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Solvent-free γ -valerolactone hydrogenation to 2-methyltetrahydrofuran catalysed by Ru/C: a reaction network analysis

Mohammad G. Al-Shaal, Adam Dzierbinski and Regina Palkovits*

2-Methyltetrahydrofuran (2-MTHF) is considered to be an attractive biomass based platform chemical with high potential as a biofuel compound and as a green solvent. 2-MTHF can be synthesised from biobased levulinic acid (LA) and γ -valerolactone (GVL). Herein the optimum reaction conditions for the hydrogenation of GVL over Ru/C have been studied. A full conversion of GVL has been obtained under solvent free conditions with a maximum yield of 2-MTHF of 43%. The optimized conditions have been employed in a mechanistic study of the synthesis of 2-MTHF. Several side reactions have been investigated to explore the full reaction network of this heterogeneously catalysed system and to elucidate the factors influencing product selectivity. Additionally an efficient solvent-free hydrogenation reaction of LA into 2-MTHF could be achieved delivering 90% conversion of LA with a yield of 2-MTHF of 61% by removing water from the system in a two-step approach.

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Introduction

While the global consumption of fossil fuels is dramatically increasing, the rapid depletion of fossil resources, coupled with the associated problem of global warming, is causing increasing concern with regard to the stability of the global economy and environment.¹ For these reasons, many research groups have focused on alternative carbon sources.² Lignocellulosic biomass, derived from wood, grass, and agricultural waste, represents one of the most viable replacements of fossil fuels.³⁻⁷ Virtually, using biomass feedstocks in biofuel production offers many advantages in comparison to fossil fuel. For example, biomass feedstocks could enable more sustainable production processes and facilitate product flexibility.8-10 Moreover lignocellulosic biomass could reduce CO₂ emissions since natural renewable resources provide a closed carbon cycle.^{11,12} In spite of the present broad research on biomass utilisation, new processes must be developed to enable its efficient conversion to fuels and chemicals.

Heterogeneous catalysis may provide an efficient methodology for biomass conversion allowing for high reaction rates and high selectivity of the target products. For this reason, the catalytic conversion of biomass to promising biomass-based chemicals over solid catalysts has received much attention in recent years.^{8,13–18} Particular attention has been paid to the production of 2-methyltetrahydrofuran (2-MTHF), a compound that can be derived based on lignocellulose. 2-MTHF may find use as an alternative solvent for many reactions^{19,20} or as a fuel component.^{21–23} The attractiveness of 2-MTHF as a green solvent and fuel is partially attributed to the wide number of feedstocks it can be derived from. Substantially, 2-MTHF can be obtained *via* the acid catalysed dehydration of cellulose, complex carbohydrates and simple C₅ and C₆ sugars to levulinic acid (LA) and furfural.^{24–27} These intermediates can undergo subsequent catalytic reduction steps to produce 2-MTHF as the desired target product (Scheme 1).^{28–30}

LA represents a platform chemical for many compounds and several studies have reported the conversion of LA to 2-MTHF. For example, Elliott et al. reported on the transformation of LA into 2-MTHF via the reaction intermediates γ -valerolactone (GVL) and 1,4-pentanediol (1,4-PDO). They tested several supported noble metals under different reaction conditions utilizing water and 1,4-dioxane as solvents.³¹ In an attempt to produce novel biofuel compounds, several studies have demonstrated that tuning the acidity and the active metal of the catalyst alternates the product distribution in the hydrogenation of LA or GVL.9,32,33 For example, Lange et al. suggested an acid-catalysed ring-opening of GVL to pentenoic acid followed by a subsequent hydrogenation to pentanoic acid and stated that a careful adjustment of the acid/metal ratio is essential to control the formation of pentenoic acid versus 2-MTHF.9,10 Further studies have focused on the conversion of LA and GVL into 2-MTHF in the presence of



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Chair for Heterogeneous Catalysis and Chemical Technology, Institut für Technische und Makromolekulare Chemie, RWTH, Aachen University, Worringerweg 1, D-52074 Aachen, Germany. E-mail: palkovits@itmc.rwth-aachen.de



Scheme 1 Example of 2-MTHF synthesis from lignocellulosic biomass.

