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Chemical Pulping

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A high molecular weight coloured component in kraft pulping black liquor originates from polysaccharide degradation

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Abstract: During kraft pulping of wood, a considerable part of biomass is solubilized, forming a black liquor from which material can be taken out as by-products. Of these, extractive-derived fractions such as tall oil and raw turpentine has long seen technical utilization, and presently, lignin degradation products have garnered a large interest. The carbohydrate degradation products, however, have seen considerably less focus. In this work, we have investigated the structure of a high molecular-weight fraction of the carbohydrate degradation products using nuclear magnetic resonance spectroscopy, finding it to be a conjugated aromatic structure rich in methyl, methylidine, alcohol and carboxylic acid groups. Based on this information, we suggest a structure based on hydroxymethylfurfural as the repeating unit, with sugar acid substituents providing additional functionality. Additionally, UV–vis data of the polymer is compared with data from the kraft cooking of cotton linters and other model systems to corroborate the hypothesis that this polymer is indeed present in black liquor and potentially responsible for some of its characteristic colour. It also reacts in the kappa number analysis, exhibiting 40 % of the permanganate consumption predicted for pure lignin. Finally, the technical significance of these carbohydrate degradation products is discussed based on the structural findings.

Keywords: kraft pulping; black liquor; alkaline carbohydrate degradation; technical lignin; colour formation

1 Introduction

The kraft pulping process retains its dominant position in the pulping industry in large part thanks to its ability to produce pulp in large scale at low costs and high yield (Ragnar et al. 2013). Another advantage of the kraft process is that the cellulose remains relatively undamaged – this probably stems from the fact that cellulose, thanks to its crystalline structure, is able to resist alkaline hydrolysis to a degree (Berglund et al. 2019; Henriksson et al. 2024). Still, even in the kraft process, significant degradation of carbohydrates is seen to occur, initially initiated by the processes of alkaline hydrolysis and peeling. In this regard, the hemicelluloses, being less crystalline than cellulose, are particularly susceptible to degradation (Henriksson et al. 2024; Nieminen et al. 2014).

In general, polysaccharides degrade by means of three different reactions under alkaline conditions, these being alkaline hydrolysis (Berglund et al. 2019; Nieminen et al. 2014), the “peeling reaction”, i.e. the endwise loss of monosaccharides from the reducing end of a polysaccharide (da Silva Perez and van Heinigen 2015; Henriksson et al. 2024), and, for polygalactouronic acids such as pectin, β-elimination (Keijbets and Pilnik 1974; Teleman et al. 1995). A schematic of these principal reactions is provided in Figure 1. Note, that neither the peeling nor the β-elimination reactions produce monosaccharides of a natural structure, but instead of modified structures. Thus, the initially released products from carbohydrate degradation will contain a mixture of natural mono-, di-, and oligosaccharides, as well as modified carbohydrates, the latter being of highest prevalence.

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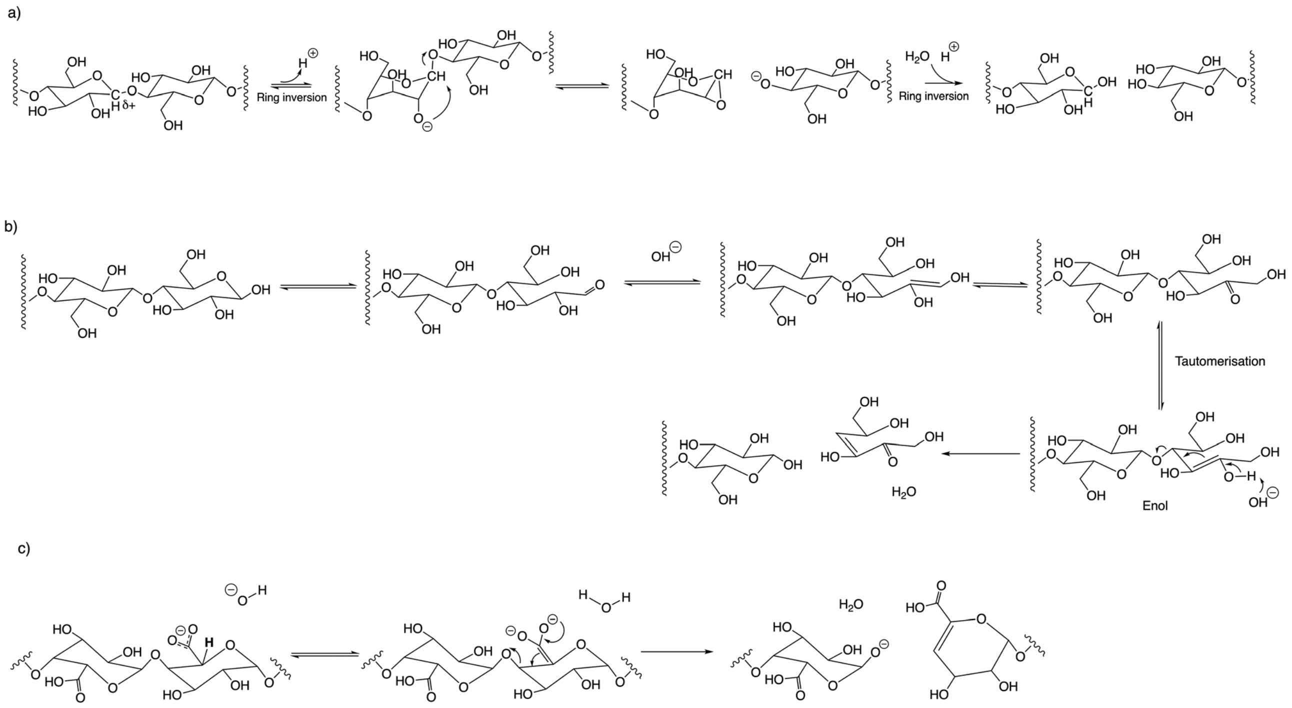

Figure 1: A schematic of the three main degradation reactions affecting polysaccharide carbohydrates, specifically a) alkaline hydrolysis of glycosidic bonds. b) Alkaline "peeling" through stepwise removal of monosaccharides from the reducing end. c) Alkaline catalysed *β*-elimination of pectin.

Once broken down into monosaccharides, the carbohydrates will, still in the presence of strong alkali, continue to react according to a new set of mechanisms. First, the monosaccharides will ring-open and tautomerise to their enediol forms, either the 1,2 enediol form or further to their 2,3 enediol form. These enediols can then undergo *β*-elimination to form the respective *α*-dicarbonyls. These *α*-dicarbonyls can then continue to react according to either benzilic acid rearrangement or *α*-dicarbonyl cleavage, producing a cascade of low molecular-weight sugar acids and other low molecular-weight degradation compounds as well as new (shorter) monosaccharides (De Bruijn et al. 1986). These mechanisms and a selection of these structures is shown in Figure 2. Additionally, other researchers were able to show the formation of minor amounts of cyclic enols, furan derivatives and phenols (Forsskåhl et al. 1976, Gellerstedt and Li 1995).

While these low molecular-weight compounds have been thoroughly characterised (MacLeod and Schroeder 1982), a polymeric fraction is also produced from carbohydrates under high temperature alkaline conditions which has eluded structural characterisation to this day despite continuous work during the past decades. It was speculated already by Ligett and Deitz (1954) based on at the time novel spectrophotometric data that the polymer could originate from *α*-dicarbonyl intermediaries. This was proven to be the case much later in the work of Kroh et al. (2008), who hypothesized a melanoidine-like structure for the polymer. Recently, two works have attempted to provide novel data on the compound: that of Luo et al. (2020) and that of Zhu et al. (2021). Luo et al. produced the polymeric degradation product from various hexoses in alkali at 60 °C, analysing the resulting product using ^{1}H-NMR, ^{13}C-NMR as well as UV-vis and FTIR. In doing so, they identified a number of functionalities, specifically carboxyl moieties, aldehyde moieties, alcoholic hydroxyl moieties, conjugated double bonds moieties, and saturated alkane moieties and further suggested aldolization of the low molecular-weight compounds as the pathway to the polymer. These functionalities were later corroborated in the work of Zhu et al., who produced the polymer from sucrose in alkali at 80 °C, also characterising their product using ^{1}H-NMR, ^{13}C-NMR as well as UV–vis and FTIR. Neither work was, however, able to attain 2D-NMR data, and while the pulse sequences used are not explicitly mentioned, the ^{13}C spectra are likely taken using a default power gate pulse sequence, meaning that the results cannot be used to estimate the quantity of any given functionality. As such, the details of the polymeric structure remain unknown to this day.

It is interesting to compare the degradation behaviour of monosaccharides in alkali to that of monosaccharides in acid. When subjected to acidic conditions and temperature, pentoses dehydrate into furfural (Sjöström 1981; Velaga and Nageswara 2022), while hexoses dehydrate into

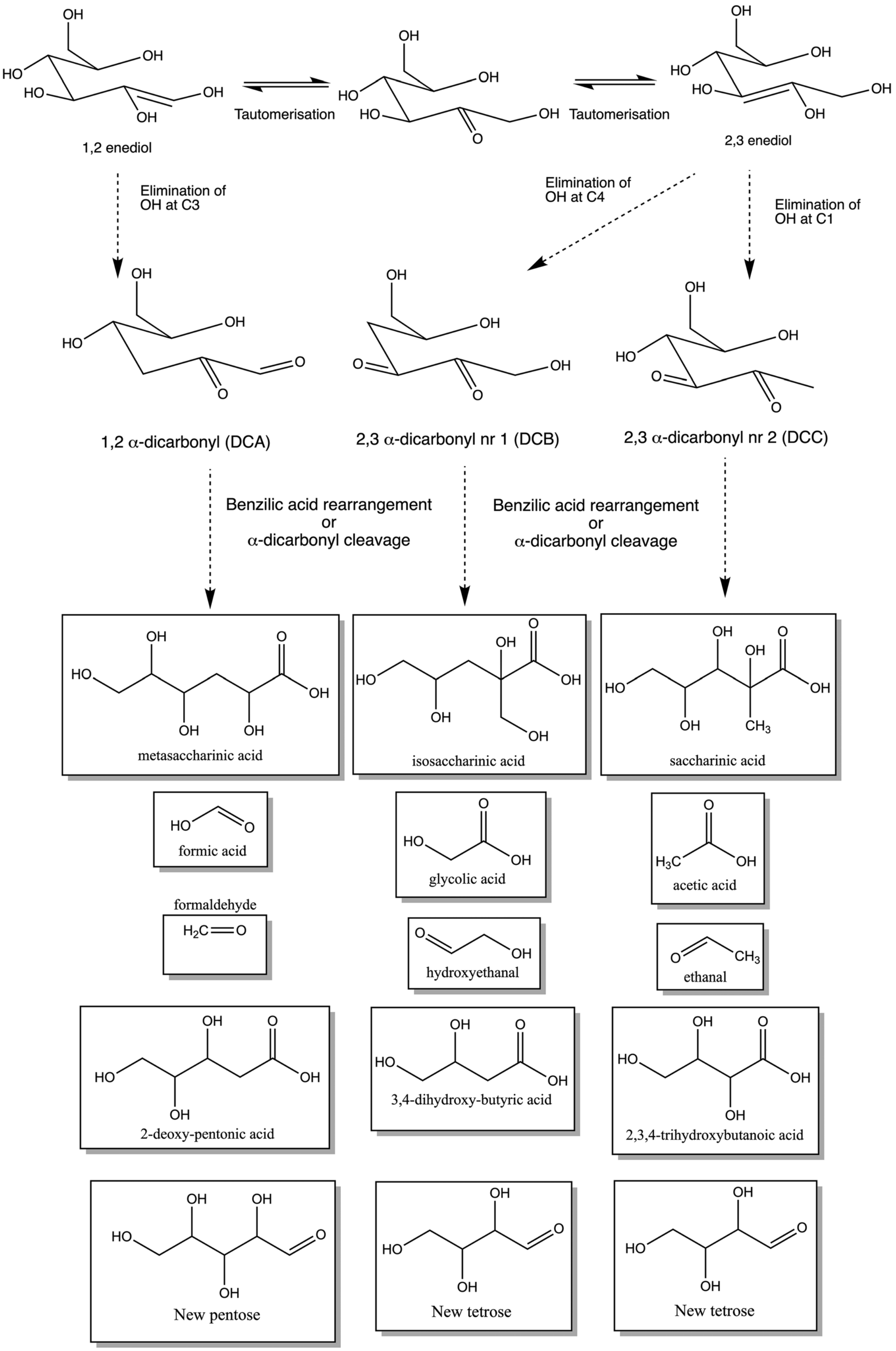

Figure 2: The formation of *α*-dicarbonyl compounds from monosaccharides followed by the formation of low molecular-weight sugar degradation products (mainly sugar acids) through benzillic acid rearrangement or *α*-dicarbonyl cleavage of the *α*-dicarbonyl intermediates.

