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Beta-irradiation of biomass in the presence of 1-alkyl-3-methyl-imidazolium ionic liquids. Identification of an unexpected product from a model compound reaction

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Abstract A combination of swelling in imidazolium ionic liquids and beta-irradiation – both common pretreatments in biomass processing on their own – leads to unexpected effects, with beta-irradiation causing degradation of the pure ionic liquid and also modification of cellulose suspended in the ionic liquid. The underlying chemistry was investigated in a series of model compound experiments. Here, we report that beta-irradiation of the ionic liquid EMIM-OAc containing equimolar amounts of benzaldehyde and D-glucose affords an unexpected condensation product $C_{17}H_{20}O_7$, of which the structure was elucidated as 5-[(1S,2R,3R)-1,2,3,4-tetrahydroxybutyl]-2-phenyl-3-furoic acid, applying a combination of analytical techniques, mainly NMR spectroscopy, after conversion into the ethyl ester derivative for

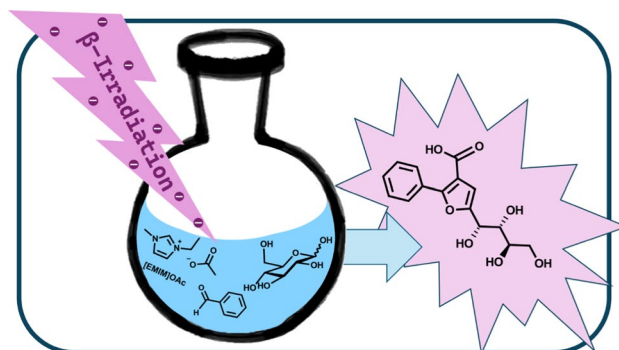
purification. No reaction at all occurred without beta-irradiation under otherwise identical conditions. Intriguingly, the acetate – the IL's anion – was incorporated into the condensation product, which can formally be regarded as the condensation product of benzoylactic acid (from benzaldehyde and the IL's acetate) and D-glucose. The reaction occurred only when all three components – acetate-type IL, glucose and PhCHO – were irradiated simultaneously. The structure elucidation of the compound is presented, along with a discussion of possible formation mechanisms. Future experiments need to address the generality of the reaction for conversion of other aldehydes and aldoses, and the question of whether a similar process occurs with the reducing end of celluloses or other polysaccharides.

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Graphical Abstract



Keywords Beta-irradiation · Cellulose · Condensation reaction · EMIM acetate · Ionic liquids

Introduction

beta-Irradiation, usually carried out in the three regimes of low (80–300 keV), medium (300 keV–5 MeV), and high (above 5 MeV) energies, has become a quite frequent pretreatment option for different biomasses, as it was shown to enhance saccharification of polysaccharide components by acidic and enzymatic hydrolysis, often accompanied by a beneficial sterilizing effect. The easier saccharification, digestion and generally increased reactivity were assumed to be due to a general increase in accessibility for enzymes and reagents, a decrease in crystallinity and a shortening of the molecular weight of the polysaccharides (Kumakura and Kaetsu 1983; Duarte et al. 2012; Shin and Sung 2008). It has been applied in particular to increase the accessibility of cellulosic pulps (Saeman et al. 1952; Ershov 1998; Dubey et al. 2004; Bouchard et al. 2006) and reactivity in preparation of cellulose derivatives (Iller et al. 2002; Ekman et al. 1984). beta-Irradiation was shown to introduce oxidized functionalities along the cellulose chains (Henniges et al. 2012, 2013), which would subsequently give rise to chain cleavage and resulting depolymerization of the polysaccharides according to beta-alkoxy-elimination mechanisms (Hosoya et al. 2018). beta-Irradiation is commonly also referred to as “electron irradiation” or “e-beaming”.

Further, swelling of biomass in ionic liquids (ILs) is one of the most common pretreatment options in

biorefinery approaches nowadays. Due to their good availability and comparatively low price, mostly ILs of the first generation, *i.e.*, of the 1,3-dialkylimidazolium type, have been used. The purposes of the treatment are improved accessibility to reagents or enzymes, facilitated saccharification, energy savings upon mechanical processing, and faster downstream processing (Brandt et al. 2012; Zhang et al. 2021; Amini et al. 2021; Quesada-Salas et al. 2022; Roy and Chundawat 2023). Earlier approaches have met considerable problems regarding the purification and recycling of the ILs and their accumulation of unused byproducts. Therefore, the recovery and reuse of ILs in such biomass pretreatments have become an integral part of corresponding biorefinery solutions (Sun et al. 2009; Mora-Pale et al. 2011; Wang et al. 2012; Tu and Hallett 2019).

The combination of biomass treatment by ILs and beta-irradiation, although proposed for similar purposes as single pretreatments (Jusri et al 2019; Zhang et al. 2021; Amini et al. 2021), has recently been put into question because beta-irradiation in the presence of imidazolium ILs was shown to alter cellulose chemically under covalent incorporation of nitrogen in considerable amounts, up to 2.5 wt% in microanalysis (Jusner et al. 2023). In the case of wood, also a macroscopic hydrophobization effect was observed (Croitoru et al. 2014; Croitoru and Patachia 2016).

We have started to study the “chemistry” of the interaction between beta-irradiation, ILs and biomass components, in particular cellulose. The mechanisms and underlying chemistry of these chemical systems are far from being understood, let alone exploited.