homogeneous ruthenium catalysts.^{23,34} Recently, Fan et al. reported a yield of 2-MTHF as high as 91% based on GVL as a substrate dissolved in ethanol and Cu/ZrO2 as a catalyst.35 However, although several studies have addressed the hydrogenation of GVL to 2-MTHF in recent years, little attention has been paid to analysing the involved reaction pathways. The present paper summarizes the influence of reaction conditions on the conversion of GVL into 2-MTHF and reveals a mechanistic study of a heterogeneously catalysed hydrogenation reaction of GVL into 2-MTHF under solvent-free conditions. Ru/C was selected as the catalyst of choice since it has been successfully employed in previous studies focusing on the hydrogenation of LA to GVL.³⁶ Aiming at a comprehensive analysis of GVL hydrogenation the reaction network has been explored elucidating the origin of other products such as 1- and 2-pentanol, 2-butanol, pentane, butene and butane, respectively. Additionally, the stability of several reaction intermediates under the applied conditions has been studied and the results were used to develop a one-pot two step reaction protocol for the direct hydrogenation of LA into 2-MTHF catalysed by Ru/C.

Results and discussion

Conversion of GVL into 2-MTHF

The production of 2-MTHF based on GVL as a substrate was investigated by several groups.^{34,35,37} However, only a few studies have focused on ruthenium catalysts in the hydrogenation of GVL.^{23,34} Horváth *et al.* obtained a conversion of 72% to 2-MTHF under 75 bar of hydrogen pressure (200 °C, 20 h) in the presence of a molecular ruthenium/phosphine system as a catalyst.³⁴ The highest yield of 2-MTHF has been reported by Leitner *et al.* with a molecular ruthenium catalyst and a triphos ligand.²³ LA-derived GVL served as a substrate and 92% yield of 2-MTHF could be reached applying 100 bar of H₂

(200 °C, 18 h). While molecular ruthenium catalysts allowed an efficient transformation of GVL into 2-MTHF, the opposite case was observed for supported ruthenium nanoparticles. Fan *et al.* reported that utilisation of 5% Ru/C enabled about 2% conversion of GVL with undetectable amounts of the target product applying 60 bar of H₂ pressure at 200 °C and 6 h with ethanol as a solvent.³⁵

These findings together with our previous results on the hydrogenation of LA to GVL motivated us to investigate the heterogeneously catalysed hydrogenation reaction of GVL to 2-MTHF over Ru/C in more detail. For this reason, different factors such as the reaction temperature, H_2 pressure and reaction time were tested applying Ru/C as a catalyst. The system was studied in the absence of a solvent. The obtained results confirm the efficient production of 2-MTHF based on GVL over Ru/C in a solvent-free reaction system.

In a first set of experiments the influence of the reaction temperature was investigated (Table 1, entries 1-3). Evidently an increase of the reaction temperature leads to higher catalytic activity. While no conversion was observed at 130 °C (Table 1, entry 1), increasing the temperature to 190 °C resulted in a moderate yield of 2-MTHF. However the hydrogenation of GVL to 2-MTHF was coupled with the formation of 2-butanol, 1,4-PDO and traces of 2-pentanol (Table 1, entries 2 and 3). Varying the H_2 pressure in a second set of experiments showed a relation between GVL conversion and the applied H₂ pressure (Table 1, entries 3-8). Obviously high hydrogen pressures are necessary to enable an efficient transformation of GVL. This effect could be related to an increasing concentration of H₂ dissolved in the liquid with enhanced H₂ pressure.38 However, future studies will focus on a full kinetic investigation of the reaction network to gain deeper insights. The highest conversion of GVL was observed after 4 h under 120 bar of H₂ at 190 °C where comparable amounts of 2-MTHF, 1,4-PDO and 2-pentanol were present in the reaction mixture (Table 1, entry 8). However due to pressure limitations of the used autoclave systems a maximum pressure of 100 bar was selected for subsequent experiments. Noteworthy, up to a H₂ pressure of 80 bar, only a minor increase in GVL conversion and 2-MTHF formation could be observed, delivering a maximum of 16% GVL conversion and 9% 2-MTHF yield.

Considering these points, a third set of experiments was dedicated to the influence of reaction time on product formation (Table 1, entries 9–12 and 3). As expected a prolonged reaction time resulted in increasing conversion of GVL as well as enhanced 2-MTHF formation. Almost full conversion of GVL was obtained after 24 h, providing a mixture of 2-MTHF, 2-butanol and small amounts of 2-pentanol (Table 1, entry 12). Interestingly the selectivity of 2-MTHF remained almost constant for the first 8 h of the reaction with around 54% but decreased subsequently to 43% after 24 h of reaction.

