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Formation of 5-methylfurfural and 2-acetylfuran from lignocellulosic biomass and by Cr^{3+}-catalyzed dehydration of 6-deoxyhexoses

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ABSTRACT

During autocatalyzed steam explosion of lignocellulose, polysaccharides in the cell wall are hydrolyzed and dehydrated to form various furaldehydes. In addition to furfural, 5-methylfurfural and 2-acetylfuran were identified in condensates from autocatalyzed steam explosion of Scandinavian softwood (Norway spruce, *Picea abies*). The presence of 5-methylfurfural can be explained by an acid-catalyzed dehydration of 6-deoxyaldohexoses, which are known to be present in lignocellulosic biomass. However, the presence of 2-acetylfuran cannot be explained by previously published reaction mechanisms since the required substrate (a 1-deoxyhexose or a 1-deoxyhexosan) is not known to be present in lignocellulosic biomass. In model experiments, it was shown that 2-acetylfuran is formed from rhamnose and fucose upon heating in the presence of the Lewis acid Cr^{3+}. Possible reaction pathways for the formation of 2-acetylfuran from 6-deoxyaldohexoses are suggested. This reaction can potentially enable the targeted production of 2-acetylfuran from renewable biomass feedstocks.

1. Introduction

Steam explosion is a physicochemical process used for breaking down biological material for processing into *e.g.* chemicals or energy carriers [1,2]. The steam explosion process was originally introduced in 1926 for producing fiberboard (trade name "Masonite") from wood [3–5] and has later been suggested as a paper fiber manufacturing ("pulping") process [6,7]. Already in 1932, steam explosion was suggested as a method for obtaining fermentable sugars from wood [8] and has later been suggested as a pretreatment process to reduce the fiber wall recalcitrance before enzymatic hydrolysis of wood [1,2,9,10]. In industrial scale, steam explosion is also used for pretreatment of mixed organic waste before biogas digestion [11–13] and for the manufacture of "brown" biofuel pellets from wood [14,15].

Steam explosion of wood is known to cause degradation of hemicelluloses [1,10], forming furfural from the wood pentosans and 5-hydroxymethylfurfural (5-HMF) from the (primarily non-cellulosic) wood hexosans. The volatile furaldehydes are found predominantly in the steam explosion condensate, which also will contain other volatile organic compounds and should not be released to the environment without effluent treatment. Furaldehydes are known to inhibit microbial growth [16,17] and may pose a challenge to biological effluent treatment systems and to the fermentation of sugars to *e.g.* ethanol. However, if these furaldehydes are formed in sufficient quantities they can be efficiently isolated and may form an additional revenue stream for a biofuel plant or a biorefinery using steam explosion to pretreat wood.

Furfural and 5-hydroxymethylfurfural have been considered some of the most promising platform chemicals from carbohydrate-containing biomass raw materials [18]. Furfural, the first furaldehyde to be isolated and identified was discovered by Döbereiner [19], and its formation by acid treatment of plant material was discovered by Stenhouse [20]. It is one of the rather few bulk chemicals produced using lignocellulosic biomass as raw material. The current world production is estimated to around 300 000 metric tons/year, with China, South Africa and the Dominican Republic being the major producers [21]. Furfural and its six-carbon analog 5-hydroxymethylfurfural (5-HMF) have recently gained considerable interest, with a noticeable increase in publications on furfural and 5-HMF since the early 2000s [22,23]. Furfural is produced industrially by hot acid treatment of lignocellulosic agricultural residues, typically corncobs or sugarcane bagasse. The feedstock is acidified and heated with steam while a mixed vapor containing >90% water, up to 6% furfural and various other volatile

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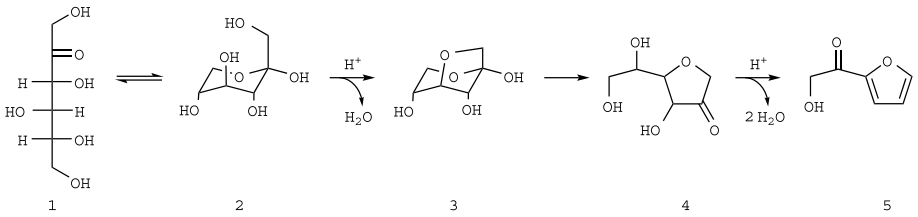


Scheme 1. Van Putten et al.'s proposed reaction pathway for the formation of 2-hydroxyacetylfuran **5** from D-sorbose **1** [41].

byproducts is vented from the reactor and condensed. The condensate is then distilled to yield >98% furfural [24–26] containing minor amounts of 5-methylfurfural (5-methylfuraldehyde, 5MF) and 2-acetylfuran (2AF, furyl methyl ketone) [26]. While 5-methylfurfural is mainly used as a flavoring agent, 2-acetylfuran is also used in the synthesis of HIV protease inhibitors [27,28] and antibiotics [29].