hydroxymethyl furfural and levulinic acid (Fitzpatrick 1997; Sjöström 1981). Just as in the alkaline case, a part of these degradation products is then known to polymerise. In the case of acidic degradation, these polymers are known as “humins” and are considered to be unwanted side products in the industrial production of hydroxymethyl furfural from carbohydrate feedstocks. Much like the case of the alkaline sugar degradation polymer, the precise structure of the humin polymer is unknown, although it is known to consist of conjugated furanic networks linked by aliphatic chains (de Jong et al. 2025).

One interesting feature of the black liquor formed during the pulping of wood is the strong colour from which this process flow takes its name. Even when a tree species with very bright wood, such as that of Norway spruce or European aspen, is pulped, the resulting black liquor is very dark (Bergbauer et al. 1991; Irfam et al. 2017). The origin of the black liquor colour, i.e., which wood component are responsible for its development, and which end compounds produce the colour remain incompletely understood, even though it has often been assumed to be related mainly to lignin degradation products such as stilbenes (Henriksson et al. 2024). However, it is also known that carbohydrates have the potential to form coloured substances (Quintas et al. 2007).

Although other organic black liquor components such as raw tall oil, raw turpentine, methanol (Aro and Fatehi 2017; Johansson 1982; Redeborn and Wernqvist 1998) and (in recent developments) lignin degradation products (Kienberger et al. 2021) have all attracted interest as valuable products for utilization in biorefinery concepts, the carbohydrate degradation products have consistently been regarded as being of low value, and are today mainly burnt in recovery boilers (Saari et al. 2021). It has been suggested, however, that carbohydrate degradation products could constitute a potential feedstock for the chemical industry (Kumar and Alén 2015) and it was recently suggested that the carbohydrate degradation products could be used in an energy efficient electrolysis for manufacturing H_2, meaning that hydrogen gas could be a possible future by-product of kraft pulping (Qui et al. 2022). Thus, there are reasons to study the chemical fate of the carbohydrate degradation products in the strong alkali and high temperature conditions of kraft pulping.

In this work, the high molecular-weight sugar degradation product was produced from glucose in an alkaline solution heated to 100 °C. The polymer was subjected to a thorough NMR-analysis with the goal of producing novel information regarding its functionality and to speculate on its reaction pathway. UV–vis data of the polymer was also acquired and used to compare the colour profile of the compound to that of components of black liquor produced via the kraft pulping of pure cellulose (cotton) and the technical significance of these results is discussed.

2 Materials and methods

2.1 Materials

Cotton linters were obtained from Crane Stockholm, Sweden. Glucose, mannose, galactose, arabinose, xylose, cellobiose, mannitol and glucuronic acid were obtained from Sigma Aldrich, St Louis, Missouri, USA. All other chemicals were of analytical grade.

2.1.1 Kraft pulping of cotton

Kraft cooking was carried out by placing 25 g of cotton linters in 200 mL of white liquor (corresponding to a liquor-to-wood ratio of 8:1) with an effective alkali charge of 18 % and a sulphidity of 35 %, in stainless steel autoclaves with a maximum capacity of 400 mL. The autoclaves were placed in a PEG bath preheated to 110 °C in an autorotating installation. The temperature of 110 °C was maintained for 1 h before it was raised to 145 °C at a rate of 5 °C per minute, with the new temperature of 145 °C being subsequently maintained for 1 additional hour. The cook was terminated by placing the autoclaves in a cooling water bath. After the autoclaves had cooled for about 20 min they were retrieved, and their content poured over a Büchner funnel with a filter, separating the pulp and the black liquor.

2.1.2 Model system preparation of carbohydrate degradation products

Batches of various monosaccharides, specifically cellobiose, galactose, arabinose, mannose, xylose, glucose, glucuronic acid and mannitol were dissolved in 1 M NaOH at concentrations of $2.5\,g\,l^{-1}$ and allowed to react for 1 h at 80 °C. In the case of glucose, an additional experiment was conducted where glucose was similarly dissolved at concentrations of $2\,g\,l^{-1}$, $4\,g\,l^{-1}$, $8\,g\,l^{-1}$, $16\,g\,l^{-1}$, $32\,g\,l^{-1}$ and $64\,g\,l^{-1}$, and the resulting samples were allowed to react as per the conditions above.

2.1.3 Bulk preparation of high molecular-weight sugar degradation product

A batch of the alkaline high molecular-weight sugar degradation product was produced in bulk as follows: glucose was dissolved in 1 M alkali at a concentration of $60\,g\,l^{-1}$ and transferred to twin 2 l stainless rotative steel autoclaves. These autoclaves were then heated in a steam-heated polyethylene glycol bath for 2 h and 30 min at a temperature of 100 °C.

The product was then transferred and concentrated using rotary evaporation at a temperature 80 °C. After concentration, the high molecular-weight fraction of the product was isolated by means of one-month continuous filtration using a Millipore XFUF07601 Solvent-resistant Stirred Cell (Billerica, MA, U.S.A) equipped with a Millipore Ultrafiltration Membrane (Billerica, MA, U.S.A) with a nominal molecular-weight limit of 30,000 Da. With the high molecular-weight product thus isolated, the enriched solution was lyophilised and used for further analysis using nuclear magnetic resonance spectroscopy.

2.1.4 Ultraviolet–visible (UV–vis) spectroscopic analysis of black liquors and carbohydrate degradation products

The UV analysis was performed using a Shimadzu UV-2550 UV-vis spectrophotometer using the UVProbe version 2.34 software from Shimadzu Corporation (Kyoto, Japan). Hellma Präazisions-kuvetten aus Quarzglas Suprasil cuvettes with light path lengths of 1 mm or 10 mm (Müllheim, Germany) were used. Experiments were performed using a sampling interval of 0.5 nm and a slit width of 0.5–2.0 nm.

2.1.5 Molecular weight determination using size-exclusion chromatography (SEC)

The molecular weight of the high molecular-weight sugar degradation product was analysed on an Ultimate-3000 HPLC system (Dionex Sunnyvale, CA, USA) equipped with an RI-detector (Waters, Milford, MA, USA) using a mobile phase of 10 mM NaOH at a flow of 1 ml min^{-1}. The oven was set to 40 °C and the cooler to 30 °C. Separation was achieved using PSS Suprema columns, specifically a guard column with dimensions 50 × 8 mm, 10 µm particle size, followed by a 30 Å column and two 100 Å columns in series, with dimensions 300 × 8 mm, 10 µm particle size. Calibration was done using 10 pullulan standards in the range of 0.342–708 kDa.

2.1.6 Kappa number determination

The kappa number of the high molecular-weight sugar degradation product was determined according to the ISO 302:2004 standard, modified as follows: a small amount of high molecular-weight sugar degradation product was weighed and dissolved in a small amount of deionised water, which was then taken as the sample and analysed as per the standard protocol.

2.1.7 Nuclear magnetic resonance (NMR) analysis of the sugar degradation product

The resulting high molecular-weight degradation product was subjected to a series of NMR experiments with the purpose of elucidating its chemical structure. With the exception of the phosphorous NMR analysis, all these experiments were conducted on a Bruker 400 DMX instrument (Bruker Corporation, Billerica, MA, USA) equipped with either a multinuclear inverse Z-grad probe (Bruker Corporation, Billerica, MA, USA) for the inverse experiments, or a BB-1H 5 mm probe (Bruker Corporation, Billerica, MA, USA) for the broadband experiments. Initial data processing was done using Bruker Topspin v1.3 patchlevel 10 (Bruker Corporation, Billerica, MA, USA) after which final processing, including apodization, phase correction and baseline correction as well as presentation was done using MestReNova v14.2.1-27684 (Mestrelab Research, Santiago de Compostela, Galicia, Spain). With the exception of the phosphorous NMR analysis, all experiments used deuterium oxide as solvent, since – without chemical modification or treatment with an exchange resin – the high molecular-weight sugar degradation product was found to be insoluble in any nonpolar solvent.

2.1.8 Quantitative carbon (^{13}C) NMR-analysis

A quantitative carbon experiment was applied to the sugar degradation product using the ‘zgig’ inverse gate pulse sequence. The matching and tuning as well as locking and shimming were all manually adjusted, after which 90° pulse widths for the proton and carbon channels were optimised by finding the corresponding 360° pulses where sample signal was minimal and then dividing resulting pulse width by four. Due to the fast T_2 relaxation delay, an acquisition time of 0.2 s was used, while a relaxation delay time of 60 s was used. 4,805 data points were used per scan, and a receiver gain of 2,298.8 was applied. The experiment was conducted at room temperature, 298.0 K.

Thus configured, a total of 640 scans were collected per day, with locking and shimming being recalibrated on a daily basis and scans cumulatively collected for a duration of 7 days, resulting in a total number of 4,480 scans.

2.1.9 Quantitative phosphorous (^{31}P) NMR-analysis

A quantitative ^{31}P NMR analysis was done according to a modified version of the protocol of Arnling Bååth et al. (2016).

Specifically, 20 mg of lyophilised degradation product was mixed with 120 mg of 1-Allyl-3-methyl-imidazolium chloride under mild heating by means of a heat gun. After cooling, 60 µl of pyridine and 130 µl of 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane were added in order to initiate the phosphorylating reaction after which 500 µl of $CDCl_3$ containing 1 mg ml^{-1} Chromium (III) acetylacetonate was added sequentially. Finally, a known amount of internal standard in the form of N-Hydroxy-5-norbornene-2,3-dicarboximide was dissolved in a mix of pyridine and $CDCl_3$ and added to the sample. The analysis was performed in duplicate.

Unlike the other experiments, the ^{31}P NMR analysis was conducted on a Bruker Advance III HD 400 MHz instrument (Bruker Corporation, Billerica, MA, USA) equipped with a BBFO probe (Bruker Corporation, Billerica, MA, USA) equipped with a Z-gradient coil. The experiments were conducted at room temperature, 295.5 K.