In attempts to detect reactive species in the system, we focused on radicals and reactive oxygen species (in dependence of the presence of atmospheric oxygen), carbenium-iminium ions and carbenes. The latter two are known to be formed relatively easily from the 1,3-dialkylimidazolium moiety (Rodríguez et al. 2011; Jahnke and Hahn 2017). To keep the system under study as simple as possible in the beginning, we used several simple model compounds that were beta-irradiated in ILs to infer intermediates and possible mechanisms from the products. The formation of benzoin from benzaldehyde, for instance, was indicative of carbene formation, which would act as a catalyst in an umpolung (*i.e.*, polarity inversion) reaction to allow the reaction between two (typically electrophilic) benzaldehyde molecules. In the presence of equimolar amounts of benzaldehyde and D-glucose in the irradiated IL, we observed the formation of a single product, of which the structure was puzzling at first. In this study, we would like to present the structure elucidation of the peculiar reaction product, along with a brief proposal and discussion of possible pathways leading to its formation.

Materials and methods

General Commercial chemicals from Sigma-Aldrich (Schnelldorf, Germany) were of the highest grade available and were used without further purification. Solvents were purchased in synthesis grade from Roth, Sigma-Aldrich and VWR and were used as received. Elemental analysis was carried out at the microanalytical laboratory of the University of Vienna on a EURO EA 3000 CHNS-O instrument (HEKAtech, Wegberg, Germany).

UV/Vis spectra were recorded on a Hitachi U-3010 UV/Vis spectrophotometer (Hitachi Global, Tokyo, Japan) with a range of 200 to 800 nm, scanning speed 300 nm min⁻¹, quartz glass cuvettes (*l*=1.0 cm). The sample **6a** was dissolved in DMSO (GC grade; *c*=0.01 mg mL⁻¹) and measured applying baseline correction with a solvent blank in a measurement setup.

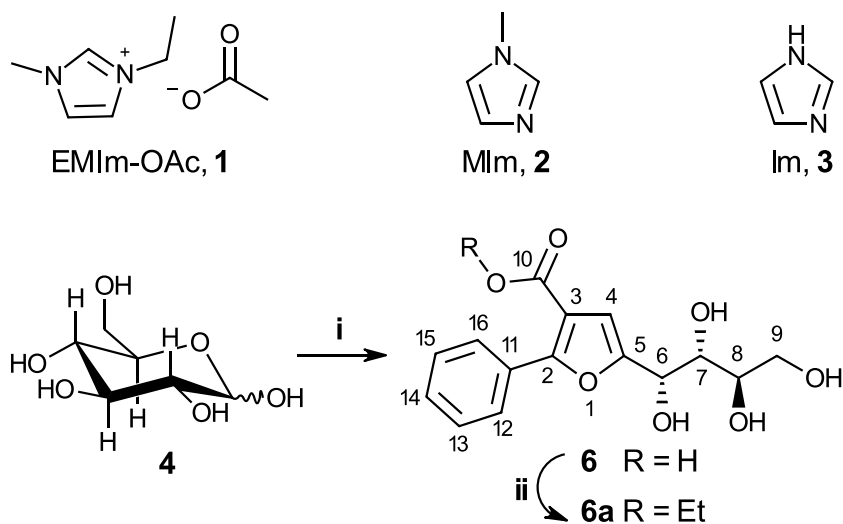
Attenuated total reflection Fourier-transformation infrared (ATR-FTIR) spectra were recorded on a Frontier IR single-range spectrometer (PerkinElmer, Waltham, MA, US) equipped with a diamond/ZnSe crystal, LiTaO₃ detector, and KBr windows. Data

processing was performed using Origin Pro 2023b software. All spectra were obtained over a spectral range of 4000–650 cm⁻¹, with a spectral resolution of 4 cm⁻¹, and 16 scans per sample.

Beta-Irradiation beta-Irradiation (electron beam irradiation) was carried out at NHV Corporation (Kyoto, Japan) on a Curetron® EBC300-60 electron beam generator at 300 keV and 10 MeV. The samples were irradiated at a liquid film thickness of 1 mm between glass slides. The samples were irradiated with a dose of 60 to 2400 kGy. For detailed procedures see Ehrhardt et al. (2005) and Henniges et al. (2012, 2013).

Gas chromatographic analysis (GC-EI-MS) GC analysis, conducted with the pertrimethylsilylated derivatives, was based on previous work (Barbini et al. 2021a and 2021b). An Agilent 5975C apparatus with MSD inert XL TAD and FID was used. Synchronized recording of FID and MS spectra was performed by a splitter mounted after the column, with one third of the flow to the MS, and two thirds to the FID. The MS detector was operated in the electron-impact (EI) mode at 70 eV at 280 °C, mass scanning range 29–1050 amu, solvent cutting time 4 min. FID parameters: temperature: 400 °C; H₂ flow: 30 mL min⁻¹; air flow: 400 mL min⁻¹; makeup flow (combined): 25 mL min⁻¹. The device was equipped with a VF-5ht UltiMetal capillary column (30 m×250 μm×0.1 μm, Agilent J&W). Column temperature program: initial T: 65 °C, isothermal for 5 min; ramp to 380 °C at a rate of 10 °C min⁻¹; maintained at 380 °C for 8 min. Helium was used as the carrier gas, with a gas flow of 2.5 mL min⁻¹. Injection (1.0 μL) was performed by an autosampler in a cold multimode inlet (MMI), which was kept at 65 °C for 6 s, by increasing the temperature to 380 °C at 500 °C min⁻¹ and then holding the temperature constant for 5 min (cold split injection). The split ratio was set to 15:1 (split flow, 37.5 mL min⁻¹). The total analysis time was 44.5 min. The MS data were collected with an Enhanced ChemStation (MSD Chemstation F.01.01.2317), deconvoluted, and then evaluated using the MassHunter Workstation software (Unknowns Analysis). The fragments were identified by comparison with the Wiley10 and NIST11 mass spectral libraries.

