

ELECTRONIC SUPPLEMENTARY INFORMATION

From batch to continuous: Au-catalysed oxidation of D-galacturonic acid in a packed bed plug flow reactor under alkaline conditions

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1. Materials

Oxygen gas (Grade 4.5, 99.995% purity) was obtained from Linde Gas. Granular Au/TiO₂ was obtained from Strem (gold on titania, Aurolite™ 1.2 wt% Au/TiO₂, AuTEK). The catalyst was pulverized in a mortar to a fine powder for experiments in batch mode, and gently crushed and sieved to obtain an equal particle size of 0.5-0.65 mm for experiments in plug flow set-up. Silicon carbide (powder, medium, 120 grit, Alfa Aesar) was used as additional filler for the plug flow reactor. Activated carbon (Norit SX 1G, bulk density 350-450 kg m⁻³, BET surface area ~1000 m² g⁻¹)¹ was used for addition to the batch experiments with Au/TiO₂, and as support material for the Au/C catalyst, which was prepared as reported previously.²

For analytical standards (HPLC-analysis), D-galacturonic acid sodium salt (purum, Sigma-Aldrich), and galactaric acid (97%, Sigma-Aldrich) were used, 5-keto-L-galactonic acid was prepared as reported.³ For the batch and plug flow experiments, D-galacturonic acid monohydrate was used (gift from Royal Cosun), and the sodium hydroxide used in these experiments was diluted from sodium hydroxide concentrate (Fixanal, 1.0 M NaOH for 1 L standard solution, Sigma-Aldrich).

D-Talose (99.8%, CarboSynth), nitric acid (65%, for analysis, Merck), and potassium carbonate (for analysis, Merck), were used as received for the synthesis of talaric acid. Sulfuric acid (95-97%, for analysis, Merck) was used to prepare the HPLC eluent, and to precipitate galactaric acid from the reaction mixture. Sicapent (with indicator, Merck) was used to dry the obtained galactaric acid.

For NMR the following solvents were used: deuterium oxide (D₂O, 99.9 atom% D, Sigma-Aldrich) and sodium deuterioxide (NaOD, 40 wt% solution in D₂O, 99+ atom % D, Sigma-Aldrich).

2. Batch reactions

2.1 General procedure & set-up

Batch oxidations were carried out in a 500 mL glass four-neck round bottom flask (diameter ~ 95 mm), which was placed in an aluminium DrySyn heating mantle, placed on a magnetic stirring/heating plate. The flask was charged with GalA solution (typical 250 mL 0.1M solution), the temperature sensor was placed inside the liquid. A glass diffuser with a porous filling (ASTM 145-175 μ) was used to generate fine oxygen bubbles (typical flow rate 300 mL min⁻¹ at atmospheric pressure). The pH was kept constant by an automated titrator (848 TitrinoPlus, Metrohm), filled with 2M NaOH solution. Stirring was performed using a magnetic stirring bar (oval shaped, 40 mm x 20 mm, VWR International), or by a mechanical stirrer ('large stirrer' = PTFE, 65 x 18 x 3 mm, length 350 mm, diameter shaft 8 mm, Heidolph-Instruments; 'small stirrer' = overhead stirrer shaft, COWIE, PTFE, with encapsulated steel reinforced drive shaft, centrifugal stirrer, 50 mm, shaft diameter 8.0 mm, shaft length 500 mm, VWR International).

In a typical experiment, the flask was charged with the GalA solution, which was heated to the desired temperature under stirring. Oxygen was bubbled through the solution at the desired flow rate. When the reaction mixture had reached the desired temperature, the pH was adjusted to the desired value using the automated titrator. Next, the catalyst (typical 550-989 mg 1 wt% Au/TiO₂) was introduced to the flask as a dry powder (marking the t = 0 h point), and NaOH consumption was monitored over time at constant pH. In some experiments, dissolved oxygen was measured as described in ESI 2.3.

2.2 Optimization of the batch oxidation set-up

Prior to the kinetic measurements (main article), the batch set-up was optimized. First, the influence of oxygen flow rate was checked, to optimize mass transfer from gas to liquid. Oxygen was supplied to the reaction mixture using a fine diffuser, and O₂ flow rates were varied between 200 – 600 mL min⁻¹. The reactions were performed at 40°C, pH 10, and using a large magnetic stirrer at 500 rpm (see specs in experimental). Fig. S1 shows the conversion of substrate over time at varying oxygen flows. The results indicate that the oxygen flow is optimal between 200 and 400 mL min⁻¹, but further increase of the oxygen flow to 500 and 600 mL min⁻¹ slows the reaction down. This can be explained by various phenomena well described by others,⁴⁻⁶ such as a change in the spatial position of the pulverized fine catalyst particles due to the lift of these solids induced by gas-bubbles moving to the surface (we did indeed visually observe a more concentrated catalyst layer at the surface of the liquid, at higher gas flow rates). It was therefore decided to keep the oxygen flow rate constant in the next steps of the investigation at an optimal constant flow rate of 300 mL min⁻¹. [Note: gas – liquid mass transfer limitations still apply, see chapter on oxygen solubility in main article].

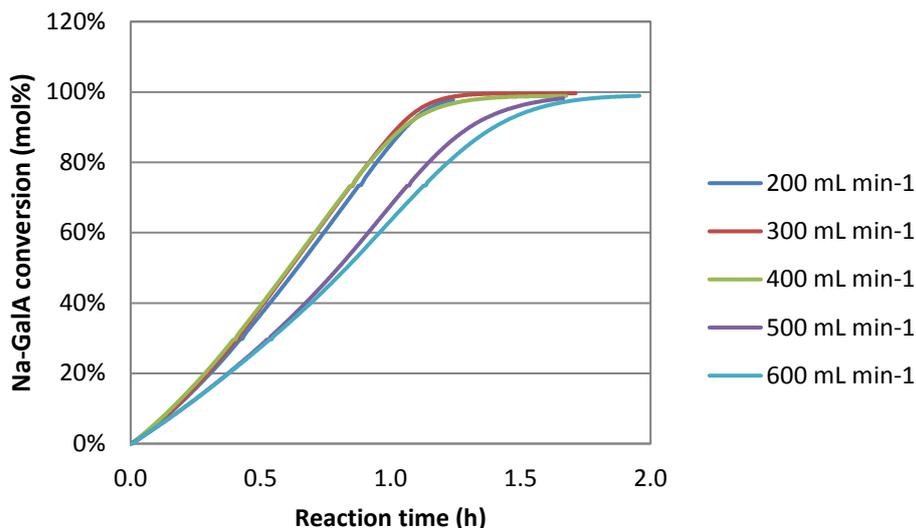


Fig. S1 Influence of oxygen flow rate on the reaction rate (Conditions: 250 mL 0.091M Na-GaIA, 0.989 g 1 wt% Au/TiO₂, pH 10, 40°C, 500 rpm magnetic stirring).

Next, the stirring speed and stirrer type were optimized to minimize catalyst - liquid mass transfer limitations. Fig. S2 shows an overview of the influence on the reaction rate for three types of stirrers: a large magnetic stirring bar, and two mechanical stirrers (a small blade and a large blade, see specs in ESI 2.1).

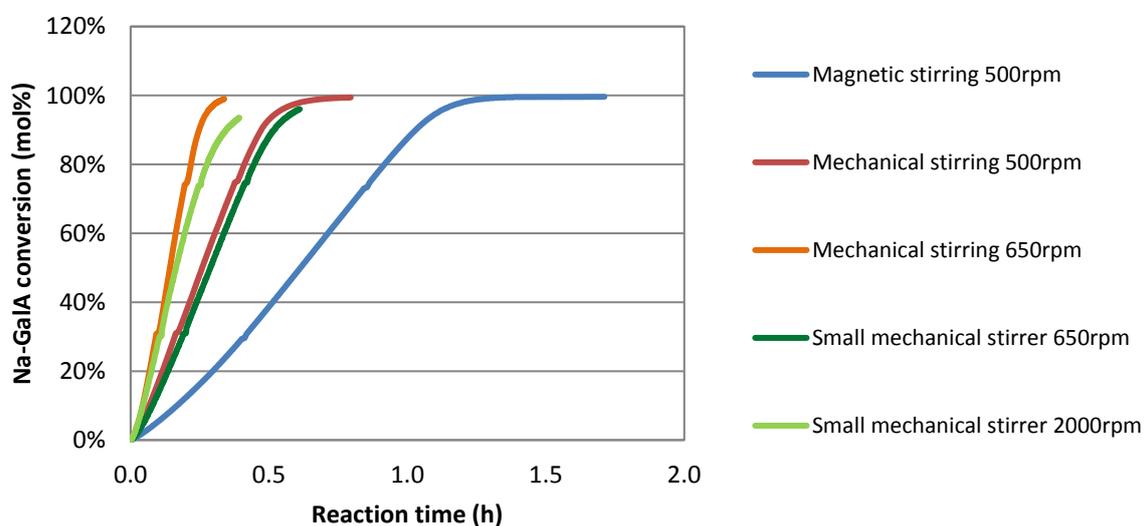


Fig. S2 Influence of stirring type and rate on the reaction rate (Conditions: 250 mL 0.091M Na-GaIA, 0.989 g 1 wt% Au/TiO₂, pH 10, 40°C, oxygen flow 300 mL min⁻¹).