The poor concentration of the reaction intermediate 1,4-PDO can be attributed to its rapid transformation into 2-MTHF.^{37,39} These findings support the fact that the formation of 1,4-PDO is the rate determining step in the hydrogenation reaction of GVL. Further investigations of the reaction

 Table 1
 GVL hydrogenation using Ru/C as a catalyst^a

Entry	T [°C]	$p{\rm H_2}^{b}$ [bar]	<i>t</i> [h]	GVL conversion [%]	2-MTHF yield [%]	2-Butanol yield [%]	1,4-PDO yield [%]	2-Pentanol yield [%]
1	130	100	4	<1	_	<1	1	<1
2	160	100	4	7	3	1	4	<1
3	190	100	4	22	12	4	5	<1
4	190	30	4	5	5	3	_	<1
5	190	40	4	8	6	3	_	<1
6	190	60	4	16	8	3	_	<1
7	190	80	4	14	9	3	1	<1
8	190	120	4	91	31	28	_	23
9	190	100	6	31	17	6	5	<1
10	190	100	8	41	22	8	6	<1
11	190	100	16	80	33	30	1	4
12	190	100	24	>99	43	36		7

^a Conditions: GVL (3 g, 29.9 mmol); Ru (5%)/support (150 mg, 0.07 mmol of Ru); solvent free. ^b Pressure at room temperature.

system and the involved reaction pathways are discussed in the following sections.

Elucidation of the main reaction pathways

With the goal of producing 2-MTHF from GVL, different studies have documented a wide variety of possible by-products including methane, butane, isobutene, 2-butanol, pentane, isopentane, 1-pentanol and 2-pentanol.^{23,29,31,34}

Initially the hydrogenation of GVL over Ru/C leads to the formation of 1,4-PDO as an intermediate which undergoes an etherification reaction to 2-MTHF. Several by-products are formed in the course of the reaction such as 1-pentanol, 2-pentanol, and 2-butanol. Additionally gas phase analysis reveals the production of further by-products including methane and butane. While the formation of 2-pentanol can be attributed to a catalytic dehydration and hydrogenation of the intermediate 1,4-PDO, the origin of 2-butanol, butane and methane requires further investigations.

Two distinct pathways may demonstrate the source of 2-butanol in the product mixture (Scheme 2). The first pathway suggests a hydration reaction of GVL to γ -hydroxyvaleric acid (GHVA) in the presence of water occurring as a by-product of 2-MTHF production. Similar to the decarboxylation reaction of fatty acids on activated carbon,⁴⁰ GHVA undergoes decarboxylation to 2-butanol. In the second pathway GVL is hydrogenated to 1,4-PDO which is in an equilibrium with 4-hydroxypentanal. A catalysed decarbonylation reaction of



Scheme 2 Proposed reaction pathways for the formation of 2-butanol. Pathway 1 includes a hydration of GVL and decarboxylation of GHVA to CO_2 and 2-butanol. Pathway 2 includes a consequent hydrogenation reaction of GVL followed by decarbonylation to CO and 2-butanol.

4-hydroxypentanal leads to the formation of 2-butanol. In order to identify the main pathway leading to the formation of 2-butanol GVL was treated for 24 hours at 190 °C under 100 bar of N₂ using an equivalent amount of water and 5% Ru/C. Analysis of the gaseous phase and the product mixture shows no conversion of GVL to GHVA or 2-butanol confirming that under the applied conditions the Ru/C catalyst is not able to facilitate the hydration reaction of GVL according to pathway 1. This finding suggests that 2-butanol is not resulting from the first reaction pathway. To confirm the second pathway as a source of 2-butanol, 1,4-PDO was used as a substrate applying 100 bar of H₂ at 190 °C. Besides the expected hydration/hydrogenation products of 1,4-PDO such as 2-pentanol and 2-MTHF, 2-butanol was formed with a yield of 11% after 4 h and 40% after 24 h, respectively. These findings emphasise that 2-butanol is predominantly formed via hydrogenation/decarbonylation reactions of GVL according to pathway 2 (Scheme 2).