Scheme 1 Chemical structure of the compounds used in this study, including the unexpected condensation product 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-phenyl-3-furoic acid (**6**) and its ethyl ester **6a** used for separation and identification (see Materials and Methods)



i: Ph-CHO (**5**), 2.5 wt% **4**, **4** : **5** = 1 : 1 (mol/mol),
 beta-irr. in EMIm-OAc (**1**), 4 h, 83 % (2400 kGy)
ii: EtOH, Al₂O₃ (acidic), 30 min, 88 %

Pertrimethylsilylation procedure for GC: To a 1.5 mL GC vial containing 5.0 mg of the analyte, 200 μ L of anhydrous pyridine containing 1.5 mg/mL of DMAP and 200 μ L of silylating agent [9:1 (v/v) of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, $\geq 99\%$, Sigma-Aldrich) and trimethylchlorosilane (TMCS, $\geq 99\%$, Sigma-Aldrich)] were added. The vial was vortexed and heated at 70 $^{\circ}$ C for 2 h. The sample was diluted with 1.0 mL ethyl acetate and directly injected into the GC-MS/FID system.

NMR analysis Solution-state NMR spectra were recorded on a Bruker Avance II 400 spectrometer equipped with a 5 mm N₂-cooled broadband observe (BBO) probe-head (CryoProbe™ Prodigy) with z-gradients at 303 K (resonance frequencies of 400.13 MHz for ¹H and 100.61 MHz for ¹³C). Chemical shifts are given in parts per million (ppm) and were referenced to the DMSO-*d*₆ residual solvent signal as an internal reference (2.50 ppm for ¹H, 39.6 ppm for ¹³C). The ¹H NMR spectrum was recorded with 32 k complex data points and apodized using a Gaussian window function (lb=-0.30 Hz and gb=0.30 Hz) prior to Fourier transformation. A *J*-modulated ¹³C NMR spectrum using WALTZ16 ¹H decoupling (Bruker pulse program “*jmod*”) was recorded with 64 k complex data points. S/N was

enhanced utilizing an exponential window function (lb=1.0 Hz) before Fourier transformation. The ¹H-¹H COSY spectrum (Bruker pulse program “*cosygpqf*”) was recorded with 2 k \times 256 data points. The multiplicity-edited ¹H-¹³C HSQC experiment (Bruker pulse program “*hsqcedetgmsp.3*”) was performed using adiabatic pulses for inversion of ¹³C and GARP-sequence for broadband ¹³C-decoupling, optimized for ¹*J*_(CH) = 145 Hz. For the determination of long-range ¹H-¹³C connectivities, an HMBC experiment (Bruker pulse program “*hmbcgpplndqf*”) with the long-range coupling constant set to 8 Hz was performed. All NMR data were processed using Bruker TopSpin 3.6.5 and/or 4.3.0 software.

Compound identification 5-[(1*S*,2*R*,3*R*)-1,2,3,4-Tetrahydroxybutyl]-2-phenyl-3-furoic acid ethyl ester (**6a**), see Scheme 1 for structure and atom numbering.

Microanalysis: calcd. C₁₇H₂₀O₇ (M=336.34 g mol⁻¹), C 60.71, H 5.99, O 33.30, found: C 60.66 / 60.81, H 5.90 / 5.94, O 33.20 / 33.27, no N.

¹H NMR (DMSO-*d*₆, 400.13 MHz, δ /ppm, *J*/Hz): 7.90 (dm, 1H, *J*=8.0, H-12+16), 7.46 (m, 2H, H-13+15), 7.43 (m, 1H, H-14), 6.68 (d, 1H, *J*=0.8, H-4), 5.27 (d, 1H, *J*=7.2, 6-OH), 4.87 (dd, *J*=7.1, 1.5, H-6), 4.67 (d, 1H, *J*=7.4, 7-OH), 4.66 (d, 1H,

$J=5.2$, 8-OH), 4.37 (t, 1H, $J=5.3$, 9-OH), 4.23 (q, 2H, $J=7.1$, H-17), 3.62 (m, 2H, H-7, H-9a), 3.54 (m, 1H, H-8), 3.44 (m, 1H, H-9b), 1.26 (t, 3H, $J=7.1$, H-18).

^{13}C NMR (DMSO- d_6 , 100.61 MHz, δ /ppm): 163.0 (C-10), 156.8 (C-5), 154.9 (C-2), 129.5 (C-11), 129.3 (C-14), 128.3 (C-13+15), 128.0 (C-12+16), 114.0 (C-3), 109.2 (C-4), 72.6 (C-7), 71.0 (C-8), 66.3 (C-6), 63.4 (C-9), 60.3 (C-17), 14.1 (C-18).

FT-IR: $\bar{\nu}$ (cm^{-1}): 3281 (broad, OH), 2933 (aliphatic CH), 1714 (C(O)OR), 1551 (aromatic CH).

MS (pertrimethylsilylated compound, $\text{C}_{29}\text{H}_{52}\text{O}_7\text{Si}_4$, $M=624.28$ g mol $^{-1}$, EI, 70 eV, m/z): 625.4 (0.1), 624.4 (0.1), 625.3 (0.15), 431.2 (30), 390.0 (45), 360.7 (30), 316.9 (100), 307.2 (20), 217.1 (40), 199.1 (25), 157.1 (30), 102.9 (50), 73.0 (90).