It is well known that the primary wall of lignified plant cells contains 6-deoxyaldohexose residues like L-rhamnan and L-fucan [30]. Thus, the presence of 5-methylfurfural in commercial furfural samples can be explained by assuming that 5-methylfurfural is formed from 6-dexoy-hexoses by the open-chain mechanism proposed for the formation of furfural from aldopentoses [31] and for the formation of 5-HMF from aldohexoses [22]. However, the presence of 2-acetylfuran in furfural samples is somewhat enigmatic.

According to Zeitsch [26], the 2-acetylfuran content in commercial samples ranges between 10% and 40% of the 5-methylfurfural content, and 2-acetylfuran is claimed to be formed from 1-deoxyhexoses (1-methyl pentoses) by the same mechanism as the more common furaldehydes (furfural and 5-HMF) are formed [24–26]. However, this reaction pathway is not very likely since 1-deoxyhexosans – unlike 6-deoxyhexosans – have not been identified in significant amounts in common lignocellulose raw materials [30].

The mechanism for the formation of furfural and related furaldehydes from glycans is well understood, although the details of the mechanism aren't completely elucidated. It is, however, generally recognized that the α carbon of the furaldehyde is formed from C(1) of the sugar [32]. For an in-depth review of the mechanistic details of furfural formation, see *e.g.* Danon et al. [31] and for the details of 5-HMF formation see *e.g.* van Putten et al. [22]. For the open-chain mechanism [33–35], it seems as if the formation of a 1,2-enediol tautomer is the initial and rate-limiting step [31,36]. Whether the reaction then proceeds via an open-chain route as proposed by Feather and Harris [35], or whether it proceeds via the formation of the keto isomer and a ring closure forming a hemiketal as proposed by Ahmad et al. [36] is still not quite determined [31]. There are indications [37] that the formation of 5-HMF from ketoses may follow a somewhat different pathway than the formation of furaldehydes from aldoses.

A 2-acetylfuran analog, 2-hydroxyacetylfuran (2HAF), was isolated by Miller and Cantor [38] after acid-catalyzed dehydration of sucrose or glucose, and Moreau et al. [39] proposed a mechanism for the formation of 2-hydroxyacetylfuran from the 1,2-enediol tautomer via a 2,3-enediol intermediate and a 2,3-diketone intermediate. However, neither this mechanism can explain the presence of 2-acetylfuran in furfural samples since according to this mechanism C(1) of the sugar would form the hydroxymethyl group of 2-hydroxyacetylfuran, and this would again require the presence of 1-deoxyhexosans in the raw material for 2-acetylfuran to be formed. On the other hand, van Putten et al. [40] showed, by converting D-[6–^{13}C]-sorbose to 2-hydroxyacetylfuran, that it is C(6) of the sugar which forms the hydroxymethyl group of 2-hydroxyacetylfuran. This led them to propose an alternative pathway (Scheme 1) via a bicyclic intermediate, 1,4-anhydro-α-D-sorbopyranose **3** [41].

In this article we report on the occurrence of 5-methylfurfural and 2-acetylfuran in condensates from steam explosion of softwood. We also report on the formation of 2-acetylfuran from the 6-deoxyhexoses L-rhamnose and L-fucose in model experiments, and we suggest possible reaction routes for the formation of 2-acetylfuran by acid-catalyzed dehydration of 6-deoxyhexoses.