Although the results indicate that 2-butanol originates from GVL and 1,4-PDO *via* a decarbonylation reaction a further analysis of the gaseous phase showed the presence of methane instead of CO. We suggest that the observed methane can be attributed to a direct methanation of CO over Ru/C.⁴¹ Another possibility is the heterogeneously catalysed hydrogenation of carbon monoxide to methanol and a dehydration reaction of methanol to methane. While methanol synthesis using a wide variety of noble metal catalysts was studied extensively,^{42–44} we have focused on the catalytic dehydration of methanol. Thus we conducted an experiment starting from methanol and heated it up under a H₂ atmosphere (190 °C and 100 H₂ bar) over 5% Ru/C. After 4 h, methanol was fully converted into a gaseous phase and GC analysis confirmed the presence of methane with 100% yield.

To identify the source of butane in GVL hydrogenation two pathways have been considered. The first route includes a decarboxylation reaction of GVL into 1-butene and CO₂. This pathway was discussed previously by Dumesic *et al.* utilising amorphous and acidic Al_2O_3/SiO_2 catalyst.⁴⁵ The acidic catalyst assists the protonation and subsequent proton transfer steps which results in decarboxylation to 1-butene and CO₂. In the



Scheme 3 Proposed mechanisms for the synthesis of butane. Pathway 1 includes a ring opening and direct decarboxylation of GVL to CO_2 and 1-butene followed by hydrogenation of 1-butene to butane. Pathway 2 includes a dehydration of 2-butanol and hydrogenation of 1-butene to butane.

second pathway of butane synthesis 1-butene can also be produced by a dehydration of 2-butanol. For both pathways, butane is the final product produced by a simultaneous hydrogenation of the obtained 1-butene. To identify the chemical route leading to the formation of 1-butene and butane in our reaction system, GVL was heated to 190 °C under 100 bar of N₂ for 24 h over 5% Ru/C as a catalyst and in the absence of water. Analysing the reaction mixture and the gaseous phase indicated no conversion of GVL into butane and CO2. This result suggests that the acidity of Ru/C is not sufficient to enable a direct decarboxylation reaction of GVL, and thus the first pathway is not likely to occur under the applied reaction conditions. Further reference experiments showed that heating of 2-butanol to 190 °C (100 bar of H2, 5% Ru/C, 4 h) results in full conversion to butane. This finding supports the hypothesis of a dehydration and hydrogenation sequence of 2-butanol according to the second reaction pathway (Scheme 3).

Stability of 2-MTHF

In addition to the determination of the origin of main by-products, we have focused on the stability of the target product 2-MTHF since its stability under the applied conditions could be a major challenge considering the maximum product selectivity. Therefore 2-MTHF was used as a substrate and heated to 190 °C under a H₂ pressure of 100 bar for 24 h applying Ru/C as a catalyst. Interestingly 2-MTHF was fully converted into 2-pentanol together with traces of pentane, 1,4-PDO and 2-butanol. These findings indicate that 2-pentanol is formed by a catalytic hydrogenation of 2-MTHF,⁴⁶ as well as a hydrogenation reaction of 1,4-PDO. As discussed in the case of 2-butanol, a dehydration/hydrogenation sequence starting from 2-pentanol leads to the formation of pentane. Finally the presence of trace amounts of 1,4-PDO and 2-butanol verifies the reversibility of the dehydration and dehydrogenation of 1,4-PDO to GVL and 4-hydroxypentanal, respectively. Further investigations concerning the stability of 2-MTHF emphasise its further transformation under the applied reaction conditions. A hydrogenation of GVL (100 bar of H₂ pressure, 190 °C, 5% Ru/C) for 48 h shows only traces of 2-MTHF and 1,4-PDO while the main products are 2-pentanol, 2-butanol and methane, respectively. This test suggests that the extended contact of the Ru/C catalyst with 2-MTHF facilitates a subsequent hydrogenation of 2-MTHF to 2-pentanol. Scheme 4 summarises the overall reaction network including the



Scheme 4 Analysis of reaction network includes the synthesis of 2-MTHF from GVL and other secondary reactions over Ru/C in a batch reactor.

discussed side and reversible reactions for a solvent free direct conversion of GVL into 2-MTHF over Ru/C.