2.1.10 Heteroatom single quantum coherence (HSQC) NMR analysis

An edited HSQC experiment was applied to the sugar degradation product using the 'hsqcedetgp' pulse sequence. The matching and tuning as well as locking and shimming were all manually adjusted, after which 90° pulse widths for the proton and carbon channels were optimised by finding the corresponding 360° pulses where sample signal was minimal and then dividing resulting pulse width by four. An acquisition time of 0.2 s was applied in the f2 dimension using a relaxation delay time of 5 s 960 × 512 increments were used, and a receiver gain of 9,195 was applied. The experiment was conducted at room temperature 297.8 K.

Thus configured, a total of 32 scans were collected per day, with locking and shimming being recalibrated on a daily basis and scans cumulatively collected for a duration of 7 days, resulting in a total number of 224 scans.

3 Results and discussion

When carbohydrates, including the polysaccharides which constitute the main components of the fibre cell wall in wood, are subjected to alkali, a series of degradation reactions occur, ultimately resulting in the formation of various low molecular-weight sugar acids as well as the formation of a high molecular-weight sugar polymer, the structure of which has yet to be determined (De Bruijn et al. 1986).

Given that all of the above criteria are present in the kraft pulping of wood, it is likely that the very same degradation products, including the high molecular-weight polymer, can be found in black liquor. It is therefore of interest to attain more information regarding the nature of the polymer, as well as its potential link to the colour of black liquor.

In order to thus elucidate the structure and colour of the carbohydrate degradation products produced by kraft pulping, samples of such degradation products were made by two means:

(1) Samples of model sugar degradation product were made by heating monosaccharides in sodium hydroxide at elevated temperatures. Of particular note, a large batch of degradation product was made from which the high molecular-weight sugar degradation product (which was the main focus of the study) was isolated.
(2) A sample of coloured liquor was made by performing kraft pulping of pure cellulose (in the form of cotton) using synthetic white liquor in an autoclave, thus allowing us to corroborate the presence of these degradation products in black liquor and their origin from polysaccharides specifically.

3.1 Analysis of the high molecular-weight degradation product using nuclear magnetic resonance spectroscopy and size-exclusion chromatography

A sample of alkaline high molecular-weight degradation product was produced in bulk by subjecting 120 g of glucose dissolved in 1 M alkali to a concentration of 60 g l^{-1} to a temperature of 100 °C for a duration of 2.5 h, after which the sample was concentrated and the high molecular-weight degradation product extracted from the solution mix using ultrafiltration. The isolated high molecular-weight degradation product was lyophilised and measured to a total weight of 886 mg, representing a yield of 0.74 %, after which the sample was redissolved in deuterium oxide. A diluted aliquot of this degradation product was subjected to molecular weight determination using size-exclusion chromatography, yielding a chromatogram as seen in Figure S1 of the Supplementary Material. The chromatogram is seen to be bifurcated, with 97 % of the area belonging to a main peak with a retention time at 22.55 min and 3 % belonging to a residual peak with a retention time of 24.79 min. The main peak of the sample is seen to correspond to a Mn of 31 kDa, a Mw of 40 kDa, and a polydispersity index of 1.27. Although this is higher than the molecular weight found by (Zhu et al. 2021), who reported a Mw of 20 kDa at a polydispersity index of 1.35, older literature has reported that the molecular weight of the polymer will vary depending on monomer concentration, temperature, and reaction times (De Bruijn et al. 1986), which could explain the disparity, given that (Zhu et al. 2021) reported using sucrose rather than glucose as well as using a lower temperature of 80 °C, and a lower pH of 13 when preparing their sample of the high molecular-weight sugar polymer. Interestingly, in the present study, the molecular weight of the high molecular-weight sugar polymer is also seen to be higher than that of a typical kraft lignin, which tends to have Mn values in the range of 8–11 kDa and Mw values in the range of 16–27 kDa (Zhu and Theliander 2015).

3.2 Investigation of chemical functionality using nuclear magnetic resonance

To elucidate the structure and chemical bonds of the high molecular-weight sugar degradation product an edited heteronuclear single quantum coherence (HSQC) analysis was applied to the sample, resulting in the data presented in Figure 3. Edited HSQC measures the intensity of carbon-proton pairs present in the sample, at the chemical shift of the protons in the direct dimension and the shift of the carbon atom in the indirect dimension. A further benefit of the edited pulse sequence is that signal can be distinguished by phase, with CH_3 and CH groups displayed as positive (red) and CH_2 groups displayed as negative (blue) in the spectrum. Quaternary carbons cannot be detected using the HSQC pulse sequence, since there is no attached proton with which to perform a polarisation transfer.

Analysing the HSQC spectrum, six distinct regions can be identified. A positive aliphatic region can be seen in the δ10-25 ^{13}C-range, followed by a negative aliphatic region in the δ25-45 ^{13}C-range. These are then followed by three regions in the chemical shift range typical for alcohols, with one positive region in the δ45-55 ^{13}C- range, one negative region in the δ60-65 ^{13}C- range, and one positive region in the δ70-80 ^{13}C- range. Interestingly, this is followed by a final positive region in the aromatic δ110-130 ^{13}C-range.

Although edited HSQC is able to give qualitative data as to the existence of chemical regions, it cannot elucidate the presence of quaternary carbons, nor give quantifiable data regarding the amount of chemical functionality in each region. In order to provide this information, a quantitative

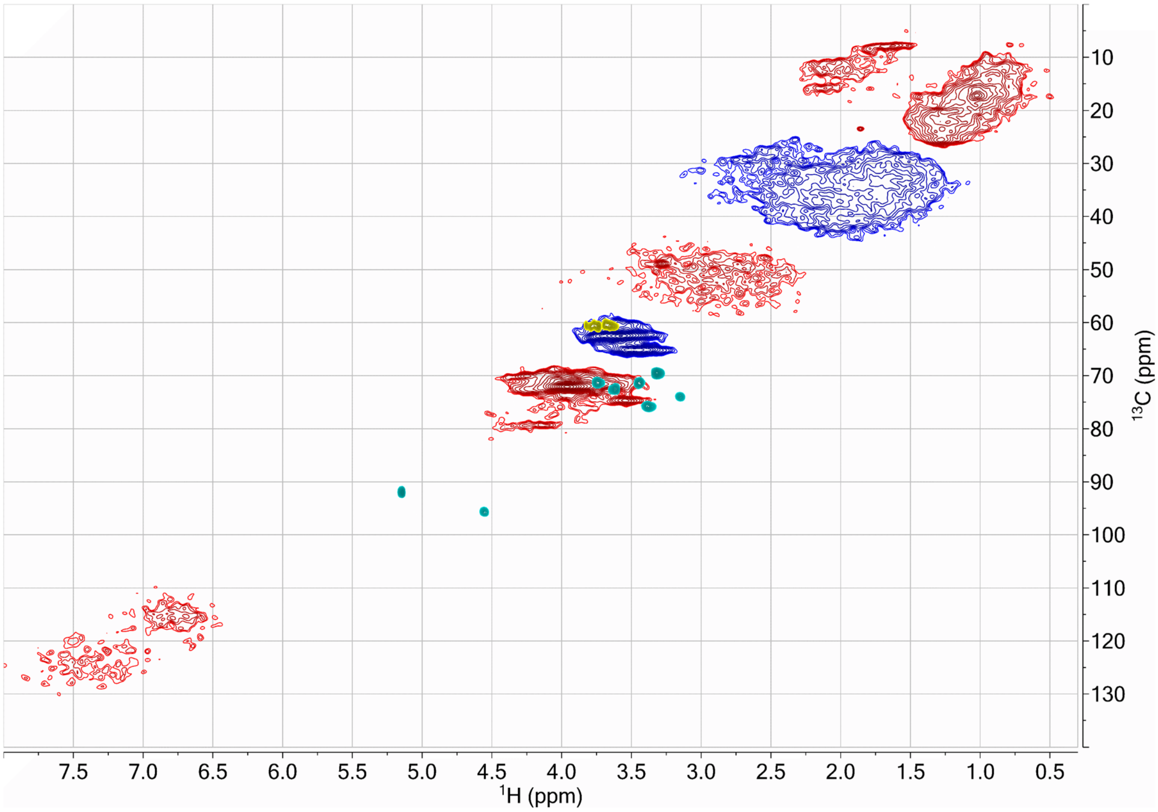

Figure 3: Edited HSQC spectrum of the high molecular-weight sugar degradation product, with (positive) red regions indicating CH_3 and CH groups and (negative) blue regions indicating CH_2 groups. For comparison and to be able to fully appreciate the significance of the new functionality thus created, a reference spectrum of the raw material, glucose, is overlayed with a 180° colour shift, with teal regions indicating CH3 and CH groups and (negative) yellow regions indicating CH_2 groups.

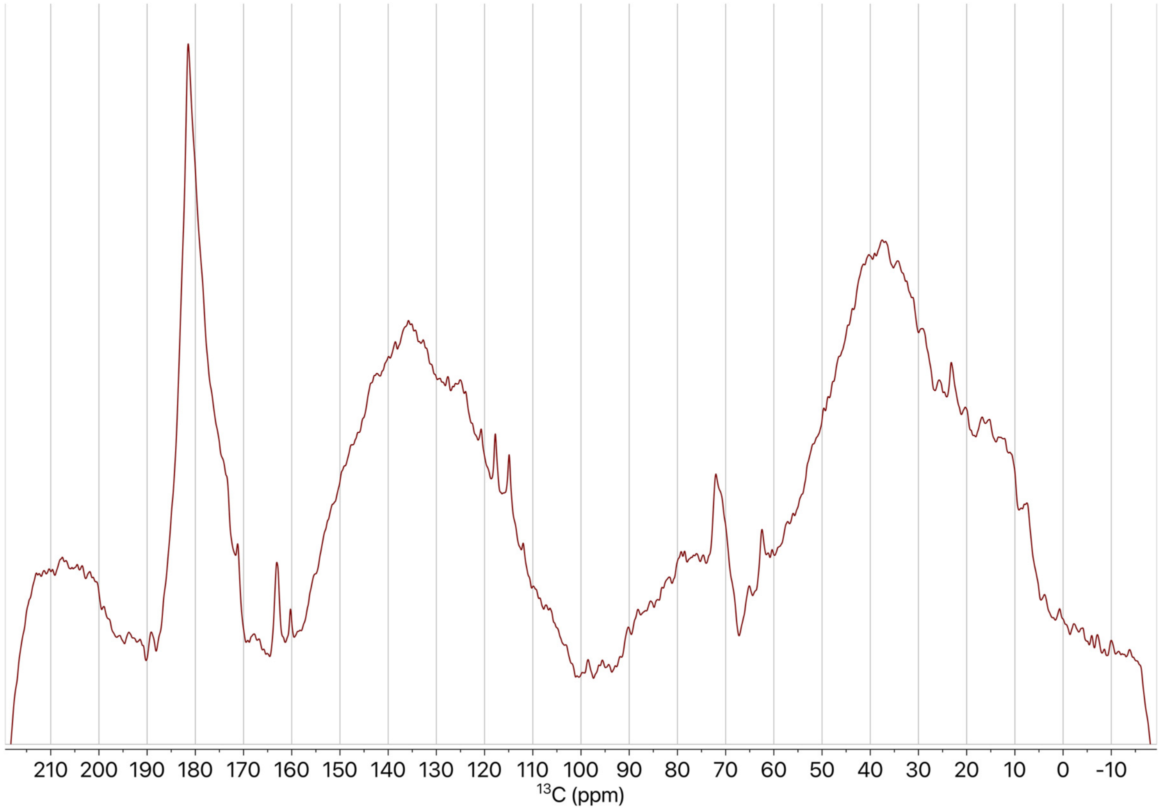

Figure 4: Quantitative inverse gate ^{13}C NMR spectrum of the high molecular-weight sugar degradation product.

carbon analysis was performed using the inverse gate ‘zgig’ pulse sequence, which allows for the collection of quantitative data by selectively applying proton decoupling only during acquisition, thus preventing distortion of integrals due to the nuclear Overhauser effect. Since the exact T_1 relaxation delay time was unknown, a large delay of 60 s was used. With this relaxation delay, data should be quantifiable with a maximum error of 5 % assuming the T_1 relaxation delay halftime is 12 s or faster.