Results and discussion

beta-Irradiation of equimolar amounts of D-glucose (**4**, 2.5 wt%, as a simple model compound for cellulose) and benzaldehyde (**5**, equimolar to **4**) in the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIM-OAc, **1**) produced a single main product (**6**). Byproducts, mainly *N*-methylimidazole (**2**) and imidazole (**3**) were formed only in trace amounts (<0.3 wt% rel. to the main product, *i.e.*, 0.0075 wt% rel. to the IL). While beta-irradiation of pure imidazolium

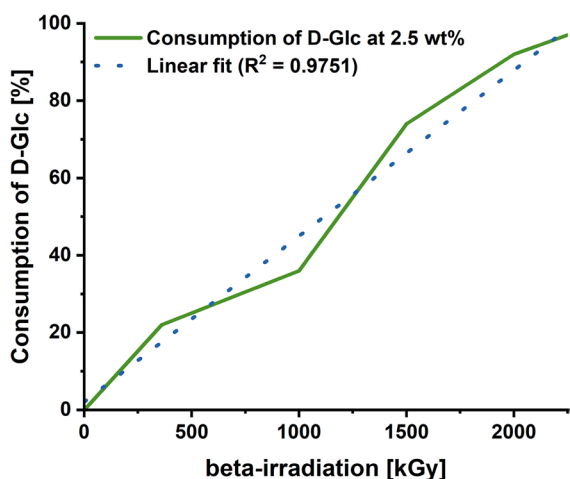


Fig. 1 Consumption of D-glucose being proportional to the beta-irradiation time

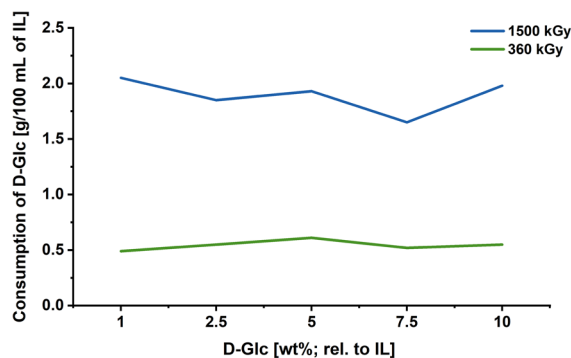


Fig. 2 Yield of product **6** being largely independent of the starting concentration of D-glucose (**4**) and benzaldehyde (**5**) (**4** in wt% relative to IL; equimolar to **5**)

ILs produces *N*-methylimidazole and imidazole in higher amounts (2 wt% relative to the IL) together with many minor degradation products, the presence of D-glucose and benzaldehyde appeared to alter the processes in such a way that parallel reactions and side processes occurring in the case of pure IL were suppressed and only one major product was formed. Notably, the reaction occurred only in an acetate ionic liquid (EMIM-OAc or its butyl counterpart), but not in the case of halide, phosphate, or hydrogensulfate anions. This indicated the involvement of the IL anion in the reaction, either directly as a reactant or as a catalyst.

The consumption of D-glucose and the formation of **6** was proportional to the irradiation time (Fig. 1), but was interestingly largely independent on the concentration of D-glucose and benzaldehyde, which were always used in equimolar ratio: the converted mass of **4** and **5** per 100 mL of ionic liquid was independent of their starting concentration (Fig. 2). This pointed towards the occurrence of an intermediate from the IL (probably as the rate-determining step) which then reacted with the dissolved model compounds according to the observed zero-order kinetics with regard to **4** and **5**. The intermediate appeared to be rather short-lived: a two-step variant of the reaction setup – first irradiating the pure IL and then adding **4** and **5** – did not give any reaction product **6** at all. All three components, EMIM-OAc (**1**), D-glucose (**4**), and benzaldehyde (**5**) had to be present simultaneously and irradiated together for **6** to form. Interestingly, the presence of water proved to be detrimental to

its yield, with even 0.2 wt% (rel. to the IL) preventing the formation of product **6** completely. Irradiation by 2400 kGy completely converted 2.5 wt% glucose (rel. to the IL) and equimolar amounts of benzaldehyde (*cf.* Scheme 1) in our setup after 4 h. The decreased isolated yield of **6** (83%) is due to isolation losses, not due to incomplete conversion of **4** and **5**. Product **6** itself appeared to be rather insensitive towards further irradiation, as additional irradiation – beyond the complete conversion of **4** and **5** – did not measurably decrease the amount of **6** already formed.

The reaction product proved to be hard to liberate from traces of the IL, which interfered with HPTLC and GC–MS analysis. As preliminary IR analysis indicated the presence of a carboxyl group, the substance was converted into its ethyl ester (ethanol/acidic aluminum oxide) and chromatographically purified using the same system. This provided an analytically pure compound that was used in all subsequent structure determination steps.

Taking all analytical input and data from the NMR and MS experiments together, compound **6** was identified as 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-phenyl-3-furoic acid. While this compound was formed upon beta-irradiation of the three components **1**, **4** and **5**, it was purified and identified as its ethyl ester derivative, ethyl 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-phenyl-3-furoate (**6a**), see Scheme 1, with the atom numbering used in the experimental part and the

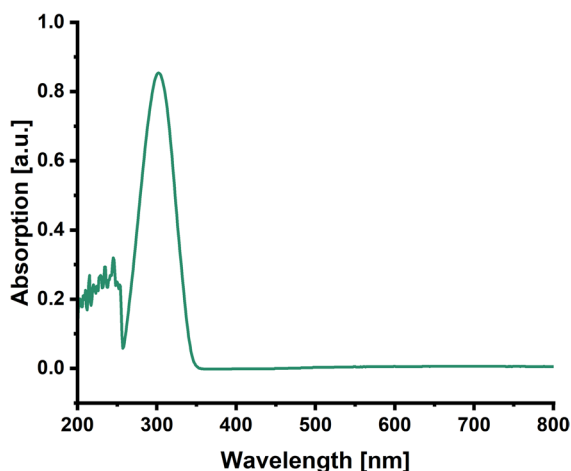


Fig. 3 UV/VIS spectrum of compound **6a** ($c=0.01$ mg mL⁻¹ in DMSO)

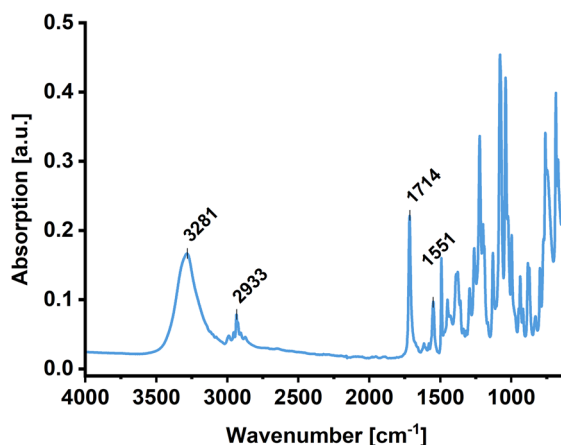


Fig. 4 ATR-FTIR spectrum of compound **6a**

stereochemistry being transferred from the parent compound D-glucose.