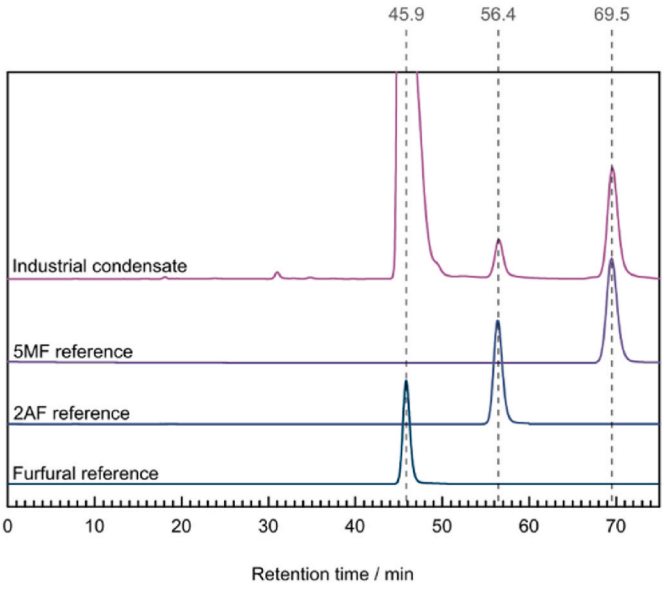


Fig. 1. Chromatograms (283 nm signal) of the industrial steam explosion condensate and the furan standards. 5 MF: 5-methylfurfural, 2AF: 2-acetylfuran. Agilent Hi-Plex H column.

2. Results and discussion

2.1. Analysis results

The HPLC chromatogram (283 nm trace) of the industrial condensate is shown in Fig. 1. In addition to the expected furfural peak at 45.9 min, two other UV-absorbing peaks of significant size can be seen.

The λ_{max} values of the peaks at 56.8 ± 0.4 min (λ_1 = 273 nm, λ_2 = 226 nm) and at 70.0 ± 0.5 min (λ_1 = 291 nm, λ_2 = 226 nm) indicated furan-like structures. After analyzing reference compounds of furans reported to be found in commercial furfural samples, it was found that the retention times and the UV spectra of the substances were in complete agreement with the retention times and the UV spectra of 2-acetylfuran and 5-methylfurfural, respectively (Figs. 1 and 3).

Considering that 1-deoxyhexosans – the postulated substrate for the formation of 2-acetylfuran – have not been identified in significant amounts in common lignocellulose materials [30] and that there is evidence of the formation of 2-hydroxyacetylfuran from ketohexoses where C(6) forms the α carbon [40,41], it was decided to investigate whether 2-acetylfuran could be formed by acid-catalyzed dehydration of 6-deoxyhexoses which are known to occur in wood carbohydrate polymers. The two 6-deoxyaldohexoses reported to have been found in lignified plant cell wall polymers (L-rhamnose and L-fucose) [30] were chosen for this investigation.

In the model experiments, addition of 6 mM $CrCl_3$ gave a strong increase in furan yield compared to the samples without added $CrCl_3$,

Table 1
Furan yields.

Sample	mmol/mol sugar added				mmol/mol sugar degraded
	Residual sugar	2-acetylfuran	5-methylfurfural	Sum furans	Sum furans
Rhamnose reference (DI H_2O)	845 ± 5	n.d.	4.7 ± 0.5	4.7 ± 0.5	30 ± 3
Fucose reference (DI H_2O)	978 ± 9	0.003	2.0 ± 0.2	2.0 ± 0.2	92 ± 10
Rhamnose + 2 mM H_2SO_4	851 ± 7	0.002	6.8 ± 0.5	6.8 ± 0.5	45 ± 4
Fucose + 2 mM H_2SO_4	983 ± 14	0.013	3.3 ± 0.3	3.3 ± 0.3	197 ± 18
Rhamnose + 2 mM H_2SO_4 + 6 mM Cr^{3+}	90 ± 10	77.0 ± 3.1	256 ± 13	333 ± 16	366 ± 17
Fucose + 2 mM H_2SO_4 + 6 mM Cr^{3+}	184 ± 20	36.2 ± 2.1	300 ± 14	336 ± 16	412 ± 20