A quantitative inverse gate carbon (^{13}C NMR) spectrum is presented in Figure 4. In this spectrum, the same regions previously identified in the HSQC spectrum can be observed in addition to additional low shifted regions stemming from quaternary carbons. Of particular note is a region of carboxylic functionality in the δ170-190 ^{13}C-range along with a region of ester functionality in the δ200-215 ^{13}C-range.

Although absolute values cannot be calculated due to the absence of an internal standard, the inverse gate ^{13}C spectrum allows for the signal contribution from each of the previously identified regions to be measured and compared. For the three aliphatic regions, signal overlap prevents direct quantification of each region, but this can be mitigated using a modified application of the method developed by Zhang and Gellerstedt (2006) for the quantification of the NMR spectra of lignins. In this method, overlapping regions in the ^{13}C spectra are resolved by their relative intensities in the HSQC spectra, which holds assuming that differences in T_2 relaxation within the region are small, as is often the case for large polymers. Normally, the HSQC integrals would be normalised by only their associated proton counts before being used as percentages but because the present work used edited HSQC, the integrals have also been normalised by their DEPT signal intensities at 135°, i.e. sin (135°)=0.71 for CH, sin (2*135°)=1.00 for CH_2 and 3* sin (135°)* cos^2 (135°) = 1.06 for CH_3. Using this method on the aliphatic regions, as well as quantifying the non-overlapping regions directly, gives relative values of signal contribution as tabulated and presented in Table 1.

Based on the information in Table 1, the alkaline high molecular-weight degradation product is seen to contain a significant amount of carbonylic functionality, specifically 7 ^{13}C-mol%, likely in the form of ketones, as well as a high amount of carboxylic functionality, 13 ^{13}C-mol%, which can be explained from the acid functionality of the precursor sugar acids being incorporated into the polymeric structure. Interestingly, a full 32 ^{13}C-mol% are contained in aromatic structures, which is surprising given the aliphatic nature of the sugar acids which are predicted to be the precursors of the polymer formation. For the aliphatic signals, only

Table 1: Summary of the quantified functionalities of the high molecular-weight sugar product according to the ^{13}C and ^{31}P data. ^{31}P data is depicted in red for clarity.

Functionality	Shift (ppm)	^{13}C-signal (mol %)	^{31}P-signal (mmol g^{-1})
Carbonylic Cq	216–192	7	–
Carboxylic OH	136–134	–	2.4
Carboxylic Cq	192–166	13	–
Aromatic CH	166–100	32	–
Aromatic OH	145–136	–	2.0
Oxygenated CH	84–68	11	–
Oxygenated CH$_2$	68–60	4	–
Aliphatic OH	150–145	–	0.9
Intermediate CH	60–45	9	–
Non-oxygenated CH$_2$	45–25	16	–
Non-oxygenated CH$_3$	25–5	9	–

15 ^{13}C-mol% are unambiguously associated with oxygenated carbons, while a full 25 ^{13}C-mol% are unambiguously non-oxygenated, suggesting significant condensation.

To corroborate the data in Table 1, a second method commonly used in the field to measure chemical functionality, ^{31}P NMR, was employed. In this analysis, hydroxyl functionalities are derivatised with a phosphorylating compound, after which a quantitative ^{31}P NMR pulse sequence is applied. In order to functionalise the hydrophilic high molecular-weight sugar degradation product, a modified version of the protocol by Arnling Bååth et al. (2016) was applied, using ionic-liquids to dissolve two samples of the product under the effects of heating before applying the phosphorylating agent, in the end yielding two spectra, the second of which is presented in Figure 5. Quantifying the regions in these spectra as usual for the protocol and averaging for the duplicate samples shows the structure to contain 0.9 mmol g^{-1} of aliphatic hydroxyls, 2.0 mmol g^{-1} of aromatic hydroxyls and 2.4 mmol g^{-1} of carboxylic hydroxyls with a total hydroxyl content of 5.3 mmol g^{-1}, replicated in Table 1.

3.3 Structural interpretation of the NMR analysis

As seen in the literature (De Bruijn et al. 1986) as well as in the present work, a strongly coloured, highly water soluble and aromatic polymer is formed from glucose in alkaline environments. Similar polymers are likely to be formed from the alkaline degradation products of cellulose during the conditions of kraft pulping.

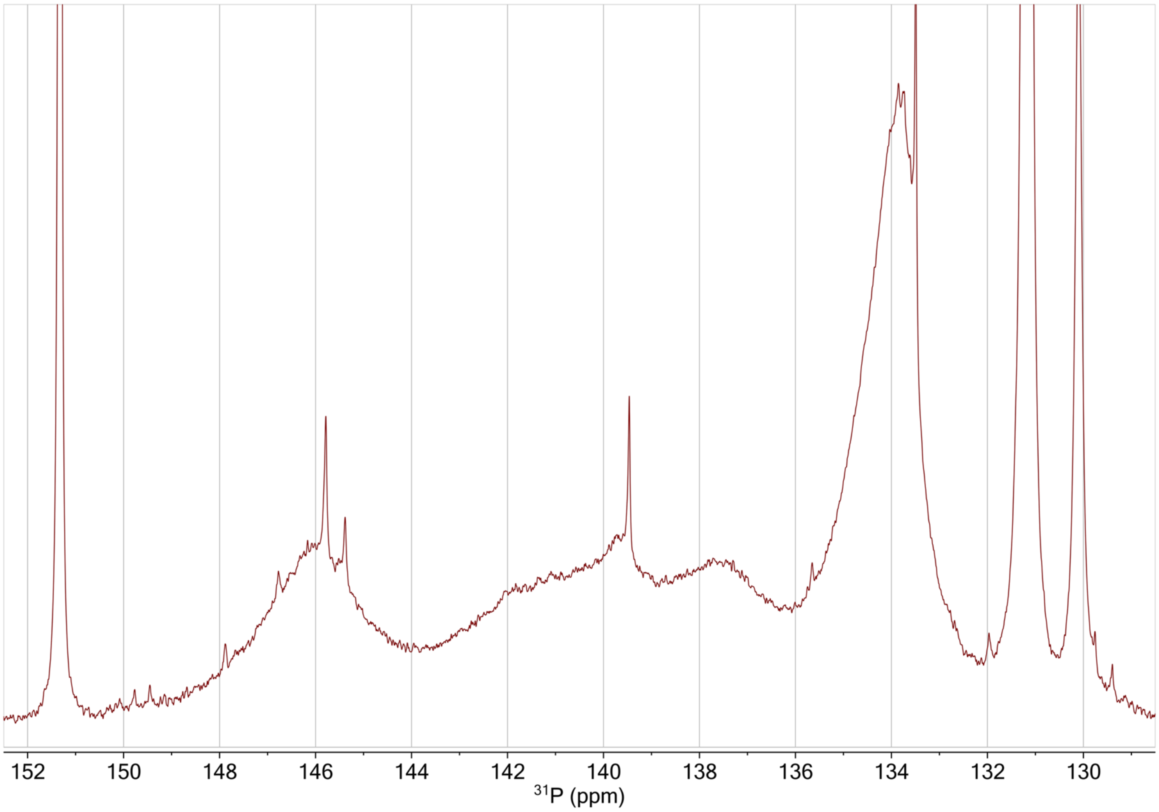

Figure 5: Quantitative inverse gate ^{31}P NMR spectrum of the high molecular-weight sugar degradation product.

Despite good effort across multiple disciplines over the decades, no work so far has been able to fully elucidate the structure of this polymer. Early literature on the nature of this polymer suggested that it is formed from *α*-dicarbonyl intermediaries (Ligett and Deitz 1954) repolymerising to form a melanoidine like substance (Kroh et al. 2008). Recently Luo et al. (2020) and Zhu et al. (2021) was able to acquire more structural information, identifying carboxyl moieties, aldehyde moieties, alcoholic hydroxyl moieties, conjugated double bonds moieties, and saturated alkane moieties to be present in the structure. In the present work, more detailed data has been ascertained, as seen above and summarised in Table 1.

In this section, we will make an attempt to use the novel structural information elucidated by this work, specifically that shown in Table 1, to form a hypothesis as to the structure of the polymeric substance.

3.3.1 Proposed reaction mechanisms

One way to unveil the structure is to follow the pathway of how carbohydrates react during alkaline conditions. It is well established that a dominating source of carbohydrate degradation products are monosaccharides from alkaline hydrolysis and peeling (Figure 1). In this study, the main model has been glucose and our discussion will thus assume it to be the starting point of the reactions, although similar reaction products are likely produced by other monosaccharides (mannose, xylose etc.) as well as by peeling products (these would have an additional double bond between C3 and C4, but would still be able to form enediols and *α*-dicarbonyls as below).

With glucose as a base, it is known that the corresponding 1,2-α-dicarbonyl (I, Figure 6) can be formed through keto-enol tautomerisation followed by *β*-elimination at high temperatures and alkaline conditions, exemplified in Figure 8. The *α*-dicarbonyl can also react further to form metasaccharinic acid (II, Figure 8). In reality, these two compounds are but representatives of a vast and complex palette of degradation products including multiple sugar acids as well as monosaccharides and carboxylic acid derivatives. A more thorough discussion of these degradation patterns is included in the Introduction, particularly in reference to Figures 1–3.

