-2.84 (m, 1H, $-C\underline{\mathbf{H}}(CH_3)-COOH$), 2.70 (dd, 1H, $-C\underline{\mathbf{H}}_2-COOH$), 2.58 (dd, 1H, $-C\underline{\mathbf{H}}_2-COOH$), 1.21 (d, 3H, $-CH(C\underline{\mathbf{H_3}})-COOH$).

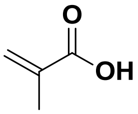
$^{13}C\{^1H\}$-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 40.0 (1C, $-\underline{\mathbf{C}}H_2-COOH$), 37.9 (1C, $-\underline{\mathbf{C}}H(CH_3)-COOH$), 16.6 (1C, $-CH(\underline{\mathbf{C}}H_3)-COOH$). Carboxylic acid carbons could not be observed.

Dimethyl methylsuccinic acid (dimethyl ester of 5, MW = 160 g/mol)



GC-MS (EI, 70 eV): m/z (rel. int., %): 130 (7), 129 (100), 128 (58), 101 (45), 100 (40), 87 (15), 74 (6), 69 (17), 59 (80), 55 (6), 42 (10), 41 (15), 39 (9).

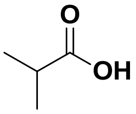
Methacrylic acid (6, MW = 86 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 6.10 (s, 1H, $C\underline{\mathbf{H}}_2=C(COOH)-$), 5.72 (s, 1H, $C\underline{\mathbf{H}}_2=C(COOH)-$), 1.91 (s, 3H, $C\underline{\mathbf{H_3}}-C(CH_2)-$).

$^{13}C\{^1H\}$-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 172.0 (1C, $-\underline{\mathbf{C}}OOH$), 136.2 (1C, $CH_2=\underline{\mathbf{C}}<$), 126.9 (1C, $\underline{\mathbf{C}}H_2=C<$), 17.5 (1C, $\geq C-\underline{\mathbf{C}}H_3$).

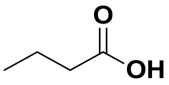
Isobutyric acid (7, MW = 88 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.60 (hp, 1H, $-C\underline{\mathbf{H}}(CH_3)_2$), 1.14 (d, 6H, $-CH(C\underline{\mathbf{H_3}})_2$).

$^{13}C\{^1H\}$-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 35.4 (1C, $-\underline{\mathbf{C}}H(CH_3)_2$), 18.7 (2C, $-CH(\underline{\mathbf{C}}H_3)_2$). Carboxylic acid carbon could not be observed.

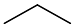
Butyric acid (8, MW = 88 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.36 (t, 2H, $-C\underline{\mathbf{H_2}}-COOH$), 1.61 (sx, 2H, $CH_3-C\underline{\mathbf{H_2}}-CH_2-$), 0.93 (t, 3H, $C\underline{\mathbf{H_3}}-CH_2-$).

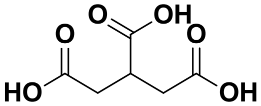
$^{13}C\{^1H\}$-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 38.3 (1C, $-\underline{\mathbf{C}}H_2-COOH$), 18.7 (1C, $CH_3-\underline{\mathbf{C}}H_2-CH_2-$), 12.9 (1C, $\underline{\mathbf{C}}H_3-CH_2-$). Carboxylic acid carbon could not be observed.

Propane (9, MW = 44 g/mol)



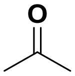
Propane was identified along with CH_4, CO and CO_2 using a Gasmet DX4000 FTIR gas analyser and Calcmet Standard software version 12.161.

Propane-1,2,3-tricarboxyllic acid (10, MW = 176 g/mol)



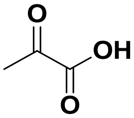
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 3.20 (quint, 1H, -C**H**-(CH_2-)$_2$), 2.76 (dd, 2H, -CH-(C**H**$_2$-)$_2$), 2.67 (dd, 2H, -CH-(C**H**$_2$-)$_2$).

Acetone (11, MW = 58 g/mol)



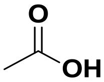
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.23 (s, 6H, C**H$_3$**-).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 30.2 (2C, **C**H_3-). Carbonyl carbon could not be observed.

Pyruvic acid (12, MW = 88 g/mol)



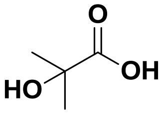
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.38 (s, 3H, C**H$_3$**-).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 29.1 (1C, **C**H_3-). Carboxylic acid and carbonyl carbons could not be observed.

Acetic acid (13, MW = 60 g/mol)



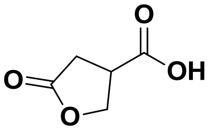
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 2.10 (s, 3H, C**H$_3$**-).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 176.9 (1C, -**C**OOH), 20.6 (1C, **C**H_3-).

2-Hydroxyisobutyric acid (MW = 104 g/mol)



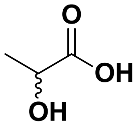
^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 1.36 (s, 6H, C**H$_3$**-).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 73.8 (1C, -**C**(OH)-(CH_3)$_2$), 26.7 (2C, **C**H_3-). Carboxylic acid carbon could not be observed.

β-Carboxy-γ-butyrolactone (MW = 130 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 4.63 (dd, 1H, -O-C**<u>H</u>**$_2$-CH<), 4.56 (dd, 1H, -O-C**<u>H</u>**$_2$-CH<), 3.64-3.54 (m, 1H, -CH_2-C**<u>H</u>**(COOH)-CH_2-), 2.93-2.86 (m, 2H, -C(=O)-C**<u>H</u>**$_2$-CH<).
^{13}C{^{1}H}-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 180.2 (1C, >CH-**<u>C</u>**OOH), 70.6 (1C, -O-**<u>C</u>**H_2-CH<), 40.4 (1C, -CH_2-**<u>C</u>**H(COOH)-CH_2-), 31.5 (1C, -C(=O)-**<u>C</u>**H_2-CH<). Carboxylic ester carbon could not be observed.

Lactic acid (MW = 90 g/mol)



^{1}H-NMR (400 MHz, H_2O/D_2O): δ (ppm) = 4.11 (q, 1H, CH_3-C**<u>H</u>**(OH)-), 1.33 (d, 3H, C**<u>H</u>**$_3$-CH(OH)-).

7. References

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