Changing the magnetic stirring bar to a mechanical stirrer at the same stirring rate (500 rpm), showed a significant improvement in the reaction rate. Further increase of the stirring rate from 500 to 650 rpm further improved the reaction rate. Due to practical limitations of the reaction set-up, the stirring rate could not be further increased using the same stirring blade. Instead, a smaller stirring blade was used at 650 rpm

(comparable to conversion with a larger blade at 500 rpm), and 2000 rpm. However, the best results were obtained using the larger mechanical stirrer at 650 rpm. Since the highest stirring speed showed the highest reaction rate, mass transfer limitations cannot be excluded.

2.3 Oxygen solubility – influence of solutes on measurements

In our kinetic study (main article and ESI 2.2) we briefly studied the influence of oxygen gas flow on the reaction rate. At that point in the investigation reaction conditions were not yet fully optimized, and reaction rates significantly increased under the more optimized conditions (e.g. 650 rpm mechanical stirring at pH 10, 50°C / pH 9, 60 °C). Others observed that at high catalyst loadings and reaction rates, glucose oxidation became limited in oxygen supply.⁷⁻⁹ It was therefore decided to investigate if this was also the case for the Na-GalA oxidation reactions at the now improved conversion rates, by online monitoring of the dissolved oxygen concentration.

In previous work on glucose oxidations, Prüße *et al.* calculated the theoretical oxygen solubility for glucose solutions (10-1000 mM) by using Henry's law constants,⁷ to estimate the experimental error during their measurements. However, these data are not available for (Na)-GalA and (diNa)-GA solutions. Since GalA and GA contain acid functionalities, the neutralized solutions are high in salinity, which also is expected to affect the oxygen solubility. Therefore, prior to determining the oxygen solubility under reaction conditions, it was decided to first determine the oxygen solubility of various Na-GalA and diNa-GA solutions (0.1-0.2 M) at pH 9 as a function of temperature, to investigate the potential influence on oxygen measurements under our reaction conditions.

Fig. S3 shows the dissolved O₂ concentration measured in mmol L⁻¹ as a function of the temperature. Between 20-50°C, the dissolved oxygen concentration was found to be mostly influenced by temperature, and not so much by the amount and type of dissolved carbohydrate (0.1-0.2 M solutions of Na-GalA and diNa-GA). Previously calculated theoretical values for 0.1 M glucose (Glc)⁷ also fit very well with our experimental data for Na-GalA and diNa-GA solutions.

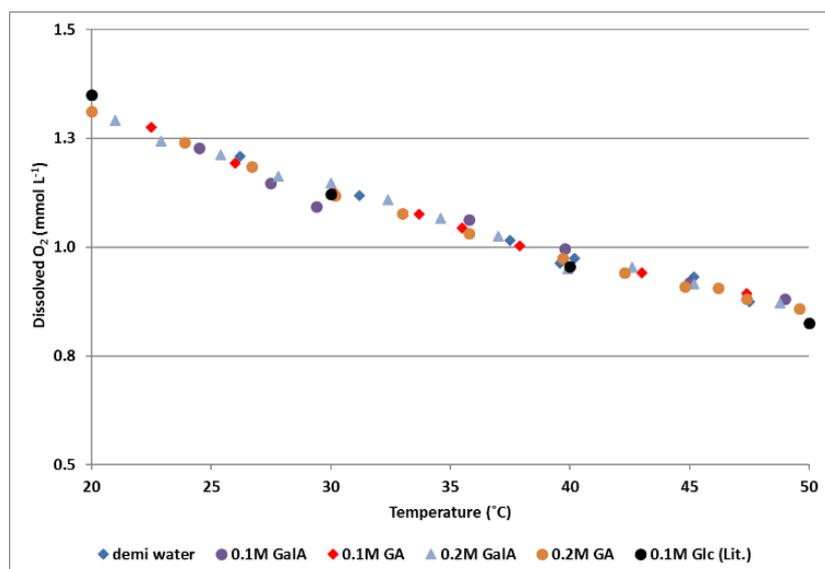


Fig. S3 Saturation values for dissolved oxygen at atmospheric oxygen pressure (pH 9), 0.1 M Glc (neutral pH) data taken from lit.⁷

Based on the data presented above, it can be concluded that the oxygen solubility is independent of the type of dissolved sugar at concentrations <0.2 M, and therefore independent of the conversion of Na-GalA to diNa-GA. So, any changes in measured dissolved oxygen concentration during reaction can solely be attributed to the consumption of oxygen.

3 Continuous Plug Flow Reactions

3.1 General procedure & set-up

Continuous flow experiments were carried out in a Parr 5400 Tubular Reactor (Hastelloy 276, fixed bed reactor, Parr Project # 914576). Catalyst particles (7.7 g 1wt% Au/TiO₂, particle size 0.5-0.65 mm) and silicon carbide powder (16.8 g, 120 grid) were placed in the fixed bed reactor (534 mm length x 8 mm inner diameter = 26.8 cm³). The catalyst bed was held in place by glass wool and a metal gauze on the top and bottom of the reactor. The temperature inside the catalyst bed was monitored by a thermocouple, and the reactor was heated by a Vecstar heating mantle (3 heating zones).

The top of the reactor was fed with oxygen gas via a mass flow controller, and the liquid phase was also fed on top of the reactor via two separate HPLC pumps. The bottom of the reactor was connected to a cooler, from which the reaction mixture entered a gas - liquid separator. The liquid phase was passed to a pressurized receiving flask controlled by a valve, and the excess gas was vented by a back pressure regulator, which also controlled the total pressure of the system. A photograph of the set-up is shown in Fig. S4, and a schematic representation is shown in Fig. S5.