We propose that 6-hydroxymethylfurfural - a cyclic aromatic compound – might form from (I, Figure 6) in the alkaline conditions present, as per Figure 7. If the full range of degradation products are taken into consideration, it is also possible that furfural might be created from pentoses via their corresponding *α*-dicarbonyls. While this might at first glance seem unorthodox in light of the mechanisms

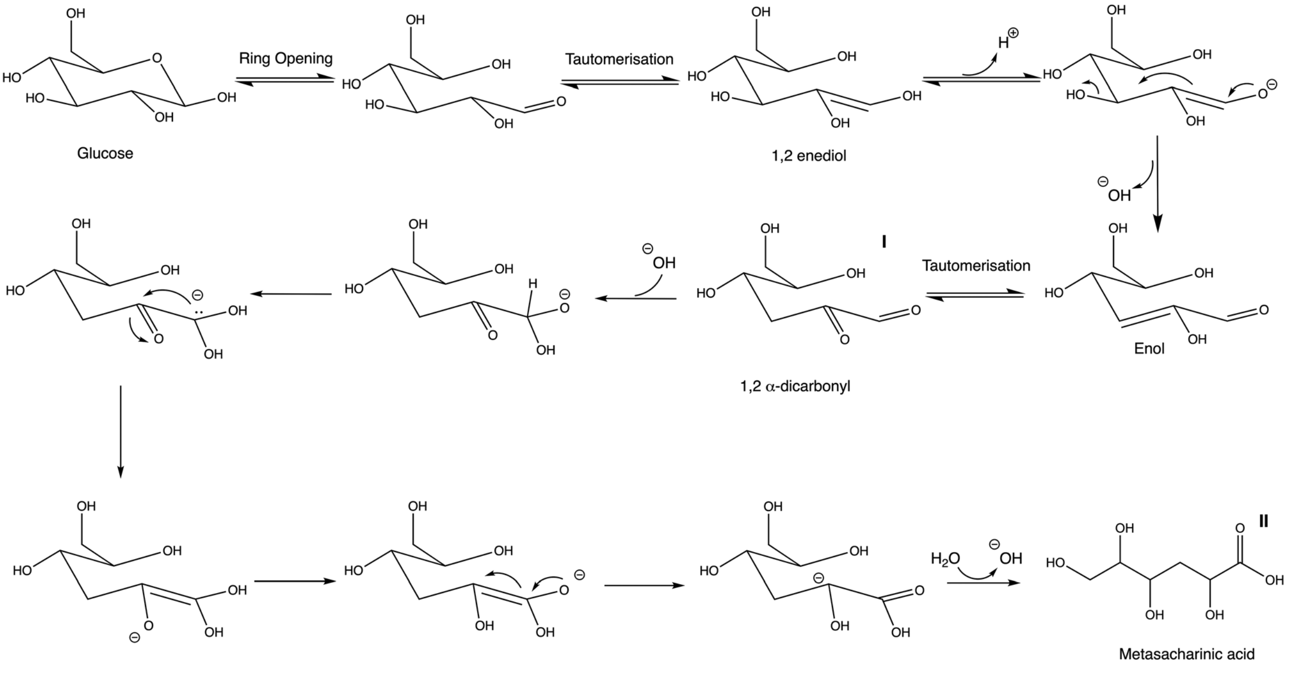

Figure 6: Proposed reactions for the formation of 1,2 *α*-dicarbonyl (I) and metasaccharinic acid (II) from glucose in alkaline conditions. Other sugar acids may also be formed. Components I and II are suggested to react further.

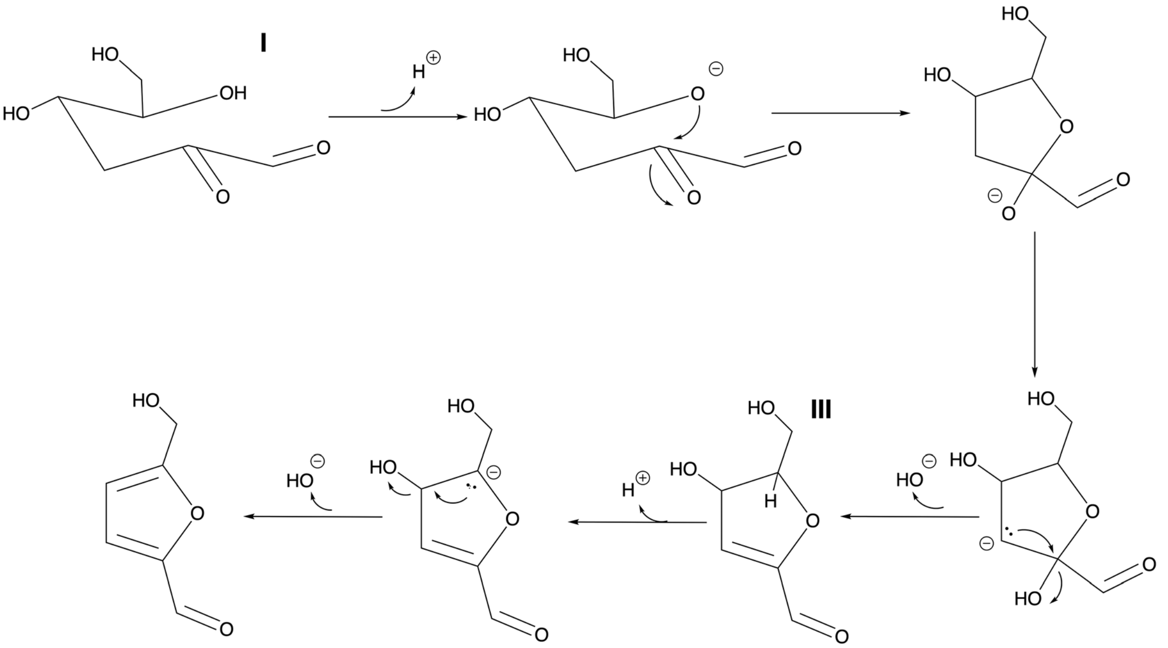

Figure 7: Formation of 6-hydroxymethylfurfural from the 1,2-α-dicarbonyl of glucose (I, Figure 6) in alkaline conditions and at high temperature. Note that a reactive intermediate (III) is created.

presented by De Bruijn et al. (1986), there is evidence to the effect that such structures are formed as per the work of Forsskåhl et al. (1976) and Gellerstedt and Li (1995).

It is possible that the aromatic monomer 6-hydroxymethylfurfural could itself polymerise in alkaline conditions, but the conjugated intermediate (III, Figure 7) might have even more potential for forming an aromatic and conjugated polymer, as exemplified in Figure 8. Take particular note of the fact that this allows for the formation of methylidene and methyl moieties, which are present in the NMR data but are difficult to account for on a mechanistic basis. Also take note of the fact that the polymerisation of (III, Figure 7) results in a highly conjugated system, which is important if we are to account for the spectroscopic data.

In addition, it is possible for sugar acids such as (II, Figure 6) to couple to the polymer, thus accounting for the carboxylic acid content observed in the data. See Figure 9a for a suggested mechanism of how this might occur. As previously mentioned, this would be but one example of such a reaction – in reality, a vast array of sugar acids would be available for similar reactions. Incorporation of carboxylic acid moieties is important not only to account for the NMR data, but also to account for the polymer's solubility over such a broad pH-interval as is observed. An alternative reaction pathway by which carboxylic acid functionality could be incorporated into the polymer is by aldehydes undergoing disproportionation into carboxylic acids and alcohols, as per Figure 9b (Cannizzaro 1853).

3.3.2 Comparison to the proposal of other authors

The proposed reaction mechanisms presented in Figure 6 through Figure 9 differ considerably from previous considerations on the topic of the alkaline sugar degradation polymer. Kroh et al. (2008) proposed a mechanism starting with *α*-dicarbonyls, forming methylglyoxal and then forming a melanoidine-like polymer through aldol condensation. This structure, however, does not seem to account for the presence of carboxylic acid moieties or aliphatic moieties.

Recently, Luo et al. (2020) proposed that low-molecular weight organic acids, aldehydes and ketones participate in aldolisation reactions which are converted into olefin aldehydes in high temperature conditions. These olefin aldehydes then polymerise by means of their unsaturated double bonds, forming a conjugated system rich in aldehydes, some of which are oxidised by air to form carboxylic acids. This mechanism does account for much of the functionality but still fails to account for the significant aliphatic part of the signal. Furthermore, it does not account for the behaviour seen in the older literature, which unambiguously identifies the *α*-dicarbonyls as key intermediaries. Finally, in our proposed mechanism, the carboxylic acid functionality is accounted for without the need of oxidation by air, which could be seen as more parsimonious.

Interestingly, the mechanisms proposed in this paper have more in common with previous work on the topic of humins (acidic sugar degradation polymers) than it has with

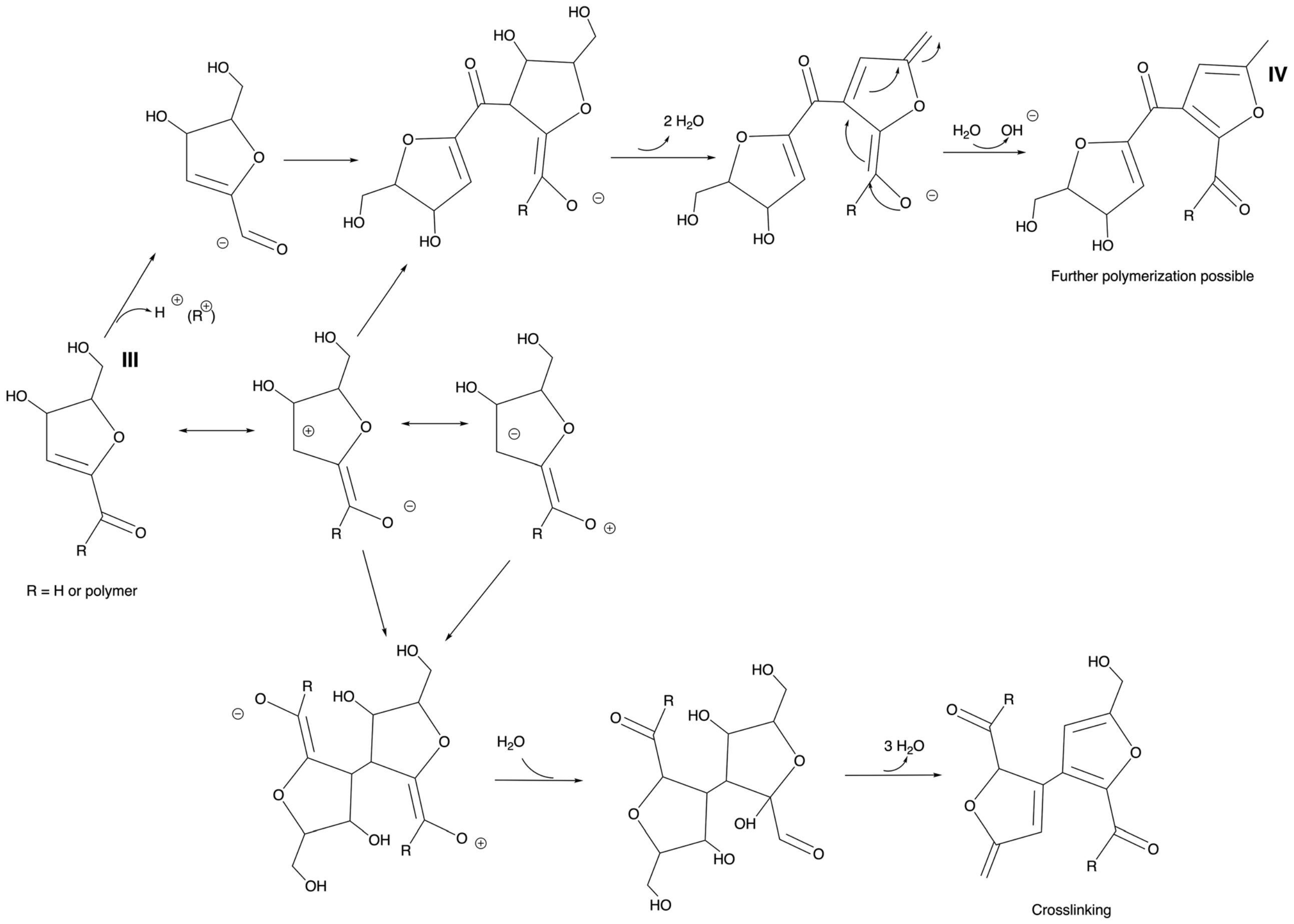

Figure 8: Suggested polymerization reactions of the 6-hydroxymethylfurfural intermediate (III, Figure 7). Note that the reaction product is a highly conjugated, partly aromatic polymer that contains methyl and methylidene groups. Some of the polymer structures (IV, Figure 8) may react further (Figure 9).

literature on the alkaline sugar degradation polymer. Although the exact mechanism for the formation of humins is also not fully known, it is believed to be formed through polymerisation of the methylhydroxyfurfural, levulinic acid and furfural degradation products which are formed from monosaccharides under acidic conditions, with some proposed mechanisms suggesting dioxohydroxyhexanal as an intermediate (de Jong et al. 2025). Of particular interest, note how dehydrated sugars similar in structure to levulinic acid (see Figure 9) are here suggested to account for the carboxylic functionality seen in the NMR data, which again show similarities to the mechanisms suggested for the formation of humins. However, nowhere in the literature of humin formation are *α*-dicarbonyls suggested as intermediates. Rather, hydration of hydroxymethylfurfural or other structures are suggested to form the relevant intermediates (de Jong et al. 2025). The comparison is further corroborated by similarities in the NMR data. In the work of Constant et al. (2024), liquid state HSQC data of industrial humins is presented and regions similar to those presented here in Figure 3 can be observed, with aliphatic, oxygenated and aromatic regions clearly visible. However, in humins, the region observed for the high molecular-weight polymer at δ84-68 ^{13}C-range is notably absent, and differences in the oxygenated region at δ68-60 ^{13}C-range and the aromatic region at δ166-100 ^{13}C-range indicates that the structures, although related, are indeed different.