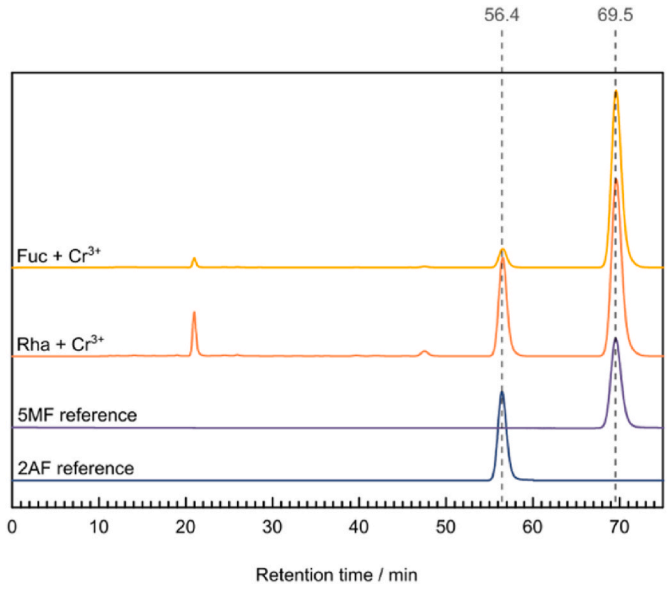


Fig. 2. Chromatograms (283 nm signal) of model experiment samples with added Cr^{3+}. Fuc: fucose, Rha: rhamnose, 5 MF: 5-methylfurfural, 2AF: 2-acetylfuran. Agilent Hi-Plex H column.

and a strong decrease in the amount of residual sugar in the sample (Table 1). In addition to the expected 5-methylfurfural peak at 70.0 ± 0.5 min, a significant peak was observed in the chromatogram at 56.8 ± 0.4 min, the retention time of 2-acetylfuran (Fig. 2). The substance had a UV spectrum indistinguishable from that of the 2-acetylfuran reference (Fig. 3b) and was therefore identified as 2-acetylfuran.

All samples without added Cr^{3+} – except the rhamnose sample without any addition of acid – showed a minor UV-absorbing peak at 56.8 ± 0.4 min (data not shown). Due to the very weak signal, UV spectra could not be recorded, but given the identification of 2-acetylfuran in the samples with added Cr^{3+}, these peaks were tentatively identified as 2-acetylfuran.