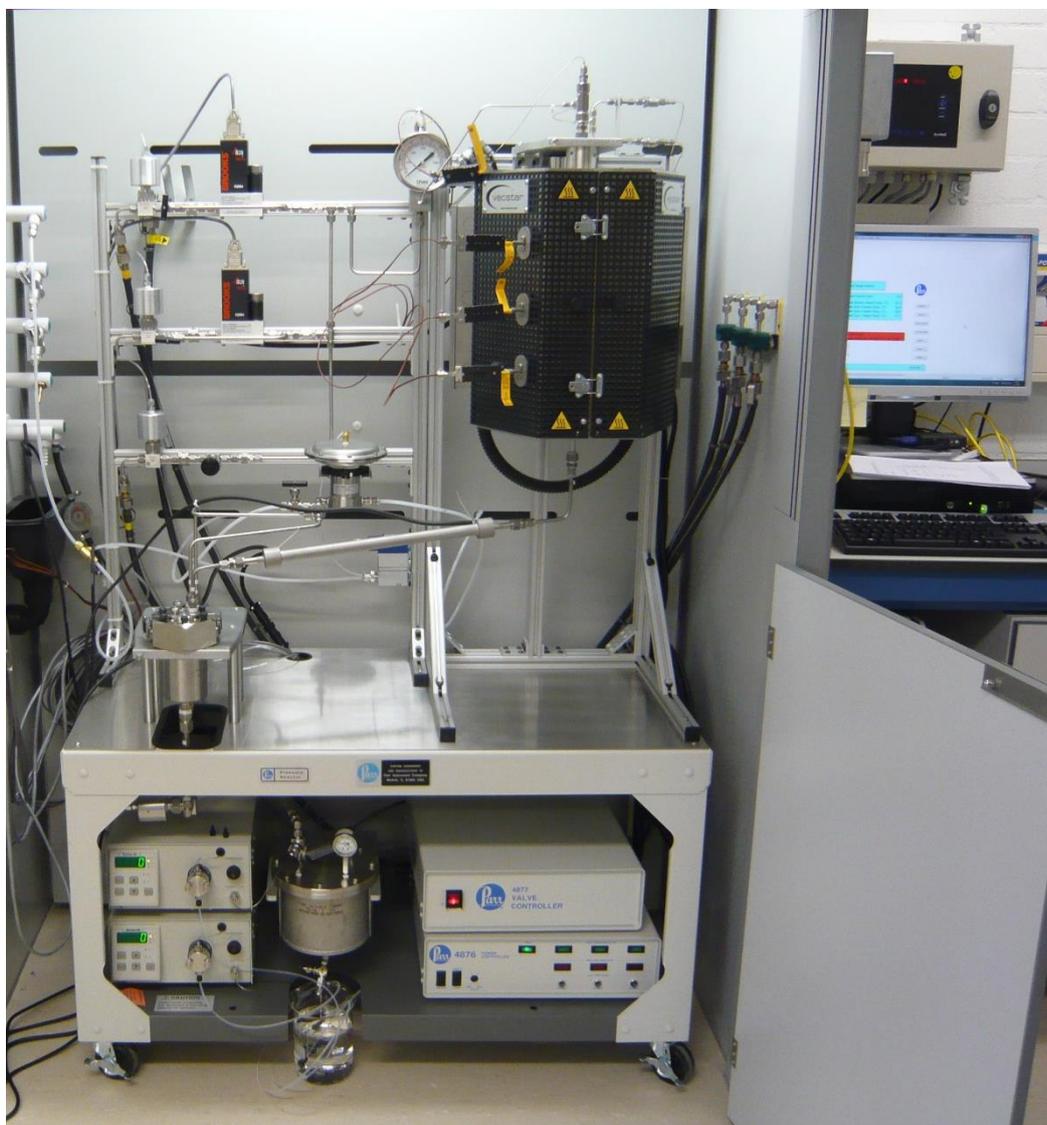


Fig. S4 Continuous plug flow reactor – photograph of the set-up.

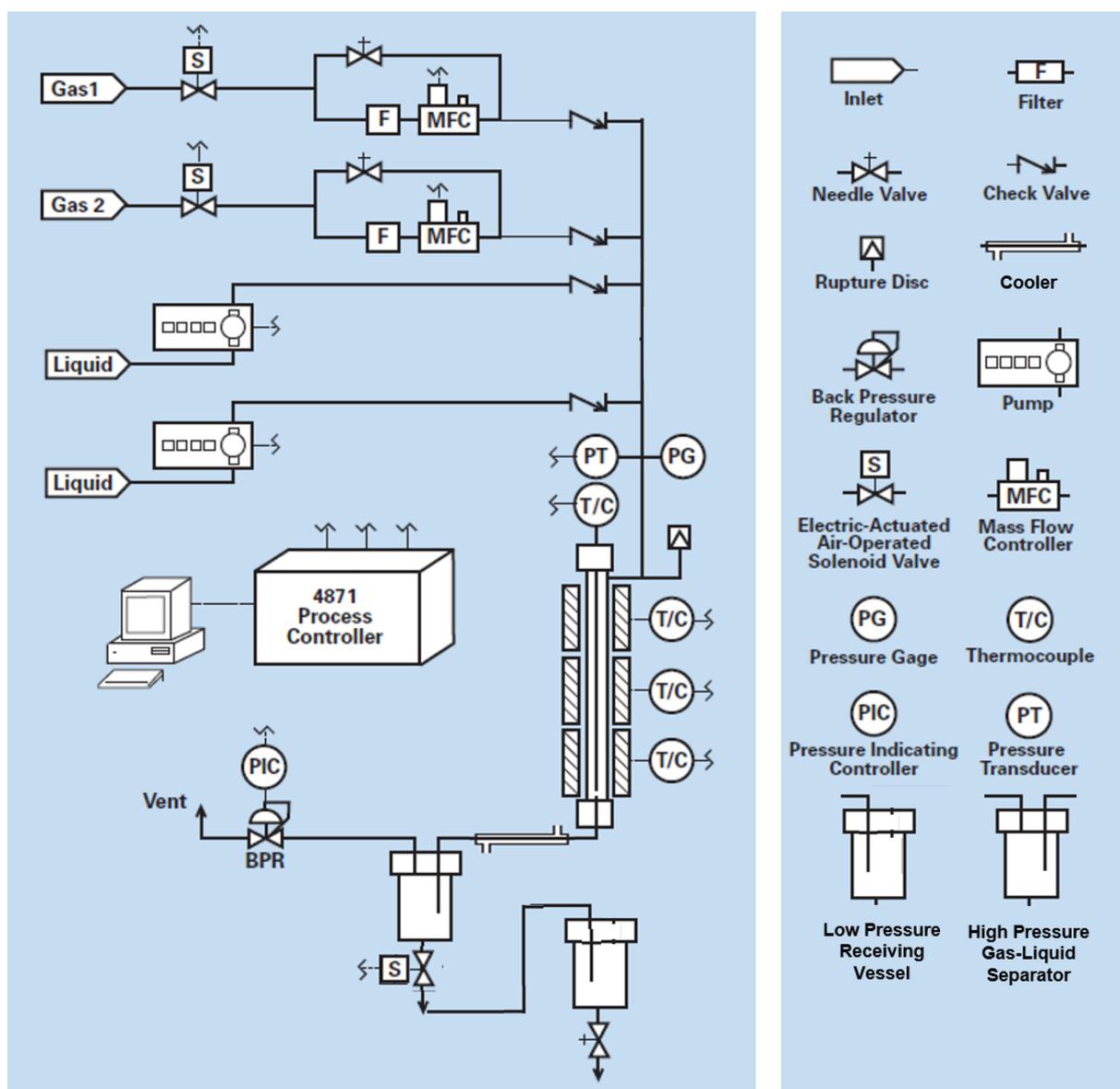


Fig. S5 Continuous plug flow reactor – schematic representation of the system.

In a typical experiment, the following protocol was used: The reactor was turned on, and oxygen gas (typical 50 mL min^{-1}) and demineralized water (typically 10 mL min^{-1}) were fed to the reactor at the desired flow rates. The back pressure regulator was set to the desired pressure (typical 10 bar over-pressure), and the heating and cooling were turned on (typical reactor bed temperature 60°C). Next, the reactor was allowed to stabilize to the desired temperature and pressures (typically $>2 \text{ h}$). After the reactor was stabilized, the liquid feed was switched from the HPLC pump running on demineralized water to the second HPLC pump running on the carbohydrate solution (typical a 0.1 M solution of sodium-d-galacturonate with 1 eq. excess NaOH). Again, the reactor was allowed to stabilize by discarding the first 500 mL liquid phase (at 10 mL min^{-1} this amounts to 50 min reaction time). Next, at least 5 samples of 100 mL reaction mixture were collected for HPLC-analysis (reaction time 50 min). After each experiment, the liquid phase was switched from the carbohydrate solution to demineralized water again, to flush the column (at least 1 h), before the settings were changed to perform another experiment. The catalyst bed was kept intact throughout the whole series of experiments.

3.2 Isolation and analysis of galactaric acid

In one experiment, GA (free acid) was isolated from the reaction mixture, using the following procedure: Liquid samples were combined (approximately 0.7 L of reaction mixture from the 0.5M Na-GalA reaction over Au/TiO₂), acidified to pH 2.5 by addition of sulphuric acid, and the solids in the resulting white suspension were collected by filtration over a type-3 glass filter, and washed with demi water. The solids were dried under vacuum at 40°C, in the presence of sicapent, to give 62.4 g GA as a white solid (85 mol% of theory).

Analysis:

FT-IR spectrum: identical to reference	(Fig. S6 & S7)
¹ H-NMR (400.17 MHz, D ₂ O/NaOD): δ = 4.29 (2 H, s), 3.96 ppm (2 H, s).	(Fig. S8)
¹³ C-NMR (100.62 MHz, D ₂ O/NaOD): δ = 71.29, 71.61, 179.32 ppm.	(Fig. S9)
HPLC-analysis (UV 210): identical to reference, purity >99%.	(Fig. S10)
HPLC-analysis (RI 410): identical to reference, purity 99%.	(Fig. S11)
Elemental analysis: Calc.	(Table . S1)