Microanalysis gave average values of 60.66 wt% C, 5.92 wt% H, and 33.23 wt% O with no N being present. Assuming the absence of any other elements, an elemental composition of C₁₇H₂₀O₇ was calculated. Interestingly, no nitrogen was contained, which was surprising since beta-irradiation of cellulose and other polysaccharides in the presence of imidazolium ILs caused covalent nitrogen fixation in the polymer (*vide supra*). If we assume the above hypothesis of an intermediate formed from the IL (cation) under beta-irradiation to be true, this species would act as a catalyst rather than as a co-reactant, being involved in the reaction, but not incorporated into the product. UV spectroscopy indicated the presence of a UV-absorbing moiety with a maximum at 300 nm, probably an aromatic unit (*cf.* Figure 3). ATR-FTIR spectroscopy revealed the presence of a phenyl moiety (1551 cm⁻¹), an ester (1714 cm⁻¹), an aliphatic CH chain (2933 cm⁻¹) and hydroxy groups (3281 cm⁻¹, broad) as structural elements very likely to be present (*cf.* Figure 4). The phenyl ring would stem from the benzaldehyde starting material, the aliphatic hydroxy groups from the carbohydrate moiety, and the ester would have formed in the purification step (see above), although the origin of the underlying carboxylic acid remained unclear.

The ¹H NMR spectrum of **6a** (Fig. 5) revealed the presence of a phenyl group with signals of the five aromatic protons at δ_{H} 7.90 and around 7.45 ppm. In addition, one olefinic proton at δ_{H} 6.68 ppm (H-4) with

Fig. 5 ^1H NMR spectrum of compound **6a** recorded in DMSO-d_6

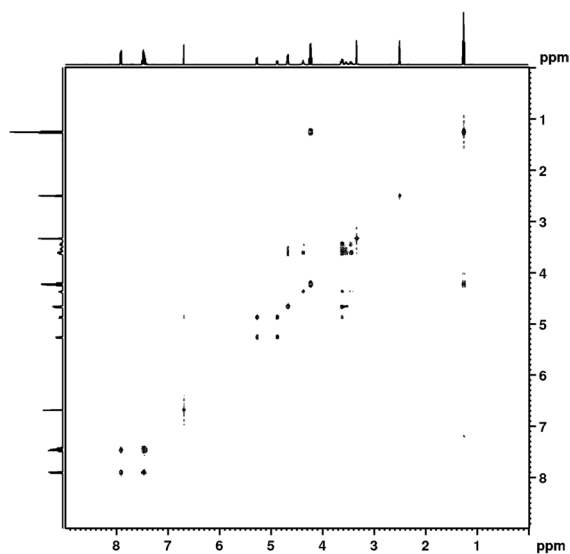
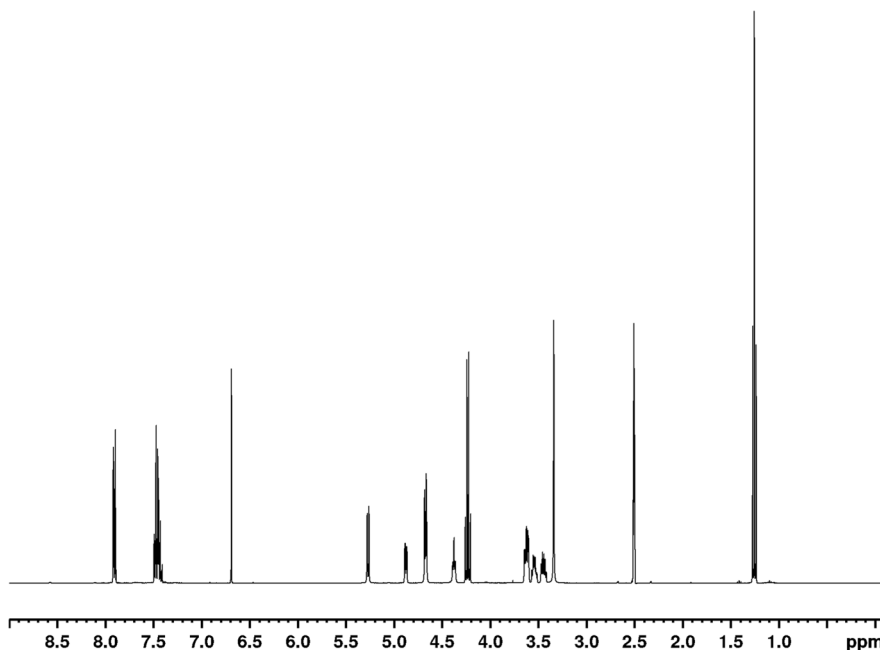


Fig. 6 ^1H - ^1H COSY NMR spectrum of compound **6a** in DMSO-d_6

a small ^1H - ^1H doublet coupling of ca. 0.8 Hz and the characteristic triplet/quadruplet pattern of an ethoxy group at δ_{H} ca. 4.20 and 1.30 ppm were detected. Besides that, nine proton resonances were localized in the oxygenated region from δ_{H} ca. 5.5–3.3 ppm, four of them turned out to be hydroxy protons due to missing cross peaks in the ^1H - ^{13}C HSQC spectrum.

Detailed analysis of the ^1H - ^1H COSY spectrum (Fig. 6) proved that all these nine resonances are part of one spin system (CH-6 to CH-9).