Conversion of LA into 2-MTHF

A direct conversion of LA to 2-MTHF was reported for the first time in 1947 where the formation of 2-MTHF was barely observed by heating LA under a pressure of H_2 (200 bar, 190 °C, 1 h) in the presence of $Cu_2Cr_2O_5$.³⁹ Similarly poor yields of 2-MTHF were reported by Elliott *et al.* for different heterogeneous catalysts in a batch system.³⁷ For instance employing 10% Ru/C enabled full conversion of LA into GVL and 1,4-PDO while the yield of 2-MTHF was only 12% after 6 h at 120 °C in 1,4-dioxane as a solvent.³¹

In an attempt to improve the yield towards 2-MTHF, we have focused on the direct hydrogenation of LA to 2-MTHF under solvent free conditions. The use of 5% Ru/C allowed the full conversion of LA after 24 h delivering a biphasic product mixture. However analysis of the liquid phase indicated the presence of 2-butanol and 2-pentanol with a selectivity close to 40% and 60%, respectively, while only trace amounts of 2-MTHF, GVL and 1-pentanol were formed. These results highlight the difference between the hydrogenation of GVL and the hydrogenation of LA into 2-MTHF under the same reaction conditions. It is plausible to argue that the production of 2-MTHF starting from GVL involves hydrogenation and dehydration of pure GVL while in a one-pot reaction the synthesis of 2-MTHF from LA comprises initially the production of water and GVL as an intermediate. Thus water resulting from the hydrogenation of LA may inhibit the later dehydration reaction of 1,4-PDO to 2-MTHF. To examine this hypothesis GVL was hydrogenated in the presence of an equivalent amount of water. Similarly to the one-pot hydrogenation of LA, 2-butanol, 2-pentanol and methane were the only products of this reaction with yields of 38%, 37% and 25% respectively. Therefore the presence of water in the reaction mixture seems indeed to inhibit 2-MTHF formation. While GVL is hydrogenated to 1,4-PDO, the presence of water prohibits the acid-catalysed dehydration of 1,4-PDO into 2-MTHF. Instead, 1,4-PDO undergoes a



Scheme 5 Catalytic hydrogenation of LA in a one pot-reaction for 24 h.

subsequent transformation into the more stable 2-butanol and 2-pentanol (Scheme 5).

Indeed removing water from the previous reaction mixture shifts the reaction towards the desired 1,4-PDO etherification reaction. For example, a high conversion of LA towards 2-MTHF was reported by Elliott et al. using a continuous process applying different supported catalysts.³¹ In fact the use of a continuous system provides a simultaneous removal of released water from the catalyst enabling a higher selectivity towards 2-MTHF. Inspired by this successful example of 2-MTHF production, we have focused on the removal of water in our batch system. Therefore a two-step hydrogenation reaction was conducted to enable an effective transformation of LA into 2-MTHF. In the first hydrogenation step, LA was totally converted to GVL under 12 bar of H₂ pressure (190 °C, 45 min).³⁶ At the end of this step the formed water was evaporated from the reaction mixture, and the catalyst was collected, washed, and dried. The second hydrogenation step was conducted using the dried catalyst and the produced GVL applying 100 bar of H_2 pressure (190 °C). Under these conditions neat GVL transforms via a hydrogenation reaction into 1,4-PDO which undergoes a subsequent etherification to 2-MTHF. After four hours of reaction we have been able to obtain 90% conversion of GVL and 61% yield of 2-MTHF confirming the possibility of a direct transformation of LA into 2-MTHF over Ru/C in a batch system.

Conclusions

We were able to demonstrate the conversion of γ -valerolactone (GVL) into 2-methyltetrahydrofuran (2-MTHF) over Ru/C in a batch reactor. The reaction conditions were optimised and full conversion of GVL with a maximum yield of 2-MTHF of 43% was obtained at 190 °C (100 bar, 24 h). Several side reactions were identified resulting in by-products such as 2-butanol, butane, 1,4-PDO, 2-pentanol, 1-pentanol, pentane and methane. Investigating the origin of the main reaction products, we have been able to introduce a comprehensive overview of the reaction network. The stability of the target product 2-MTHF was examined under the mentioned reaction conditions emphasising that 2-MTHF undergoes a hydrogenation reaction to 2-pentanol for reaction times longer than 24 h.

The study also focused on the conversion of levulinic acid (LA) into 2-MTHF in a solvent free one-pot reaction. We could demonstrate that the addition and the formation of water in

the system inhibits the dehydration step and shifts the main reaction toward the formation of 2-pentanol instead of the desired production of 2-MTHF. In line with this, a two-step reaction including an intermediate removal of water enables a full conversion of LA together with 61% yield of 2-MTHF.