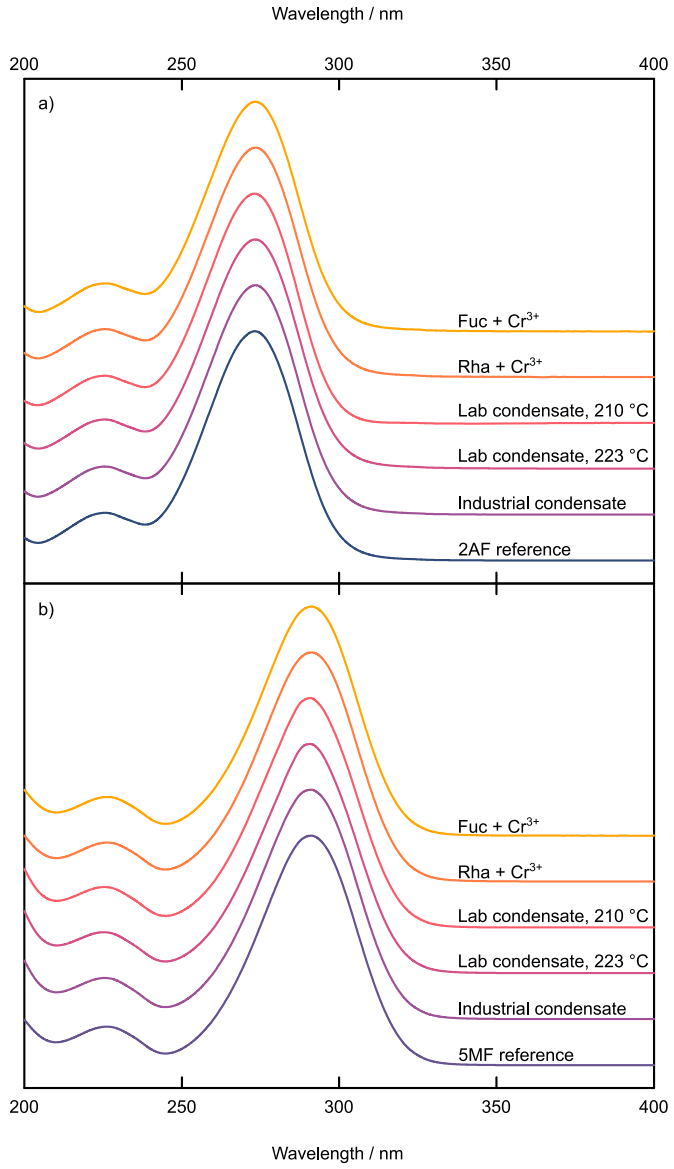


Fig. 3. Comparison of the UV spectra of 2-acetylfuran (2AF) and 5-methylfurfural (5 MF) reference samples, and of the substances identified as such in steam explosion condensates and in the model substance experiments. **a)** RT = 56.8 ± 0.4 min (2AF retention time), **b)** RT = 70.0 ± 0.5 min (5 MF retention time).

To confirm the results from the HPLC analyses, the samples with added Cr^{3+} were analyzed by ^1H NMR. The NMR spectra (Fig. 4) show that both samples contained 2-acetylfuran in addition to 5-methylfurfural (see Fig. 5).

Furan yields are given in Table 1. While the total furan (5 MF + 2AF) yield on added carbohydrate was identical within experimental error for both samples with added Cr^{3+} (333 ± 16 mmol/mol for rhamnose, 336 ± 16 mmol/mol for fucose), the 2-acetylfuran yield was noticeably higher for the rhamnose sample than for the fucose sample (77 ± 3 mmol/mol and 36 ± 2 mmol/mol, respectively). Table 1 also shows an increase in yield on sugar degraded upon addition of Cr^{3+}, indicating an improved specificity for furan formation.

2.1. Mechanistic considerations

The initial and rate-limiting step of one of the recognized mechanisms for the formation of furfural and 5-hydroxymethylfurfural from pentoses and hexoses respectively is the keto-enol tautomerism [31,36],