The ^{13}C NMR spectrum showed 15 carbon resonances (Fig. 7). Considering the already identified phenyl and ethoxy moieties as well as the before-mentioned four-carbon spin system, additionally one carboxyl carbon at δ_{C} 163.0 ppm, two oxygenated quaternary carbons at δ_{C} 156.8 and 154.9 ppm, and one quaternary carbon at δ_{C} 114.0 ppm were detected. The combination of the different substructures was established by detailed analysis of the ^1H - ^{13}C HSQC (Fig. 8) and ^1H - ^{13}C HMBC (Fig. 9) spectra. The ethoxy group was linked to the carboxyl carbon δ_{C} 163.0 (C-10), seen by a long-range cross peak from H-17 to form an ester function. Cross peaks from 6-OH (δ_{H} 5.27 ppm) and H-7 (δ_{H} 3.62 ppm) to the carbon at δ_{C} 156.8 (C-5) and from H-6 (δ_{H} 4.87 ppm) to C-4 (δ_{C} 109.2 ppm) extended the carbon chain of the spin system C6-C9. C-2 was identified with a long-range cross peak from H-12,16 to the resonance at δ_{C} 154.9 ppm. The final structure of a 2,3,5-trisubstituted furan derivative was determined by the crucial HMBC cross peaks from H-4 to C-2, C-3, C-5, and C-10 (see inset in Fig. 9).

The structure of the compound – and its purity – was further confirmed by GC-EI-MS, after pertrimethylsilylation of the OH groups (Fig. 10). A signal

Fig. 7 J -modulated ^{13}C NMR spectrum of compound **6a** in DMSO-d_6

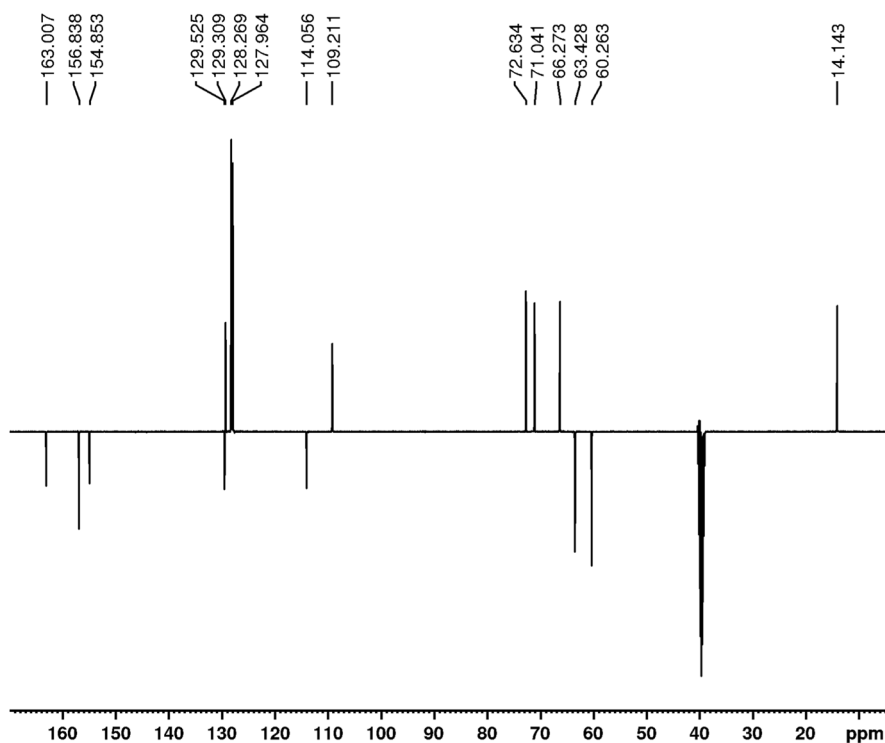
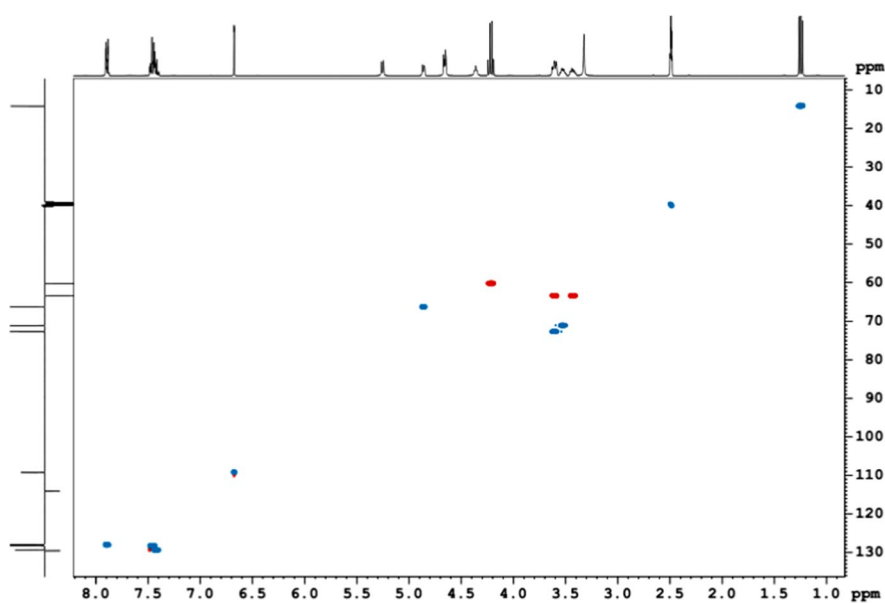


Fig. 8 Edited ^1H - ^{13}C HSQC NMR spectrum of compound **6a** in DMSO-d_6 (positive phases (CH_3/CH) shown in blue, negative ones (CH_2) in red)



at $m/z = 624.3$ was observed corresponding to the parent ion $[\text{C}_{29}\text{H}_{52}\text{O}_7\text{Si}_4]^+$. Owing to the high fragmentation in EI-mode, the silylated parent ion was low in abundance and several characteristic fragments dominated (see experimental section).