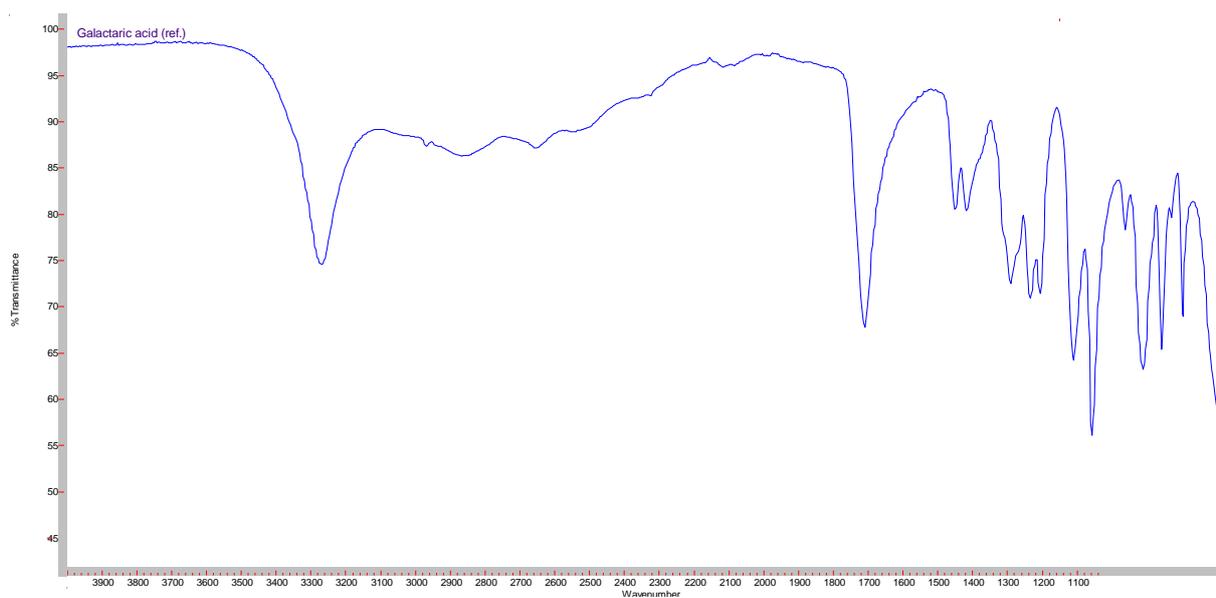


Fig. S6 FT-IR spectrum of Galactaric acid (Reference from Sigma-Aldrich)

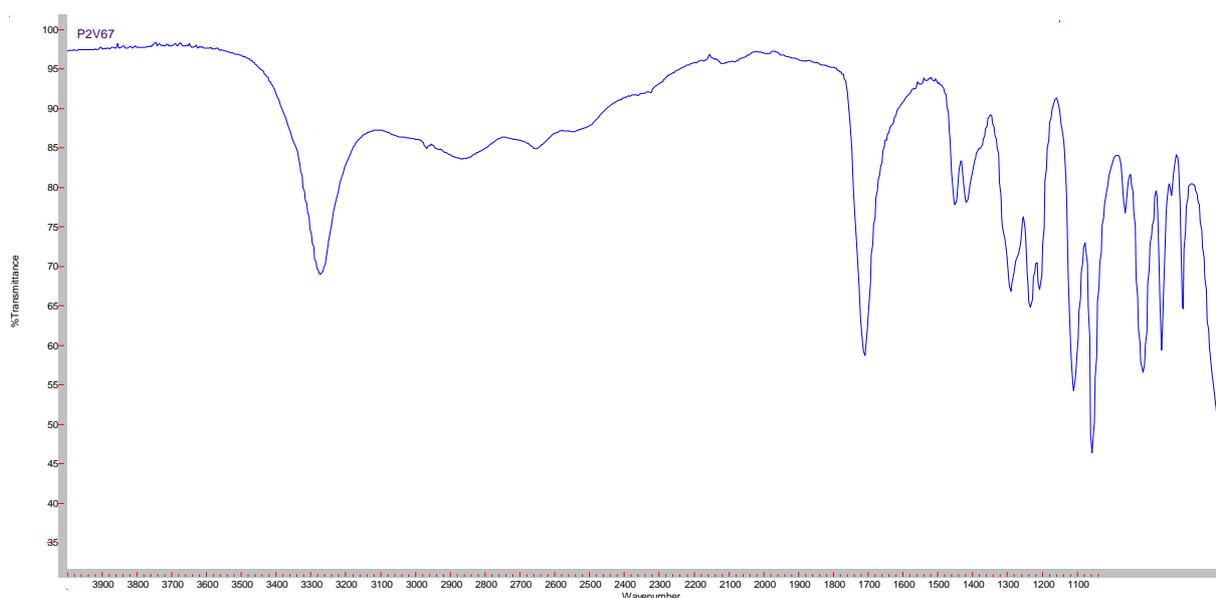


Fig. S7 FT-IR spectrum of Galactaric acid (Isolated from reaction mixture)

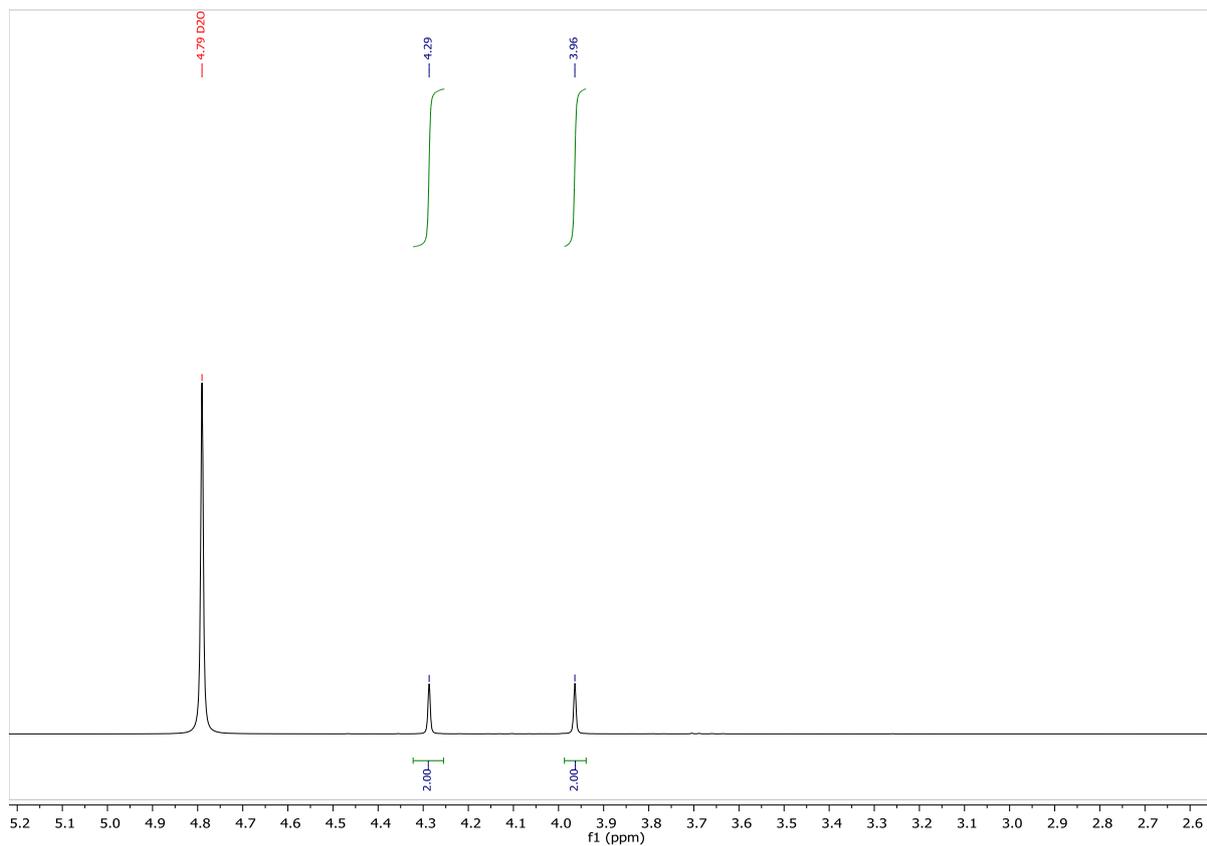


Fig. S8 $^1\text{H-NMR}$ spectrum (D_2O) Galactaric acid (Isolated from reaction mixture)