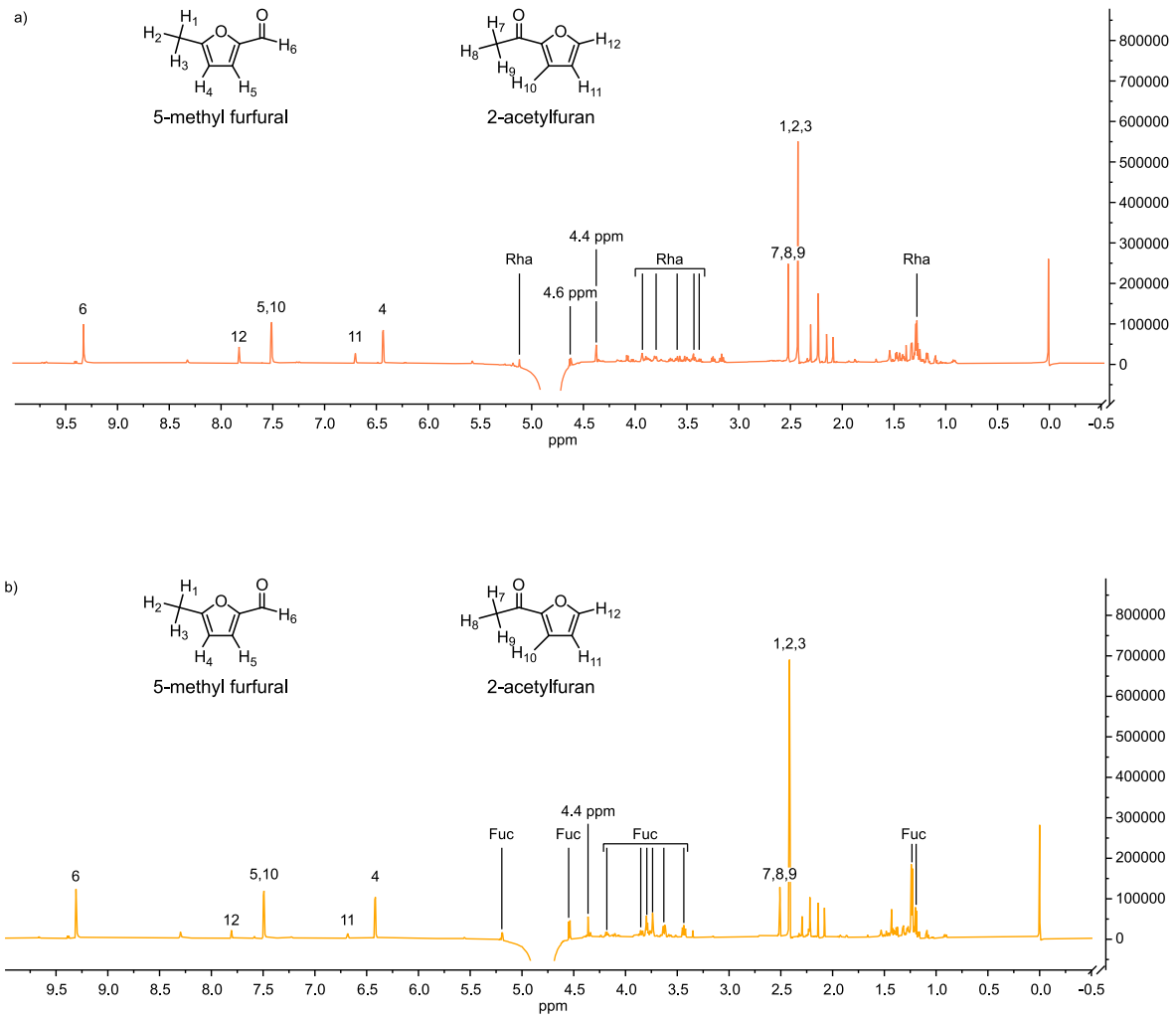


Fig. 4. ^{1}H NMR spectra of the **a)** rhamnose + Cr^{3+} sample and **b)** fucose + Cr^{3+} sample. Rha: rhamnose; Fuc: fucose.

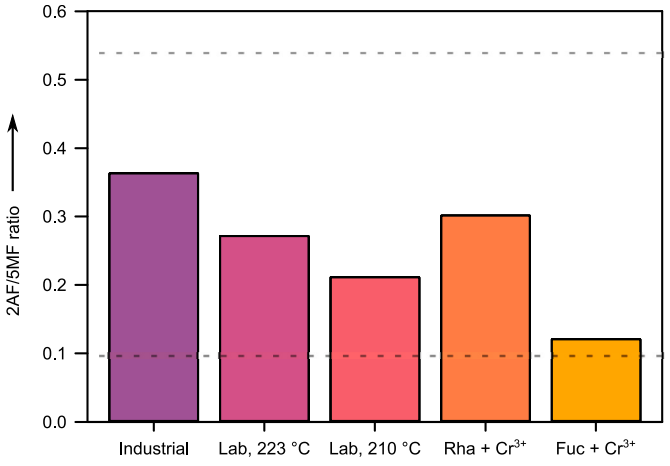


Fig. 5. 2-Acetylfuran/5-methylfurfural ratio in the analyzed samples. Dotted horizontal lines show maximum and minimum ratios found in the literature [26].

and the α carbon on the furan is formed from C(1) on the carbohydrate by a 2,5-dehydration. It is reasonable to assume that the formation of 5-methylfurfural from 6-deoxyhexoses follows the same mechanism. Since Cr^{3+} has been shown to promote the enolization of xylose and the formation of furfural from xylose [42], this can explain the strong increase in 5-methylfurfural yield upon addition of Cr^{3+}. However, it still does not explain the formation of 2-acetylfuran.

While it is impossible to ascertain whether the hydroxyacetyl group on 2-hydroxyacetylfuran is be formed from C(1) and C(2) or from C(5) and C(6) on the hexose unless isotope-labeled substrates are used, the acetyl group on 2-acetylfuran must be formed from C(5) and C(6) on the deoxyhexose. This requires that the furan ring is formed by a 1,4-dehydration rather than by a 2,5-dehydration which is the accepted reaction route for the formation of furfural, 5-hydroxymethylfurfural or 5-methylfurfural.

If the keto-enol tautomerization is promoted by Cr^{3+}, this should promote the formation of L-rhamnulose (6-deoxy-L-fructose) from rhamnose and L-fuculose (6-deoxy-L-tagatose) from fucose, and also other 6-deoxysugars via multiple keto-enol isomerizations. The monosaccharide region of the chromatograms showed multiple peaks for the samples with added Cr^{3+} (Fig. 6). This is interpreted as a strong indication of isomerization of the substrate. The NMR spectra (Fig. 4) supported the indications of carbohydrate isomerization. Both NMR spectra show an unidentified signal at 4.4 ppm, and the spectrum for the rhamnose + Cr^{3+} sample shows a minor signal at 4.6 ppm consistent with H(1) on fucose.