Furthermore, in a recent series on chromophoric degradation products from hexenuronic acids, Rosenau et al. (2017a, 2017b) were able to demonstrate the formation of ladder-type oligomers consisting of mixed furanoid/benzoid-moieties and with a mixed aromatic/quinoid nature from either Methyl 4-deoxy-β-L-threo-hex-4-enopyranosiduronic acid or from various mixtures of 5-formylfuran-2-carboxylic acid and furan-2- carboxylic acid under acidic conditions. These oligomers were found to be strongly chromophoric, with a yellow tint at even nanomolar concentrations. Structurally, however, they seem to differ considerably from

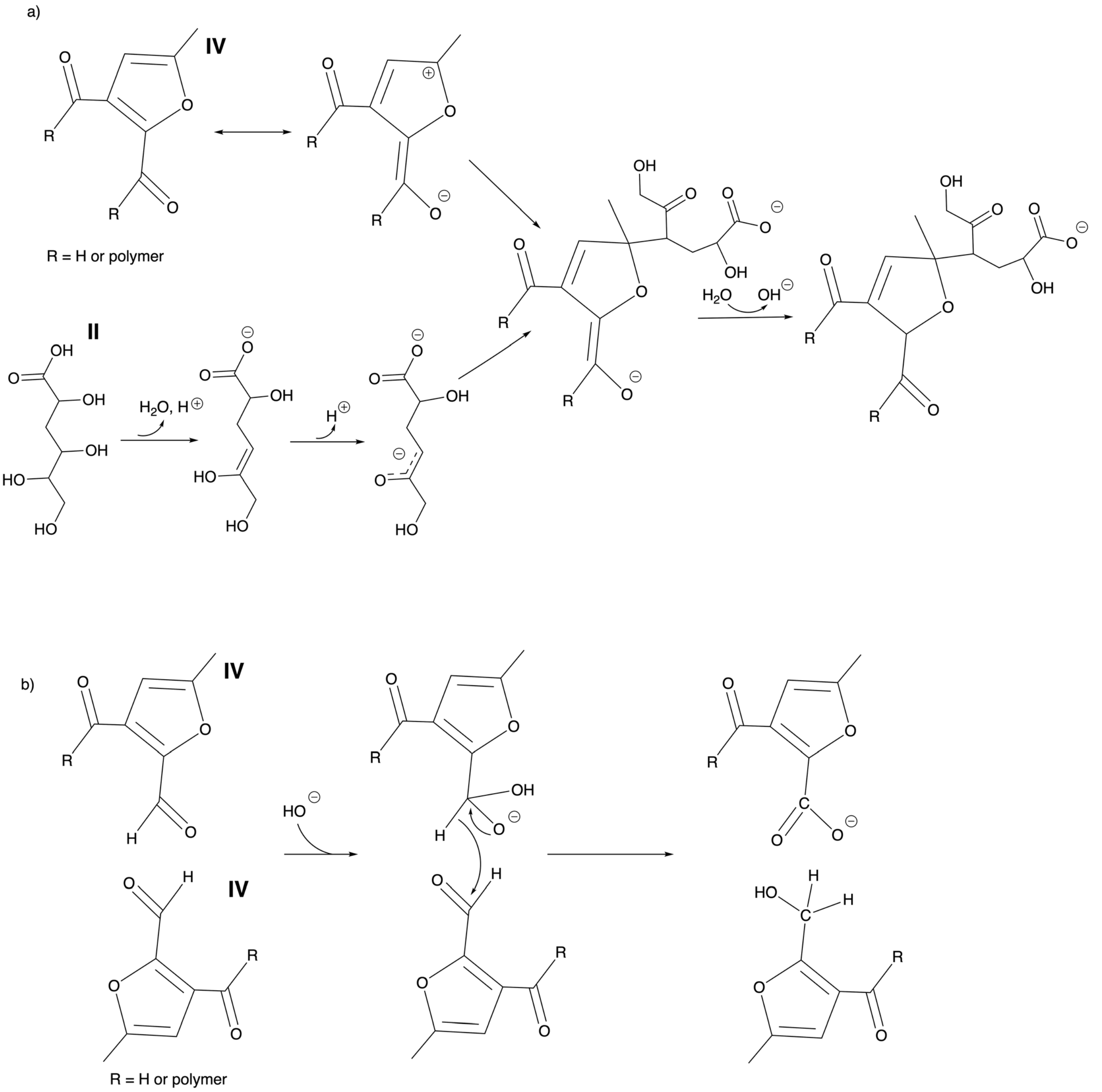

Figure 9: Hypothetical origin of the carboxylic acid functionality of the polymer. a) The carboxylic acid moiety formed from monosaccharides by alkaline reactions (II, Figure 6), is here suggested to couple to the polymeric structure (IV) formed in Figure 8. b) aldehydes in the polymeric structures are disproportioning to carboxylic acids and alcohols.

the alkaline sugar degradation polymer observed in the present work, exhibiting an almost completely aromatic and/or quinoid structure whereas such functionality only accounts for 32 | mol% in the present work. Furthermore, much like humins, but unlike the alkaline high molecular-weight polymer, further reaction saw the formation of a brown film insoluble in any solvent.

Conversely, Urbisch et al. (2018) proposed a mechanism where *α*-ketoglutaraldehyde acts as a key intermediate and 4H-chromen-4-one as well as 2,3-dihydroxybenzaldehyde act as key partners together with typical carbohydrate degradation products to form a polyphenolic system and propose this mechanism to be viable in both acidic and alkaline environments, although consistently assuming an acidic environment in their examples. Interestingly, while 6-hydroxymethyl furfural had long been assumed to be the monomer for both the uncatalyzed and the acidic versions of the high molecular-weight degradation polymer, an earlier work by Kroh (1994) argued against this, suggesting osuloses to be more important to the formation of these versions of the polymer.

3.3.3 Proposed structure of the high molecular-weight sugar degradation product

To summarise, by means of the reaction mechanisms suggested in Figure 6 through Figure 9, we are able to obtain, from monosaccharides, a polymer which:

- is aromatic,
- is highly conjugated,
- contains methyl, methylidene, alcohol and carboxylic acid groups.

As such, it fits well with the NMR data presented in Table 1. A tentative suggested structure based on these mechanisms is presented in Figure 10.

It seems likely that a similar material is formed during kraft pulping and is present in the black liquor. Interestingly, while there are substantial differences between the presented structure and technical lignin (it is based on 5-rings rather than 6-rings; it is connected through carbon-carbon bonds instead of ethers; it contains carboxylic acids unlike lignin), it is in fact similar to technical lignin in terms of colour and NMR-functionality, as can be seen by comparing the data of Figures 3 and 5 with example spectra of Lignoboost kraft lignin, an example HSQC spectrum is provided in Figure S3 and an example ^{31}P spectrum In Figure S4 in the Supplementary Material. It might therefore be possible that kraft lignin, as prepared by Lignoboost (Theliander 2008) or other methods, could consist in part of material with a polysaccharide origin. This could explain certain peculiarities of technical lignin, such as their content of carboxylic acids. It may also explain the poor accountability of lignin inter-units in kraft lignins obtained by NMR, since some of the aromatic signals adopted for the quantitation may actually originate from carbohydrate sources, thereby leading to an underestimation.

3.4 Investigation and comparison of colour profiles using ultraviolet–visible (UV–vis) spectroscopy

The high molecular-weight sugar degradation product obtained from the model compound experiment was seen to be strongly coloured. The UV–vis absorption spectrum product dissolved in water at a concentration of 65 mg l^{-1} is shown in Figure 11a, recalculated to weight-based extinction coefficient per wavelength. The resulting spectrum is seen to have strong colour at all visible wavelengths, but particularly below 400 nm, where the extinction coefficient is >5 l $g^{-1}cm^{-1}$. A hump is seen right after, around 370 nm, rising to a peak at around 260 nm in the UV region.

This colour profile is strikingly similar to earlier absorption spectra seen in our group for the degradation of glucose, although in those cases the high molecular-weight polymer was not separated from the low molecular-weight sugar acids. Still, an interesting example can be seen in Figure S6 in the Supplementary Material, showing the

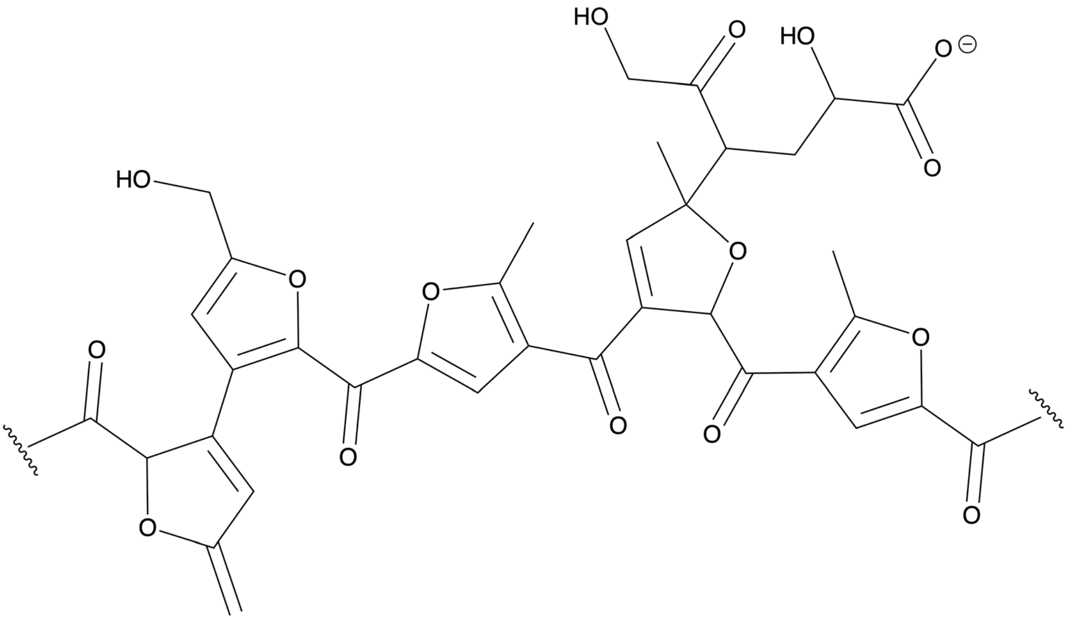

Figure 10: Tentative suggested structure of the polymer created from glucose under alkaline conditions. This structure can be formed from glucose by the reactions presented in Figure 6 through Figure 9.