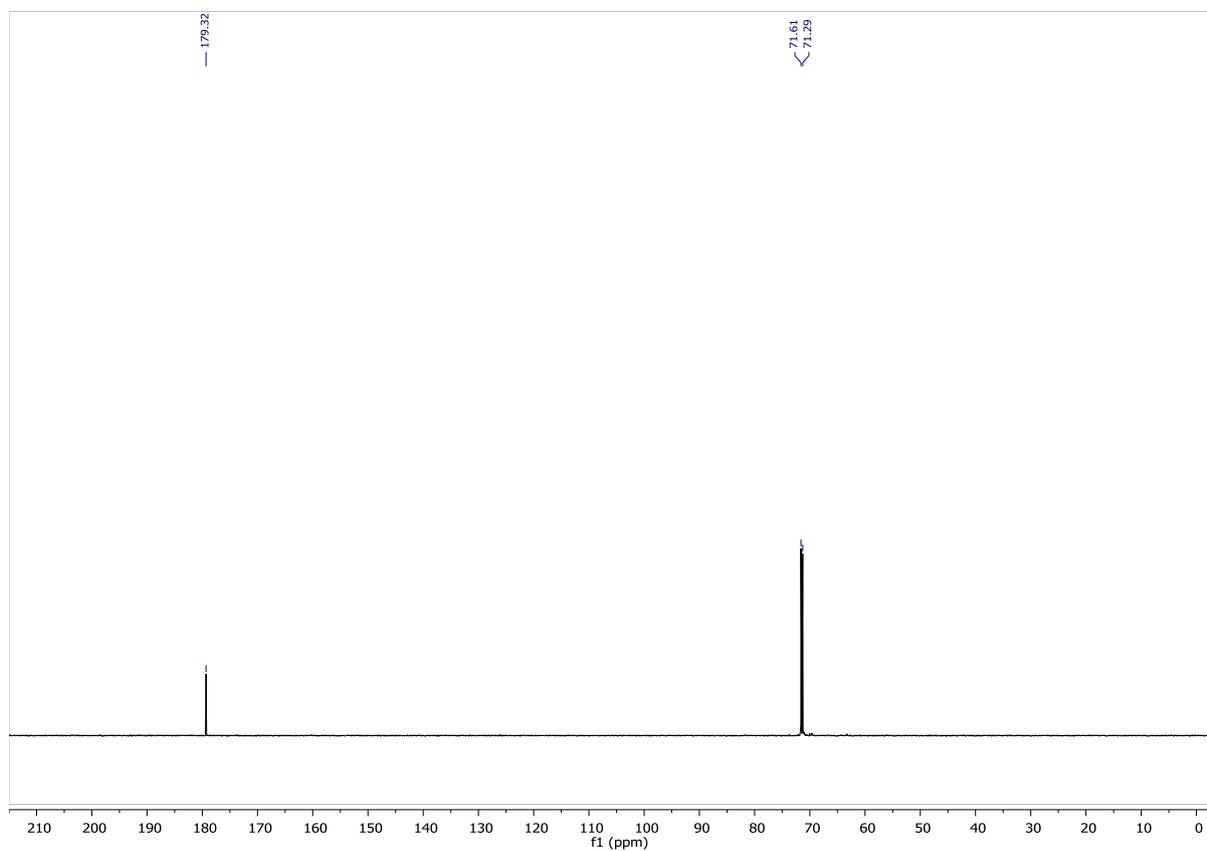
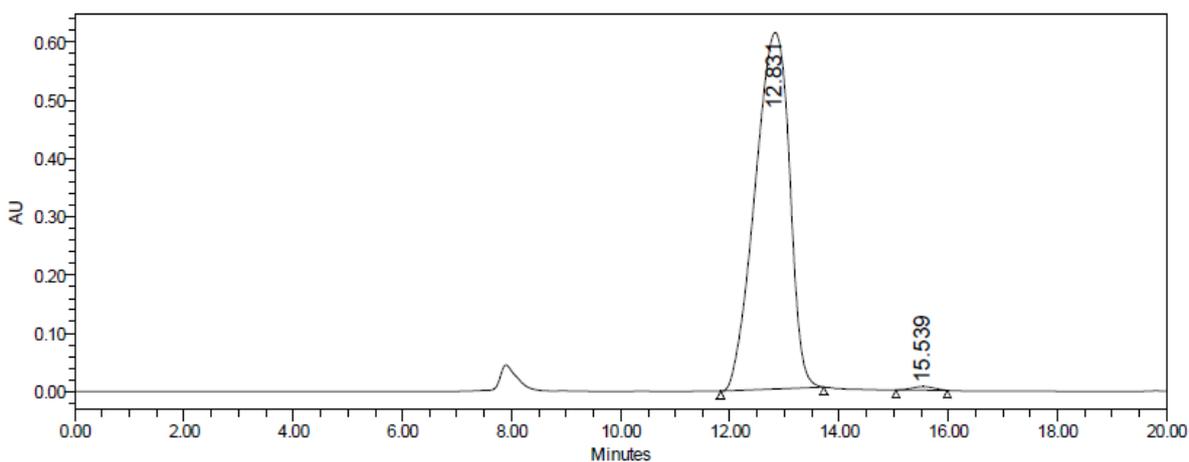


Fig. S9 $^{13}\text{C-NMR}$ spectrum (D_2O) Galactaric acid (Isolated from reaction mixture)

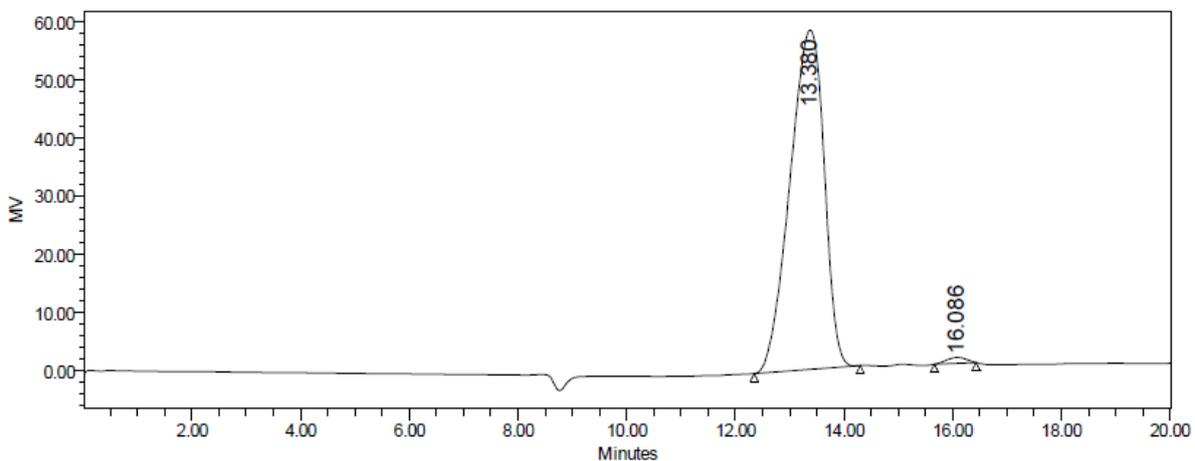
SAMPLE INFORMATION			
Sample Name:	P2V67solid_N	Acquired By:	Linda
Sample Type:	Unknown	Sample Set Name	P2V67solid_P2V69
Vial:	1	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method	P2V67
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 210nm
Date Acquired:	7/17/2017 4:46:54 PM CEST		
Date Processed:	4/24/2018 11:29:47 AM CEST		



	RT	Area	% Area	Height
1	12.83	26835122	99.37	611613
2	15.54	169000	0.63	6024

Fig. S10 HPLC-analysis (UV 210) Galactaric acid (R_t 12.83 min., Isolated from reaction mixture); R_t 7.8 min. = injection peak.

SAMPLE INFORMATION			
Sample Name:	P2V67solid_N	Acquired By:	Linda
Sample Type:	Unknown	Sample Set Name:	P2V67solid_P2V69
Vial:	1	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method:	P2V67_solidRI
Injection Volume:	10.00 ul	Channel Name:	410
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	410
Date Acquired:	7/17/2017 4:46:54 PM CEST		
Date Processed:	4/24/2018 11:36:09 AM CEST		



	RT	Area	% Area	Height
1	13.38	2555619	98.98	58384
2	16.09	26243	1.02	1027

Fig. S11 HPLC-analysis (RI 410) Galactaric acid (R_t 13.39 min., Isolated from reaction mixture); R_t 8.5 min. = injection peak.

The elemental composition the of the isolated galactaric acid was measured in duplicate, and corresponds to the calculated elemental composition (Table S1)

Table S1. Elemental Analysis Galactaric acid (Isolated from reaction mixture)

Element	Calculated (wt %)	Measurement 1 (wt %)	Measurement 2 (wt %)
C	34.29	33.32	33.30
H	4.80	4.75	4.76
N	-	0.01	0.02
Moisture	-	0.41	0.39

3.3 Contact time calculations

The internal reactor volume is 26.8 cm^3 , and the liquid flow rate (with dissolved substrate) is 10 mL min^{-1} .