From the structure of **6** and its ester **6a**, it can be concluded that D-glucose , benzaldehyde and acetate (anion from IL) are incorporated into the product in an equimolar (1:1:1) ratio. The ethyl moiety of the ester was introduced upon purification. The

Fig. 9 ^1H - ^{13}C HMBC NMR spectrum of compound **6a** in DMSO-d_6 , the inset showing selected ^1H , ^{13}C HMBC cross peaks confirming the structure

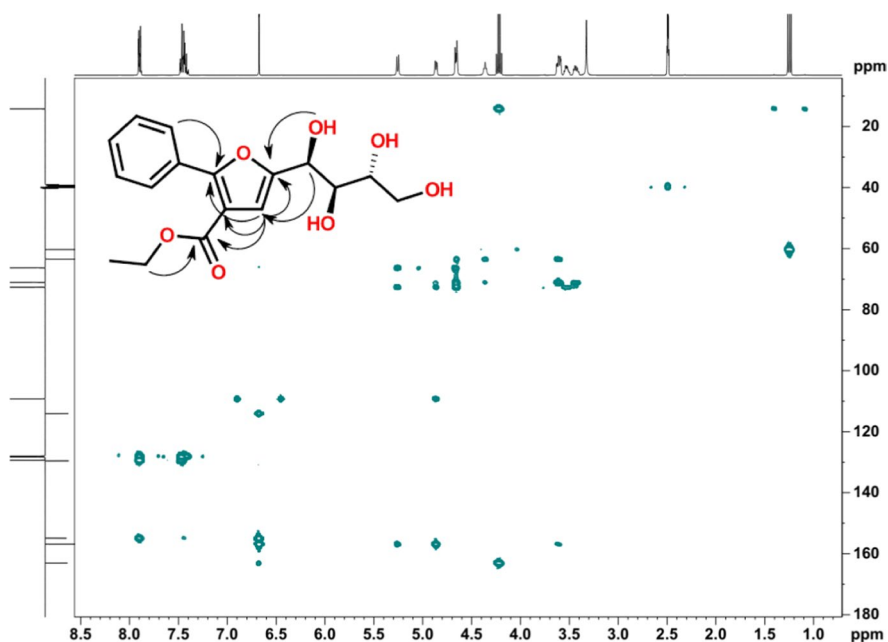
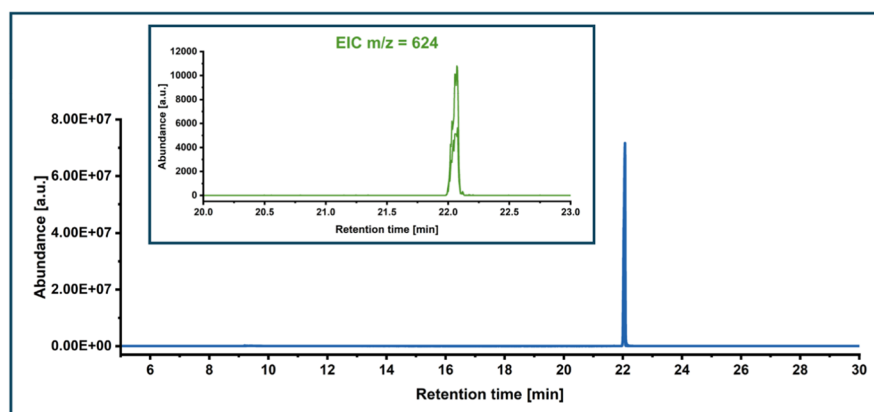


Fig. 10 GC-EI-MS chromatogram (total ion chromatogram (TIC), bottom) and extracted ion chromatogram (EIC) for $m/z = 624$ [M^+] (inset)

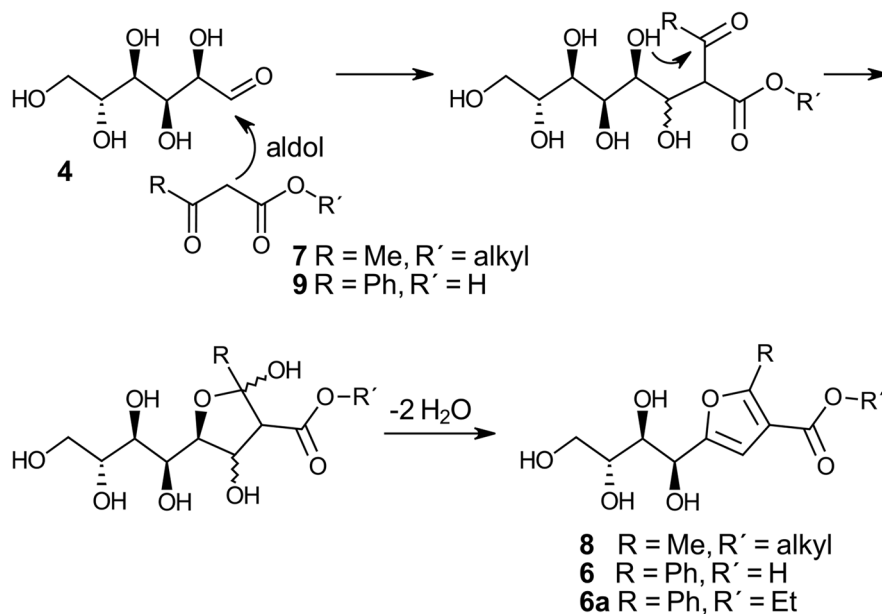


mechanism of the formation reaction is still under study. An initial hypothesis, the formation of an *N*-heterocyclic carbene (NHC) at C-2 of the imidazolium by beta-irradiation, was rejected. Such carbene formation is known to occur easily in the presence of bases (Jahnke and Hahn 2017). It was also likely to be the cause of benzoin formation when irradiating only Ph-CHO in the imidazolium ionic liquid. However, such NHCs react as strong nucleophiles with carbonyl compounds, causing an umpolung, and subsequent reaction with another aldehyde. The carbene is cleaved off again and thus regenerated: it acts as a catalyst in the benzoin condensation process (Breslow 1958; Burstein and Glorius 2004; Sohn et al. 2004).