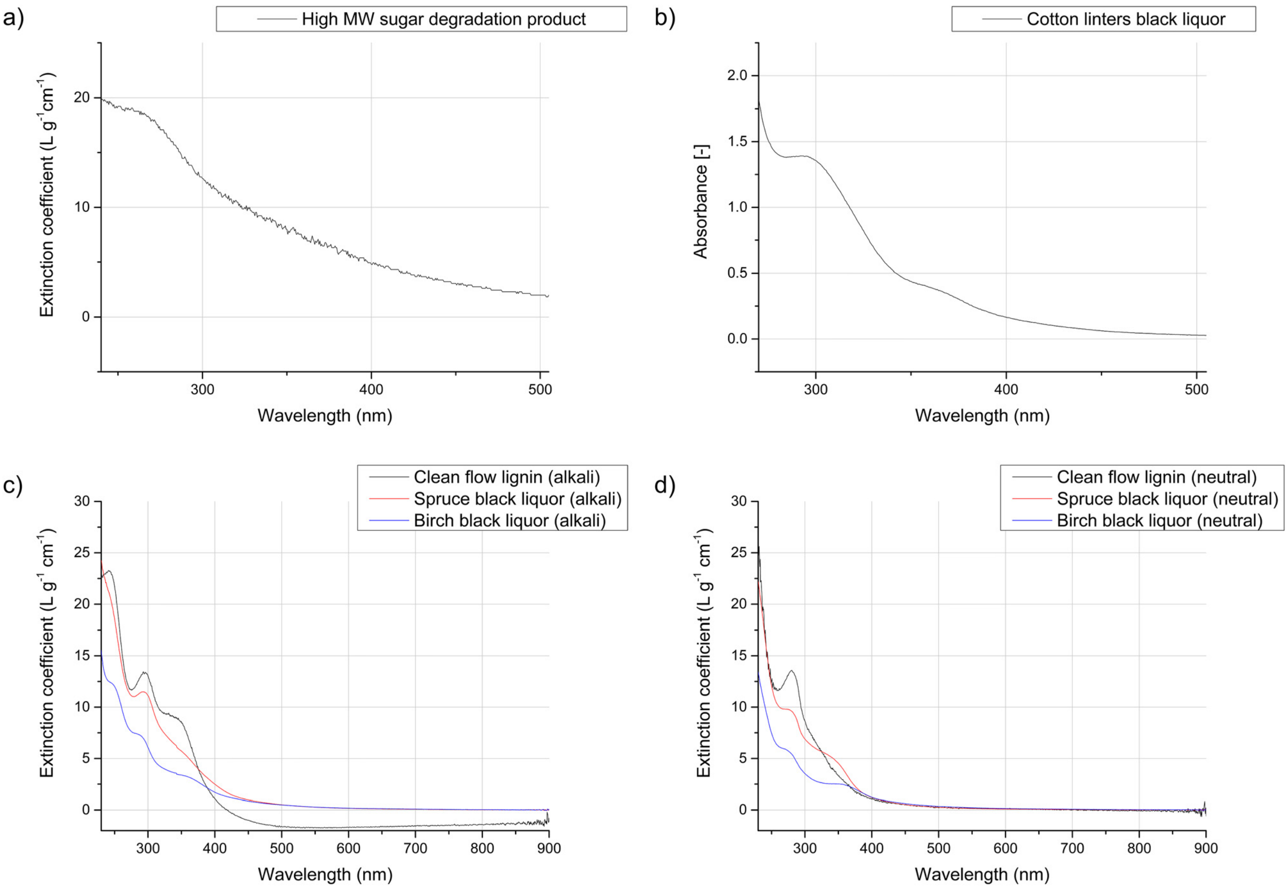

Figure 11: UV-vis spectra of various substances of interest, specifically of the high molecular-weight sugar polymer (a); glucose alkaline degradation products (including small amounts of the high molecular-weight sugar polymer) formed from the kraft cooking of cotton linters (b); clean flow lignin and precipitated lignin from spruce black liquor as well as from birch black liquor, all in the original alkaline forms (c) as well as in the corresponding neutralised forms (d).

absorption spectra of glucose after reaction in alkali at various glucose concentrations. In all cases, significant absorbance is seen above 400 nm, with a bump observed shortly thereafter and a peak observed later at around 260 nm in the UV region. As another point of comparison, an absorption spectrum of various monosugars, after reaction with alkali, is shown in Figure S7 in the Supplementary Material, all of which show a similar profile, albeit with differing extinction coefficients.

One disadvantage with all these model compound experiments, however, is that it is not immediately obvious whether the same behaviour would be seen for polymeric sugars. Although the authors of this work do feel confident in the elementary degradation reaction pathway presented thus far, it would be ideal to corroborate this hypothesis with experimental data. To this end, a UV-vis spectrum from the degradation of cotton linters is provided in Figure 11b. In this experiment, cotton linters were kraft cooked using a white liquor prepared to 18 % EA and 35 % sulphidity at a liquor to wood ratio of 8:1 (corresponding to an [OH-] concentration of 0.56 M and a [HS-] concentration of 0.12 M). The cotton linters were impregnated at 110 °C for 1 h and cooked at 145 °C for another hour and the resulting black liquor collected and subjected to UV-vis analysis. The UV-vis spectrum in question is seen to have colour, particularly below 400 nm, with a bump around 370 nm, rising to a peak around 300 nm.

Comparing the spectrum from cotton linters black liquor with the spectrum from the sugar degradation product, it can be seen to have a similar absorption profile. Unfortunately, given that the black liquor is a mixture of unknown purity, it is not possible to calculate an absorption coefficient for the black liquor solution, making a more thorough comparison with the high molecular-weight polymer impossible. It is, however, striking that the absorption profiles are as similar as they are, showing that it is not an unreasonable hypothesis that the high molecular-weight sugar degradation product is also formed during the kraft cooking of polymeric carbohydrates.

As a final comparison, the UV-vis spectra of precipitated spruce lignin, birch lignin and clean flow lignin are also presented in Figure 11 with the alkaline form presented in (c) and the neutralised form presented in (d). While the spectra observed for these lignin samples are not exactly the same as those seen for the carbohydrates, some similarities can be observed, with the neutralised form showing significant absorption below 400 nm, with a hump closely following (although at 340 nm) and a peak below 300 nm (although at 290 nm). Given these similarities, it might not be unreasonable to believe that these sugar degradation products could be related to certain forms of pseudo-lignin.

3.5 Kappa number determination

Given all of the evidence in the sections above regarding a possible connection to the pseudo-lignin that has been speculated to be formed during kraft cooking of wood, a sample of the high molecular-weight sugar polymer was used for a kappa number determination, a method typically used in the pulping field to quantify lignin content in pulp. Using 80 mg of the product, the kappa number was found to be 257.

Although the kappa number of pure lignin cannot be measured directly, it can be estimated using established values for the consumption of permanganate per lignin C9 unit. According to Li and Gellerstedt (1998), typical consumption values for birch kraft dissolved lignin are in the range of 11.1–11.7 equivalents, with a suggested molecular weight of 183 g mol^{-1}. Since the kappa number analysis is standardised to use permanganate concentrations of 0.02 M (corresponding to 0.1 *N*) the resulting permanganate number (which will be the same as the kappa number under ideal conditions except for the unit) is 623 ml g^{-1}.

As such, the kappa number of the high molecular-weight sugar degradation product is seen to be roughly 40 % of what we would expect from pure lignin. This discrepancy could be explained by the large non-oxygenated aliphatic content of the polymer, as seen in Table 1, totalling 25 ^{13}C-mol% of the structure. Curiously, adding together the aromatic and carbonylic structures (which would be expected to be most prone to reaction with permanganate) in Table 1 yields a total of 39 ^{13}C-mol%, in agreement with the experimental data.

Thus, while the high molecular-weight sugar polymer does not quite display the same magnitude of permanganate consumption as true lignin, it is still large enough that if present in sufficiently large quantities, the high molecular-weight sugar degradation product might indeed be able to act as a form of pseudo-lignin.

4 Conclusions

When any monosaccharide is heated in alkali, coloured compounds are produced in the form of sugar acids, α-dicarbonyls and a high molecular-weight sugar degradation product (De Bruijn et al. 1986). This was also found to be the case in the present study, both when model monosaccharides were heated in alkali and when cotton linters were cooked in white liquor. In either case, a characteristic UV-vis spectrum was obtained where significant absorption was seen below 400 nm, with a hump around 370 nm and a peak below 300 nm. Curiously, it was later found that the purified high molecular-weight sugar degradation product itself gave a similar characteristic spectrum.

In this work, bulk amounts of sugar degradation products were made, and the high molecular-weight sugar degradation product was isolated by means of ultrafiltration or dialysis. The isolated high molecular-weight sugar degradation product was analysed by size exclusion chromatography and found to have a Mw of 40 kDa, after which it was subjected to a quantitative nuclear magnetic resonance analysis, indicating that a full 32 mol% can be attributed to aromatic carbons and a full 25 mol% to aliphatic moieties with significant carbonylic moieties, carboxylic moieties and hydroxylic moieties also being present in the structure as per the data shown in Table 1.

Based on the functionalities obtained from the NMR-study and knowledge of key intermediaries as discussed in the literature, we propose a mechanism for, and a final structure of, the sugar polymer. Specifically, we propose that α-dicarbonyls (which are known to be intermediaries in the polymerisation reaction) can react to form 6-hydroxymethylfurfural as well as conjugated hydroxymethylfurfural intermediates, which can then polymerise in alkaline conditions. Additional functionalities can be introduced through the addition of any of the low molecular-weight sugar acids which are also known to be produced from sugars under alkaline conditions. This would produce an aromatic, highly conjugated, methyl-containing, methylidene-containing, alcohol-containing and carboxylic acid-containing polymer which agrees with the NMR-data observed in this work.

5 Technical significance

Since it is likely to be the case that components which are essentially identical to the compounds characterized here are created during the kraft pulping of wood from carbohydrate degradation products, one can conclude that the carbohydrate components of wood might contribute to the dark colour of black liquor, and possibly also to the colour of unbleached kraft pulp.

It is known that large amounts of carbohydrate degradation products are formed during kraft pulping and that these ultimately end up in the black liquor. It is certainly an attractive possibility, then, to use them as valuable by-products. This work corroborates earlier studies indicating that these components are heterogenous and diverse, and thus the observation that the natural carbohydrate structure can be difficult to use as a raw material for chemical synthesis, or even as feedstock to microbes as is done in fermentation, for example. However, the richness of alcohol moieties makes the material suitable for electrochemical hydrogen production (Qui et al. 2022).