The internal volume (available for liquid phase with dissolved substrate) is however lowered by the following:

1) Au/TiO₂-catalyst: 7.7 g (bulk density is 4.26 g cm^{-3})
 $\Rightarrow 7.7/4.26 = 1.8 \text{ cm}^3$

2) SiC-filler: 16.8 g (bulk density is 3.16 g cm^{-3})
 $\Rightarrow 16.8/3.16 = 5.3 \text{ cm}^3$

3) Thermocouple: diameter = 0.3 cm , length = 41.5 cm
 $\Rightarrow \pi \times 0.15^2 \times 41.5 = 2.9 \text{ cm}^3$

Total volume (available for both liquid phase & oxygen gas phase):
 $\Rightarrow 26.8 - (1.8 + 5.3 + 2.9) = 16.8 \text{ cm}^3$

Furthermore, the oxygen gas phase occupies the following space:

4) Oxygen gas flow: 50 mL min^{-1} at a pressure of 10 bar
 $\Rightarrow 50/10 = 5 \text{ cm}^3$ (input at top of reactor)

Part of the oxygen is however consumed during the oxidation reaction: Assuming 100% conversion, out of the 50 mL min^{-1} oxygen input ($2.2 \text{ mmol min}^{-1}$), $0.5 \text{ mmol min}^{-1}$ will be consumed. Minimum excess of oxygen gas phase $\Rightarrow 1.7/2.2 \times 5 = 3.9 \text{ cm}^3$

Note: This amount might be lower, given that part of the oxygen might dissolve in the liquid phase.

So, the internal volume available for the liquid phase is $16.8 - 3.9 = 12.9 \text{ cm}^3$, and with a liquid flow rate of 10 mL min^{-1} , this amounts to a contact time of around 1.3 min .

3.4 Spent catalyst analysis

The spent catalyst after the long term experiment was washed with demineralized water, and subsequently dried in an oven at 105°C. The fresh catalyst (crushed and sieved, but unwashed) was used as received without any treatment. The gold-loading was determined by elemental analysis (ICP), and compared to the gold loading of the fresh catalyst. Both samples were measured in duplicate. The results are summarized in Table S2.

Table S2. Au-loading (wt%) of spent Au/TiO₂ catalyst and fresh Au/TiO₂ catalyst.

Catalyst	Au-loading (wt%)	
	Measurement 1	Measurement 2
Au/TiO ₂ (spent)	0.99	1.01
Au/TiO ₂ (fresh)	1.13	1.14

3.5 Side product identification

In the main article, Scheme 2 provides a route to the main (so far prophetic) side product D-talaric acid. This product appears in chromatograms as a small peak directly after the desired galactaric acid (product). In an attempt to provide more proof for the formation of this product, the following additional experiments were performed:

- 1) In the proposed route (Scheme 2, main article), the formation of D-talaric acid proceeds via the isomerization of GalA to TalA, followed by subsequent oxidation. Another potential route to the same product is the isomerization of galactaric acid to D-talaric acid. This alkaline isomerization was described by Fisher in 1891, who subjected galactaric acid to boiling pyridine for prolonged time.¹⁰ Accordingly, we have subjected a neutralized suspension of diNa-galactarate (20 g) in water (100 mL) to high temperature (70 °C) for 3 days. The HPLC-analysis of the dissolved fraction (after 3 days) is shown in Fig. S12. [Note: Due to the replacement of the HPLC column, the retention times in this section slightly differ from the other sections.]

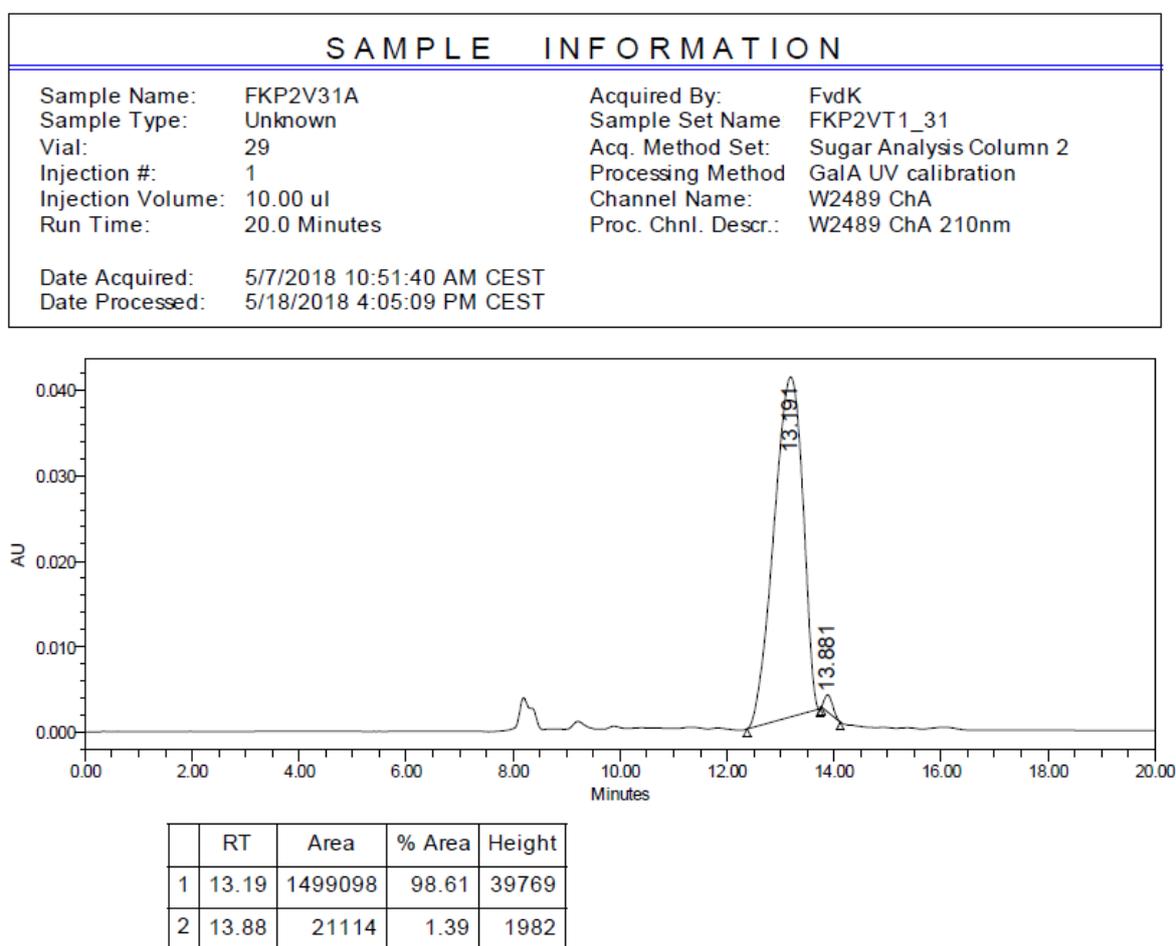
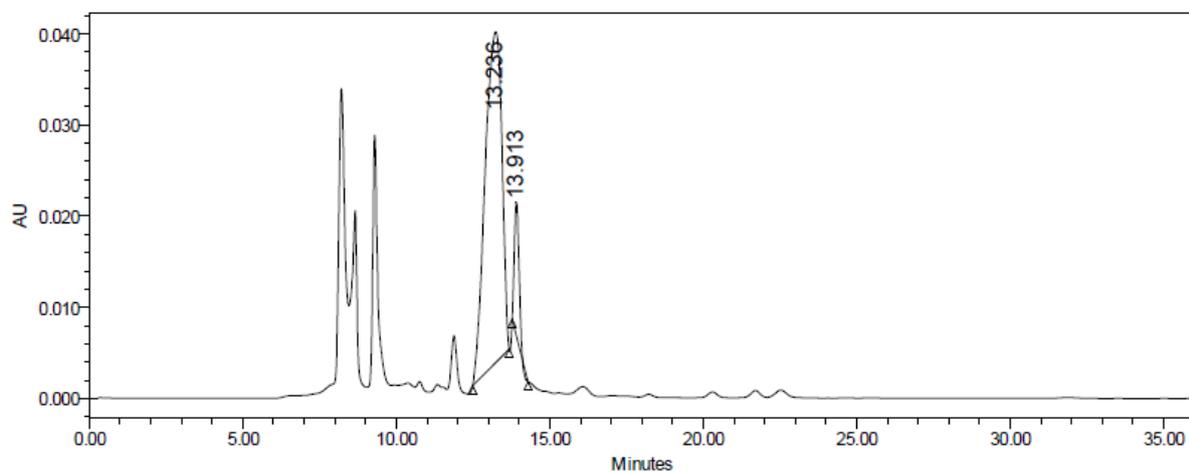


Fig. S12 HPLC-analysis (UV 210) Dissolved fraction of crude reaction mixture (suspension of diNa-GA in water, pH 7) (GA: R_t 13.19 min., side product 2 / Talaric acid: R_t 13.88 min.; R_t 8-10 min. = injection / salt peaks).

Next, by removal of the suspended solid (diNa-GA), followed by subsequent acidification of the filtrate with conc. HCl to pH 2.3 to precipitate GA (free acid), a mixture enriched in the side product was obtained.