One alternative for a 1,4-dehydration could then be the formation of the corresponding deoxyhexulose by the keto-enol isomerization, followed by a direct 1,4-dehydration of the deoxyhexulose similar to the route suggested by van Putten et al. [41] (Scheme 1). However, a

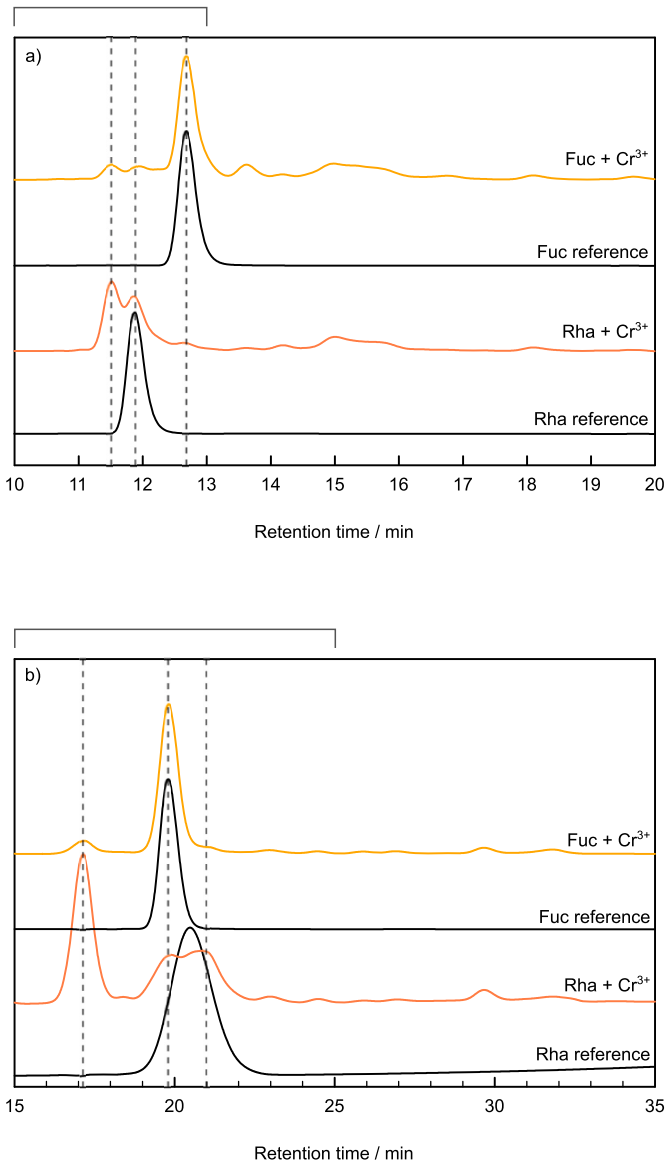


Fig. 6. Normalized chromatograms (RI signal) of model experiment samples with and without added Cr^{3+}. **a)** Agilent Hi-Plex H column, **b)** Agilent Hi-Plex Pb column. Brackets indicate typical retention times for monosaccharides and dotted lines indicate peaks with similar retention times.

bicyclic intermediate analogous to 1,4-anhydro-α-D-sorbopyranose (**3**) is unlikely to form. The absence of a hydroxyl group on C(6) in rhamnose and fucose precludes the formation of a 2,6-linked pyranose ring, thus the only possible ring form for a 6-deoxyketohexose is a 2,5-linked furanose ring. A bicyclic 1,4-anhydrofuranose structure analogous to the bicyclic intermediate 1,4-anhydro-α-D-sorbopyranose (**3**) is unlikely to form due to the bond angle strain imposed on the furanose ring by the 1,4-anhydro bridge. MM2 force field [43] calculations showed that the steric free energy of the hypothetical bicyclic 1,4-anhydrofuranose intermediates from rhamnose and fucose is approximately 16 times higher than the steric free energy of the bicyclic 1,4-anhydro-α-D-sorbopyranose intermediate (**3**) postulated by van Putten et al. [41].