The high molecular-weight fraction that was the main subject of this study appears to be polyphenolic and is therefore not totally unsimilar to kraft lignin. In fact, it might turn out to be the case that some of the technical lignins that are today produced from kraft and soda mills are in fact partly of polysaccharide origin. If so, and if these structures could remain in the pulp by some means, this would corroborate the work of Li and Gellerstedt (1998) and might even explain the origin of at least some of the 'non-lignin' that they named in their work as contributing to the kappa number beside lignin and hexenuronic acid but was unable to elucidate the structure of. It would also corroborate their further suggestion (Li and Gellerstedt 2004) that furan structures in black liquor significantly interfere with the UV-vis based acid-soluble lignin analysis. Additionally, it would also corroborate the work and suggestions of Paulsen-Thorensen et al. (2023) who observed that the existence of so called humin-lignin hybrids would parsimoniously explain abnormalities in the analytical data and properties of organosolv lignins.

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Data availability: The raw data can be obtained on request from the corresponding author.

References

Arnling Bååth, J., Giummarella, N., Klaubauf, S., Lawoko, M., and Olsson, L. (2016). A glucuronyl esterase from *Acremonium alcalophilum* cleaves native lignin-carbohydrate ester bonds. *FEBS Lett.* 590: 2611–2618, https://doi.org/10.1002/1873-3468.12290.

Aro, T. and Fatehi, P. (2017). Tall oil production from black liquor: challenges and opportunities. *Sep. Purif. Technol.* V175: 469–480, https://doi.org/10.1016/j.seppur.2016.10.027.

Bergbauer, M., Eggert, C., and Kraepelin, G. (1991). Degradation of chlorinated lignin compounds in a bleach plant effluent by the white-rot fungus *Trametes versicolor*. *Appl. Microbiol. Biotechnol.* 35: 105–109, https://doi.org/10.1007/bf00180645.

Berglund, J., Azhar, S., Lawoko, M., Lindström, M.E., Vilaplana, F., Wohlert, J., and Henriksson, G. (2019). The structure of galactoglucomannan impacts the degradation under alkaline conditions. *Cellulose* 26: 2155–2175, https://doi.org/10.1007/s10570-018-1737-z.

Cannizzaro, S. (1853). Ueber den der Benzoësäure entsprechenden alkohol [On the alcohol corresponding to benzoic acid]. *Adv. Cycloaddit.* 88: 129–130, https://doi.org/10.1002/jlac.18530880114.

Constant S., Lancefield C.S., Vogelzang W., Pazhavelikkakath Purushothaman R.K., Frissen A.E., Houben K., de Peinder P., Baldus M., Weckhuysen B.M., van Es D.S, et al. (2024) Molecular structure and composition elucidation of an industrial humin and its fractions. *Green Chem.* 26: 7739–7751, https://doi.org/10.1039/d4gc00429a.

da Silva Perez, D. and van Heiningen, A. (2015). Prediction of alkaline pulping yield: equation derivation and validation. *Cellulose* 22: 3967–3979, https://doi.org/10.1007/s10570-015-0735-7.

De Bruijn, J.M., Kieboom, A.P.G., Van Beckum, H., and Van der Poel, P.W. (1986). Reactions of monosaccharides in aqueous alkaline solutions. *Sugar Technol. Rev.* 13: 21–52.

de Jong, E., Mascal, M., Constant, S., Claessen, T., Tosi, P., and Mija, A. (2025). The origin, composition and applications of industrial humins – a review. *Green Chem.* 27: 3136–3166, https://doi.org/10.1039/d4gc06244b.

Fitzpatrick, S.W. (1997). Production of levulinic acid from carbohydrate-containing materials. *US patent* 5: 105.

Forsskåhl, I., Popoff, T., and Theander, O. (1976). Reactions of ᴅ-xylose and ᴅ-glucose in alkaline aqueous solutions. *Carbohydr. Res.* 48: 13–21, https://doi.org/10.1016/s0008-6215(00)83510-7.

Gellerstedt, G. and Li, J. (1995). Xylan degradation products from birch kraft pulp. In: *8th Int. symp. wood pulping chem.*, Vol. 1. Proceedings, Helsinki, Finland, pp. 533–537.

Henriksson, G., Germgård, U., and Lindström, M. (2024). A review on chemical mechanisms of kraft pulping. *Nord. Pulp Pap. Res. J.* 39: 297–311.

Irfam, M., Butt, T., Imtiaz, N., Abbas, N., Khan, R.A., and Shafique, A. (2017). The removal of COD, TSS and colour of black liquor by coagulation – flocculation process at optimized pH, settling and dosing rate. *Arab. J. Chem.* V10: S2307–S2318.

Johansson, A. (1982). By-product recovery and valorization in the kraft industry: a review of current trends in the recovery and use of turpentine and tall oil derivatives. *Biomass* V2: 103–113.

Keijbets, M.J.H. and Pilnik, W. (1974). Betaelimination of pectin in the presence of anions and cations. *Carbohydr. Res.* 33: 359–362, https://doi.org/10.1016/s0008-6215(00)82815-3.

Kienberger, M., Maitz, S., Pichler, T., and Demmelmayer, P. (2021). Systematic review on isolation processes for technical lignin. *Processes* 9: 804–821, https://doi.org/10.3390/pr9050804.

Kroh, L.W., Fiedler, T., and Wagner, J. (2008). α-Dicarbonyl compounds – key intermediates for the formation of carbohydrate-based melanoidins. *Ann. N.Y. Acad. Sci.* 1126: 210–215, https://doi.org/10.1196/annals.1433.058.

Kroh, L.W. (1994). Caramelisation in food and beverages. *Food Chem.* 51: 373–379, https://doi.org/10.1016/0308-8146(94)90188-0.

Kumar, H. and Alén, R. (2015). Recovery of aliphatic low-molecular- mass carboxylic acids from hardwood kraft black liquor. *Sep. Pur. Technol.* V142: 293–298.

Li, J. and Gellerstedt, G. (1998). On the structural significance of the kappa number measurement. *Nord. Pulp Pap. Res. J.* 13: 153–158, https://doi.org/10.3183/npprj-1998-13-02-p153-158.

Li, J. and Gellerstedt, G. (2004). Acid soluble lignin content in kraft pulps, an artifact. In: Jin, Y.C., and Xie, H.F. (Eds.), *2nd international symposium on technologies of pulping, papermaking and biotechnology on fiber plants. Proceedings*. Nanjing Forestry Univ, Nanjing, pp. 53–57.

Ligett, R.W. and Deitz, V.R. (1954). Color and turbidity of sugar products. *Adv. Carbohydr. Chem.* 9: 247–284, https://doi.org/10.1016/s0096-5332(08)60377-x.

Luo, W.J., Lu, H.Q., Lei, F.H., Cheng, L.Y., Li, K., and Li, W. (2020). Structural elucidation of high-molecular-weight alkaline degradation products of hexoses. *Food. Sci. Nutr.* 8: 2848–2853, https://doi.org/10.1002/fsn3.1584.

MacLeod, J.M. and Schroeder, L.R. (1982). Alkaline degradation of cellobiose, 3,6-anhydro-4-0-(β-D-glucopuranosyl)-D-glucose, 3,6-anhydro-4-O-methyl-D-glucose, and D-glucose[1]. *J. Wood Chem. Technol.* 2: 187–205, https://doi.org/10.1080/02773818208085129.

Nieminen K., Paananen M. and Sixta H. (2014) Kinetic model for carbohydrate degradation and dissolution during kraft pulping *Ind. Eng. Chem. Res.* 53: 11292–11302, https://doi.org/10.1021/ie501359p.

Paulsen-Thorensen, P., Lange, H., Rova, U., Christakopoulos, P., and Matsakas, L. (2023). Covalently bound humin-lignin hybrids as important novel substructures in organosolv spruce lignins. *Int. J. Biol. Macromol.* 233: 123471, https://doi.org/10.1016/j.ijbiomac.2023.123471.

Qui, Z., Martin-Yerga, D., Lindén, P.A., Henriksson, G., and Cornell, A. (2022). Green hydrogen production via electrochemical conversion of components from alkaline carbohydrate degradation. *Int. J. Hydrogen Energy* V47: 3644–3654.

Quintas, M.A.C., Brandâo, T.R.S., and Silva, C.L.M. (2007). Modelling colour changes during caramelization reaction. *J. Food Eng.* V83: 483–491.

Ragnar, M., Henriksson, G., Lindström, M.E., Wimby, M., and Süttinger, R. (2013). Pulp. In: *Ullman encyclopedia of industrial chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA., Weinheim, Germany, pp. 1–89.

Redeborn, M. and Wernqcist (1998). Adaptable calculation method for segregation of contaminants in vapours formed from Black liquor. *Nord. Pulp Pap. Res. J.* V 13: 172–179.

Rosenau, T., Potthast, A., Zwirchmayr, N.S., Hettegger, H., Plasser, F., Hosoya, T., Bacher, M., Krainz, K., and Dietz, T. (2017a). Chromophores from hexeneuronic acids: identification of HexA-derived chromophores. *Cellulose* 24: 3671–3687, https://doi.org/10.1007/s10570-017-1397-4.

Rosenau, T., Potthast, A., Zwirchmayr, N.S., Hosoya, T., Hettegger, H., Bacher, M., Krainz, K., Yoneda, Y., Plasser, F., and Dietz, T. (2017b). Chromophores from hexeneuronic acids: synthesis of model compounds and primary degradation intermediates. *Cellulose* 24: 3703–3723, https://doi.org/10.1007/s10570-017-1396-5.

Saari, J., Sermyagina, E., Kaikko, J., Haidar, Hamaguchi M., and Vakkilainen, E. (2021). Evaluation of the energy efficiency improvements potential through back-end heat recovery in the kraft recovery boiler. *Energies* 14: 1550–1570, https://doi.org/10.3390/en14061550.

Sjöström, E. (1981). *Wood chemistry: fundamentals and applications*. Academic Press, Inc., Orlando, Florida, U.S.A, pp. 43.

Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., and Vuorinen, T. (1995). Characterisation of 4-deoxy-β-L-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by 1 H and 13C NMR spectroscopy. *Carbohyd. Res* 272: 55–71, https://doi.org/10.1016/0008-6215(95)96873-m.

Theliander, H. (2008). *Withdrawing lignin from Black liquor by precipitation, filtration and washing*. Nordic Wood Biorefinery Conference, Stockholm, Sweden, pp. 36–42.

Urbisch, A., Einhorn-Stoll, U., Kastner, H., Drusch, S., and Kroh, L.W. (2018). Formation of phenolic compounds from d-galacturonic acid. *J. Agric. Food Chem.* 66: 11407–11413, https://doi.org/10.1021/acs.jafc.8b04158.

Velaga B., Nageswara R.P. (2022) Levulinic acid production from furfural: process development and techno-economics. *Green Chem.* 24: 3326–3343, https://doi.org/10.1039/d2gc00089j.

Zhang, L. and Gellerstedt, G. (2006). Quantitative 2D HSQC NMR determination of polymer structures by selecting suitable internal standard references. *Magn. Reson. Chem.* 45: 37–45, https://doi.org/10.1002/mrc.1914.

Zhu, W. and Theliander, H. (2015). Precipitation of lignin from softwood Black liquor: an investigation of the equilibrium and molecular properties of lignin. *BioResources* 10: 1696–1714, https://doi.org/10.15376/biores.10.1.1696-1715.

Zhu, Z., Li, K., and Li, W. (2021). Preliminary structural analysis of high molecular weight alkaline degradation products of sucrose. *Sugar Tech* 23: 461–465, https://doi.org/10.1007/s12355-020-00902-2.

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