Next, the sample was conc. on a rotary evaporator, 50 °C, and the obtained solid was re-suspended and treated with potassium carbonate (see section 3.5.2). The HPLC-analysis results are shown below (Fig. S13 – S14):

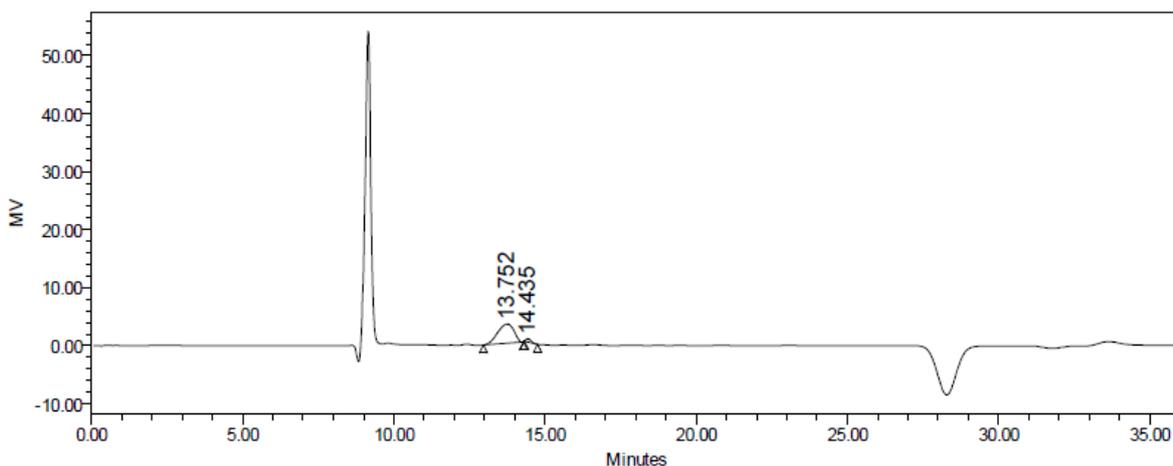
SAMPLE INFORMATION			
Sample Name:	FKP2V31C	Acquired By:	David
Sample Type:	Unknown	Sample Set Name	calibration im is 34
Vial:	25	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method	Default
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	36.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 210nm
Date Acquired:	5/17/2018 4:25:12 PM CEST		
Date Processed:	5/18/2018 1:18:01 PM CEST		



	RT	Area	% Area	Height
1	13.24	1378620	89.30	36278
2	13.91	165219	10.70	14645

Fig. S13 HPLC-analysis (UV 210) Dissolved fraction after K₂CO₃ treatment (GA: R_t 13.24 min., side product 2 / Talaric acid: R_t 13.91 min.); R_t 8-10 min. = injection / salt peaks.

SAMPLE INFORMATION			
Sample Name:	FKP2V31C	Acquired By:	David
Sample Type:	Unknown	Sample Set Name	calibration im is 34
Vial:	25	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method	Default
Injection Volume:	10.00 ul	Channel Name:	410
Run Time:	36.0 Minutes	Proc. Chnl. Descr.:	410
Date Acquired:	5/17/2018 4:25:12 PM CEST		
Date Processed:	5/18/2018 1:10:00 PM CEST		



	RT	Area	% Area	Height
1	13.75	123730	94.77	3312
2	14.44	6821	5.23	584

Fig. S14 HPLC-analysis (RI 410) Dissolved fraction after K_2CO_3 treatment (GA: R_t 13.75 min., side product 2 / Talaric acid: R_t 14.44 min.; R_t 9 min. = injection / salt peak).

- Next, D-talaric acid was prepared by the nitric acid oxidation of D-talose (300 mg scale) by following a previously reported literature procedure.¹¹ To confirm the formation of D-talose, the 1H -NMR spectrum (D_2O) was recorded, which was in agreement with the two previously reported spectra^{11, 12} (Fig, S15).

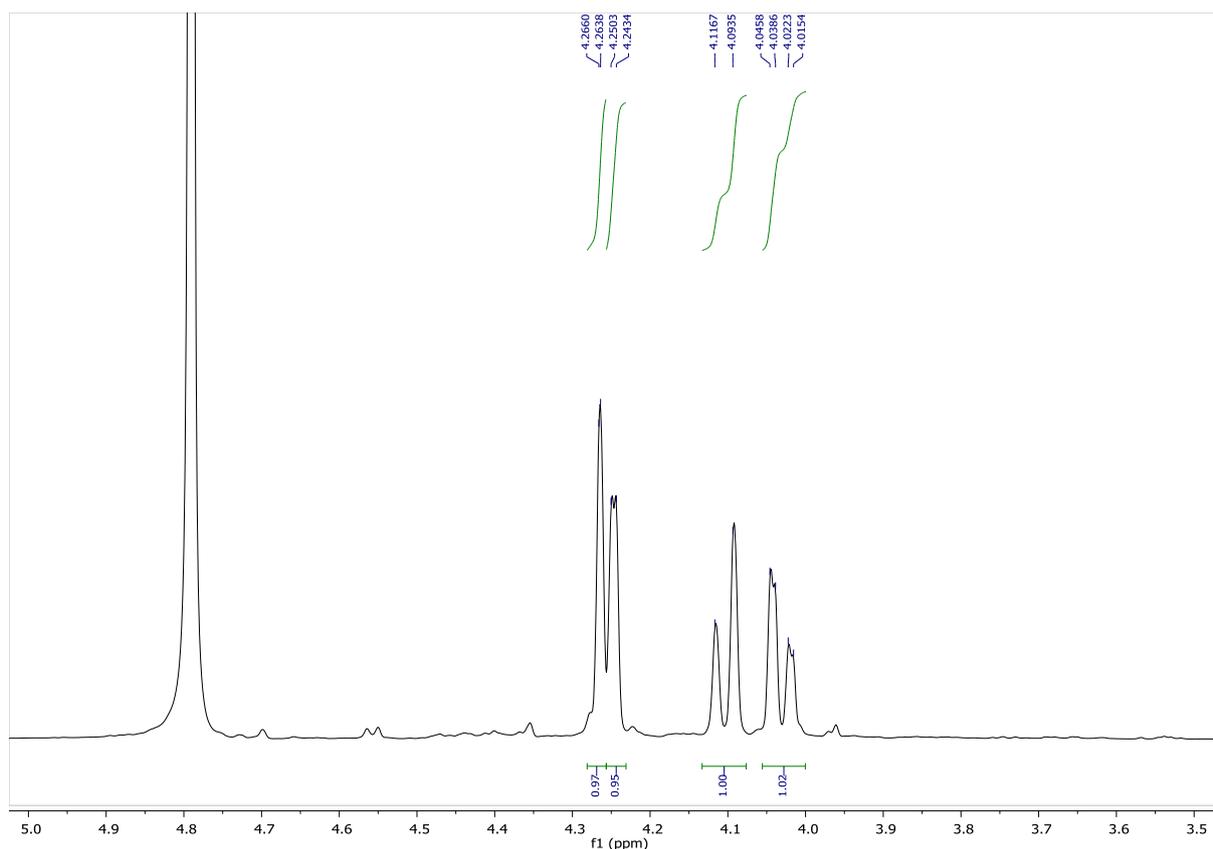
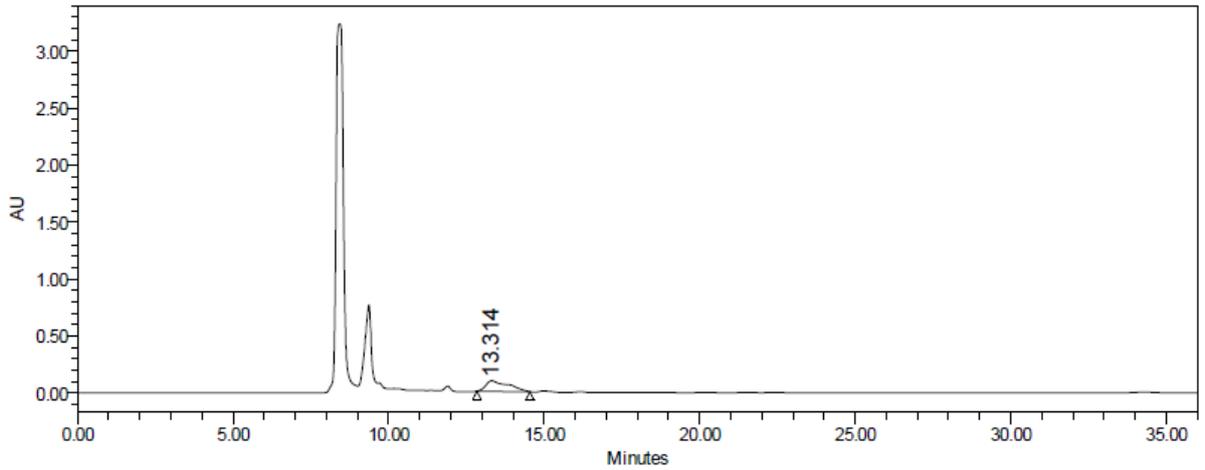


Fig. S15 ^1H -NMR spectrum of Talaric acid (crude product): ^1H -NMR (400.17 MHz, $\text{D}_2\text{O}/\text{NaOD}$): $\delta = 4.28 - 4.25$ (1 H, m), 4.25 (1 H, d, $J = 2.8$ Hz), 4.11 (1H, d, $J = 9.3$ Hz), 4.03 ppm (1H, dd, $J = 9.3, 2.8$ Hz).