In the present case, the two carbonyl groups (CHO in benzaldehyde, CHO in glucose) should have reacted with each other according to such a mechanism, but in **6** both “former” CHO are linked to the “former” methyl group of the acetate. Another hypothesis, the formation of keteniminium ions – known to proceed from imidazolium cations, albeit under rather drastic conditions ($T > 150\text{ }^\circ\text{C}$) – was rejected for similar polarity considerations.

The literature describes a reaction of aldoses that produces structurally very similar compounds, the condensation with acetoacetic acid esters and amides that leads to trisubstituted furans, with an ester or amide group at C-3, the methyl substituent

Scheme 2 Proposed mechanism of the reaction upon irradiation by analogy to the García-González reaction known from literature



from the acetoacetic acid moiety at C-2 and the carbohydrate residue (from C-3 on) at C-5 (Gonzalez 1956; Gonzalez and Sanchez 1965). In this reaction, the aldoses' reducing end condenses with the methylene-active CH₂ group in acetoacetic acid alkyl esters (7) in an aldol-type process, subsequently the C-2 hydroxy group of the aldose attacks the acyl keto group nucleophilically under tetrahydrofuran ring formation, in which water elimination and rearomatization finally lead to formation of the aromatic furan ring (see Scheme 2 with D-glucose as an aldose co-reactant). The generated furans **8**, 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-methyl-3-furoates, incorporate C-1 and C-2 of the aldose and C-2' and C-3' of the acetoacetate. Their structure is very similar to furan **6** which was generated upon irradiation (*cf.* Scheme 1), with the methyl group in **8** being replaced by the phenyl ring in **6**, and the alkyl ester moiety of **8** by the COOH group in **6**. This structural resemblance makes a similar formation mechanism likely, although we cannot account for the formation of the β-ketoacid (ester) in the case of irradiation. This condensation reaction is the basis of the “furan endwise-peeling” of celluloses with acetoacetates, which depolymerizes cellulose from the reducing end by individual glucose units and converts them into 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-methyl-3-furoates (**8**) in excellent yields (Rosenau et al. 2008).

Assuming the presence of benzoylacetate (**9**) in the present irradiation case, this reaction mechanism would readily explain the formation of product **6** from D-glucose. However, the problem persists, how this benzoylacetate could have formed from benzaldehyde and acetate under the prevailing conditions. Irradiation of benzaldehyde alone in EMIM-OAc did not provide any benzoylacetate, so we cannot assume an initial benzoylacetate generation process which is followed by the reaction with glucose. However, it is known that high-energy input at high ionicity can cause the condensation of non-activated acetic acid moieties in an aldol-type fashion. *N,N*-Dimethylacetamide, for instance, condenses to *N,N*-dimethylacetacetamide when refluxed in the presence of dissolved LiCl via intermediate *N,N*-dimethylketeniminium ions (Potthast et al. 2002). This process occurs only in the absence of water (Chrapava et al. 2003). The same thermal condensation reaction occurs with sodium acetate and acetic acid to give sodium acetoacetate via intermediate ketene formation (Snell and McElvain 1933; Spence and Degering 1944; Sullivan et al. 1977; Helmchen et al. 1985).

We could assume a similar high-energy, aldol-type condensation process for the present case, with the energy input not being thermal, but through radiation. Benzaldehyde would replace one of the two acetates in the condensation, always reacting as the carbonyl component (as it has no CH-acidic, methylene-active

carbon). Formally, the intermediate benzoylacetate (**9**) would condense with D-glucose (**4**) to afford the observed trisubstituted furan **6** (Scheme 2). The observed sensitivity of the formation of **6** towards the presence of water would support such a hypothesis, but the exact role of the beta-irradiation, and the chemical processes it triggers, remains elusive.

Conclusions

The beta-irradiation of EMIM-OAc ionic liquid in the presence of equimolar amounts of D-glucose and benzaldehyde produces 5-[(1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl]-2-phenyl-3-furoic acid (**6**). At an irradiation dose of 2.4 MGy, the aldose was completely consumed, forming 83% of the product, which is an astonishingly high yield considering that beta-irradiation is a high-energy treatment usually connected with random fragmentation and arbitrary bond cleavage, as, for instance, in electron-impact ionization in mass spectrometry. The reaction is limited to water-free systems – as common commercially available imidazolium ILs contain between 1 and 3% water, the reaction yielding **6** is unlikely to occur in these systems. Carefully dried ILs are a prerequisite to use beta-irradiation for any “synthesis” purposes based on the described reaction.

At present, we are not able to offer a satisfactory, conclusive mechanistic explanation for the formation of the β -keto-acid precursor for compound **6** in the irradiation system. Analogies to the García-González reaction involving a Knoevenagel condensation reaction argue in favor of its formation and a condensation of benzoylacetate with D-glucose to the furan system. The β -ketoacid would be formed from the IL's acetate anions and benzaldehyde under the high-energy action of the beta-irradiation, although the detailed process remains unclear. We will continue to pursue the elucidation of the mechanism and communicate our findings as appropriate. This is not exclusively of academic interest: the formation of **6** as the sole major product may well have some interesting synthesis potential for the production of highly substituted furans with defined stereochemistry in the substituents, provided of course that the reaction with other aldose and aldehyde components proceeds as smoothly as in the model system presented here. Selective modification of the reducing end of

cellulose (or other polysaccharides) would be another interesting and worthwhile application option.

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Declarations

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