Experimental procedures

Chemicals

2-Butanol (99.5%), GVL (99%), 1-hexanol (99.5%), LA (\geq 98%), 2-MTHF (99.5%), 1,4-PDO (99%), 1-pentanol (\geq 99%), 2-pentanol (\geq 98%) and ruthenium on carbon (5 wt%) were purchased from Sigma-Aldrich. Methanol (99.8%) and ethanol (99.9%) were purchased from Chemsolute. All chemicals were used without further purification or drying.

General procedure

Each experiment was conducted in a Schlesinger B18rb250-01 autoclave reactor with a volume of 50 mL being charged with the substrate and Ru/C. The agitation of these compounds was provided by a magnetic bar. Prior to the reaction the autoclaves were flushed four times with hydrogen before applying 100 bar of hydrogen pressure and heating to 190 °C.

After termination of the respective reaction periods, the autoclave was cooled down and a sample of the gaseous phase for gas chromatographic (GC) analysis was collected. The depressurisation was followed by the collection and filtration of the liquid phase. Analogously the liquid samples were analysed by GC and HPLC.

Time dependent screenings

In the time dependent screening experiments, GVL (3 g, 30.0 mmol) and Ru/C (150 mg, 0.07 mmol of Ru) were charged into an autoclave, 100 bar of hydrogen pressure were applied and the mixture was heated to 190 °C varying the reaction time (4, 6, 8, 16, 24, and 48 h).

Mechanistic study

The mechanistic study focused on the investigation of further substrates under the previously optimised reaction conditions. Experiments involving GVL (3 g, 30.0 mmol), 1,4-PDO (3.12 g, 30.0 mmol) and methanol (0.96 g, 30.0 mmol) were conducted for 4 hours, while experiments using LA (3.47 g, 30.0 mmol), 2-pentanol (2.64 g, 30.0 mmol), 2-MTHF (1.0 g, 11.6 mmol) and 2-butanol (2.22 g, 30.0 mmol) lasted for 24 hours. All reactions were performed at 190 °C under 100 bar of hydrogen pressure.

Sample analysis

Gaseous reaction products were analysed by GC using an Agilent HP6890 chromatograph and a Restek Shincarbon ST column with dimensions of 2 m \times 1 mm and a thermal conductivity detector (TCD). The carrier gas was helium with a constant flow rate of 15 mL min⁻¹ and an inlet temperature of 100 °C. The following temperature program was used in the

analysis of a gas volume of 100 $\mu L:$ 35 °C (5 min)–8 °C min $^{-1}$ – 200 °C (5 min).

The aqueous phases for one-pot LA hydrogenation reactions were analysed with a Shimadzu lc 2020 liquid chromatograph using three Organic-Acid/CS columns with dimensions of 300 mm × 8 mm, 100 × 8 mm and 40 mm × 8 mm and a refractive index detector (RI). The eluent was a solution of 154 μ L of trifluoroacetic acid in 1 L water with a flow rate of 1 mL min⁻¹ and a retention time of 40 min.

The organic liquid phases of all reactions were analysed with an Agilent HP6890 gas chromatograph using a CP-Sil-Pona-CB column with dimensions of 50 m × 210 μ m × 0.5 μ m and a flame ionisation detector (FID). The carrier gas was nitrogen with a flow rate of 1.5 mL min⁻¹, an inlet temperature of 250 °C and a split flow of 50 mL min⁻¹. The following temperature program was used in the analysis of a liquid volume of 1 μ L: 50 °C (5 min)–8 °C min⁻¹–250 °C (15 min).

To confirm the presence of pentane and 2-butanol sample analysis was performed by a gas chromatograph-mass spectrometer (GC-MS). A Trace GC 1310 instrument and a Thermo Scientific ISQ mass spectrometer were employed. A helium carrier gas with a flow rate of 1 mL min⁻¹ and an inlet temperature of 250 °C was purged through a Restek Rxi-1 ms column with dimensions of 60 m × 250 μ m × 0.5 μ m. The following temperature program was applied: 50 °C (5 min)–8 °C min⁻¹–250 °C (15 min). The temperature of the transfer tubing as well as the ion source was 250 °C, and the spectrometer used an electron impact (EI) ionisation mode with 70 eV of electron energy.

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