Next, the product was analyzed by HPLC (Fig. S16-17), and compared to the reaction mixture in the previous section ESI 3.5.1, (Fig. S13-14). Unfortunately, the product suffers from severe additional peaks in the HPLC-analysis (both UV and RI). This is probably due to the presence of (highly UV active) nitrate salts. The retention time of the prepared D-talaric acid (potassium salt), is however in the same range as the observed additional peak of the side product from GalA oxidation (sodium salt).

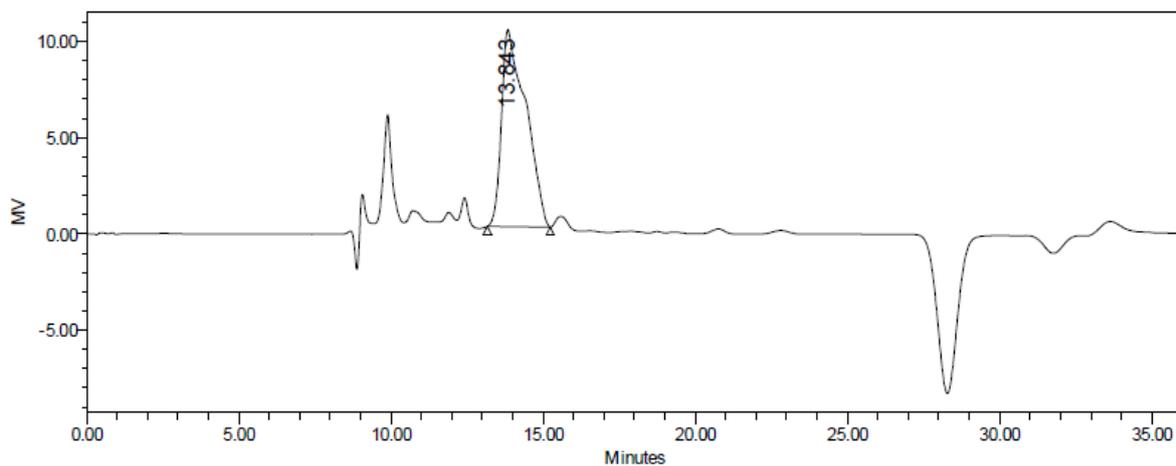
SAMPLE INFORMATION			
Sample Name:	FKP2VT1A	Acquired By:	David
Sample Type:	Unknown	Sample Set Name	calibration im is 34
Vial:	26	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method	Default
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	36.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 210nm
Date Acquired:	5/17/2018 5:39:06 PM CEST		
Date Processed:	5/18/2018 1:17:12 PM CEST		



	RT	Area	% Area	Height
1	13.31	4723137	100.00	93377

Fig. S16 HPLC-analysis (UV 210) Talaric acid after K_2CO_3 treatment (Talaric acid: R_t 13.31 min.; R_t 8-10 min. = injection / salt peaks.)

SAMPLE INFORMATION			
Sample Name:	FKP2VT1A	Acquired By:	David
Sample Type:	Unknown	Sample Set Name	calibration im is 34
Vial:	26	Acq. Method Set:	Sugar Analysis Column 2
Injection #:	1	Processing Method	Default
Injection Volume:	10.00 ul	Channel Name:	410
Run Time:	36.0 Minutes	Proc. Chnl. Descr.:	410
Date Acquired:	5/17/2018 5:39:06 PM CEST		
Date Processed:	5/18/2018 1:09:30 PM CEST		



	RT	Area	% Area	Height
1	13.84	566910	100.00	10228

Fig. S17 HPLC-analysis (RI 410) Talaric acid after K_2CO_3 treatment (Talaric acid: R_t 13.84 min.; R_t 8-10 min. = injection / salt peaks.)

So, although we have to admit that we cannot give a 100% proof for the formation of talaric acid under our conditions, we think that based on the reported literature (GalA isomerization to TalA,¹² and isomerization of galactaric acid to talaric acid)¹⁰, and our additional experiments, this is the most likely candidate for side product 2.

4 Analytical equipment

4.1 HPLC-analysis

HPLC-analyses were performed on a Waters e2695 HPLC instrument, equipped with a Concise Corogel Ion 300 (30 cm length) column, maintained at 65 °C, using H₂SO₄ (3 mM) in MilliQ water as the eluent, with a flow rate of 0.4 mL min⁻¹. The components were identified using a Waters 2489 UV/Vis Detector (210 nm) and a Waters 2414 RI detector. Observed products were compared to the retention times (both RI and UV) of the pure standards (Table S3).

Table S3. HPLC retention times (UV and RI) for commercial / reference compounds.

Compound	R _t UV (min)	R _t RI (min)
D-Galacturonic acid	13.86	14.40
Galactaric acid	12.77	13.31
5-keto-L-galactonic acid	14.36	14.90

Measurements were performed using an InoLab® Oxl 7310 “dissolved oxygen sensor”, which was calibrated to air. Due to limitations of the oxygen sensor, the highest temperature at which dissolved oxygen could be measured was 50°C, and the highest stirring speed allowing stable measurements was 500 rpm. The temperature dependent oxygen solubility of the carbohydrate solutions was determined by slowly heating and subsequent cooling (~2°C min⁻¹) of stirred and oxygenated (300 mL O₂ min⁻¹) solutions (300 mL), while temperature, time, and dissolved oxygen were recorded. Online measurements during catalytic oxidation were performed by simply placing the probe inside the reaction mixture.

4.3 FT-IR

Fourier transform infrared (FT-IR) spectra were obtained on a Varian Scimitar 1000 FT-IR spectrometer equipped with a Pike MIRacle ATR Diamond/ZnSe single reflection plate and a DTSG-detector. The measurement resolution was set at 4 cm⁻¹, and the spectra were collected in the range 4000-650 cm⁻¹ with 64 co-added scans.

4.4 NMR

NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.17 MHz (¹H) and 100.62 MHz (¹³C). Proton NMR chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak. Carbon NMR was fully decoupled by broad band decoupling.

4.5 Elemental analysis

Elemental analysis (CHN) and catalyst Au-loadings were determined by Mikroanalytisches Laboratorium Kolbe (Mikrolab Kolbe), Osterfelder Str. 3, 46047 Oberhausen, Germany.

5 References

1. Z. Li, D. Wu, Y. Liang, F. Xu and R. Fu, *Nanoscale*, 2013, **5**, 10824-10828.
2. R. K. Pazhavelikkakath Purushothaman, F. van der Klis, A. E. Frissen, J. van Haveren, A. Mayoral, A. van der Bent and D. S. van Es, *Green Chem.*, 2018, DOI: 10.1039/c1038gc00103k.
3. F. van der Klis, J. van Haveren, D. S. van Es and J. H. Bitter, *ChemSusChem*, 2017, **10**, 1460-1468.
4. O. Deutschmann, *Modeling and Simulation of Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
5. J. A. Raffensberger, B. J. Glasser and J. G. Khinast, *AIChE J.*, 2005, **51**, 1482-1496.
6. X. Zhang and G. Ahmadi, *Chem. Eng. Sci.*, 2005, **60**, 5089-5104.
7. U. Prüße, S. Heidinger and C. Baatz, *Landbauforschung - vTI Agriculture and Forestry Research*, 2011, **3**, 261-272.
8. U. Prüße, K. Heidkamp, N. Decker, M. Herrmann and K. D. Vorlop, *Chem. Ing. Tech.*, 2010, **82**, 1231-1237.
9. U. Prüße, M. Herrmann, C. Baatz and N. Decker, *Appl. Catal., A*, 2011, **406**, 89-93.
10. E. Fischer, *Ber. Dtsch. Chem. Ges.*, 1891, **24**, 3622-3629.
11. M. Takenaka, X. Yan, H. Ono, M. Yoshida, T. Nagata and T. Nakanishi, *J. Agric. Food Chem.*, 2003, **51**, 793-796.
12. W. S. Yew, A. A. Fedorov, E. V. Fedorov, J. F. Rakus, R. W. Pierce, S. C. Almo and J. A. Gerlt, *Biochemistry*, 2006, **45**, 14582-14597.