If a monocyclic 1,4-anhydrodeoxyhexose can form directly from the open-chain form of the 6-deoxyketose, a reaction pathway analogous to the pathway proposed by van Putten et al. [41] is possible. Thus, assuming that 2-acetylfuran is formed from deoxyhexoses in a similar way as suggested for the formation of 2-hydroxyacetylfuran from ketohexoses, Scheme 2 is a possible pathway for the formation of 2-acetylfuran (**10**) from rhamnose (**6**) and fucose (**11**). The initial step is the same equilibrium forming the keto-enol tautomer (**7**, **12**) as for dehydration of aldopentoses and aldohexoses, but is then followed by isomerization to the corresponding 6-deoxyketohexose (**8**, **13**). 1, 4-dehydration of the open-chain keto isomer would then directly form a 1,4-anhydro intermediate (**9**, **14**) analogous to the 1,4-anhydro-D-sorbose intermediate **4** in van Putten et al.'s suggested mechanism for the formation of 2-hydroxyacetylfuran.

If a 4,5-enediol is formed via multiple keto-enol tautomerisms (Scheme 3) similar to what was suggested by Moreau et al. [39] for the formation of 2-hydroxyacetylfuran from fructose, 2-acetylfuran may be formed. This may happen either via a cyclic pathway analogous to the route suggested by Ahmad et al. [36] for furfural formation (Scheme 4) or via an open-chain pathway analogous to the open-chain pathway proposed by Feather and Harris [35] (Scheme 5). Considering that consensus still hasn't been reached about which reaction route is the preferred for formation of furfural from xylose [31], all the three suggested routes for 2-acetylfuran formation may be possible.

The high furan yield, the fact that the total furan yield from the two 6-deoxyhexoses investigated was the same within experimental error, and indications of isomerization of the substrates when Cr^{3+} was added all indicate that the addition of Cr^{3+} promotes the enolization of 6-deoxyhexoses similar to the effect of Cr^{3+} on xylose [42], leading to increased formation of the corresponding furans. The formation of 2-acetylfuran from 6-deoxyaldoses opens the possibility for producing 2-acetylfuran from rhamnose-rich biological raw materials like *e.g.*, pectin rhamnogalacturonans.

3. Conclusions

2-acetylfuran and 5-methylfurfural were unambiguously identified in condensates from autocatalyzed steam explosion of Norway spruce (*Picea abies*), both in industrial scale and in laboratory scale. Model experiments using L-rhamnose and L-fucose as substrates showed the formation of 2-acetylfuran from the two 6-deoxyaldohexoses. This supports the hypothesis that both 2-acetylfuran and 5-methylfurfural are formed by acid-catalyzed hydrolysis and subsequent acid-catalyzed dehydration of 6-deoxyhexosans known to be present in the fiber wall of softwood. Possible reaction pathways have been suggested.

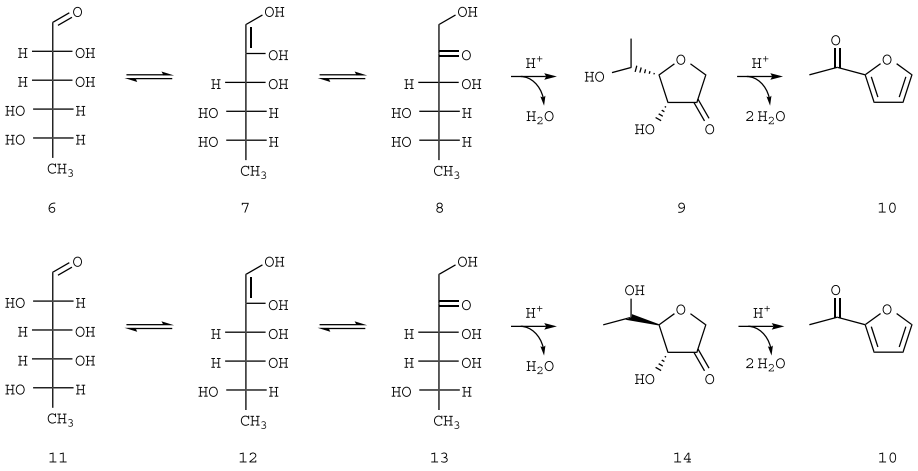
4. Experimental

4.1. Steam explosion condensates

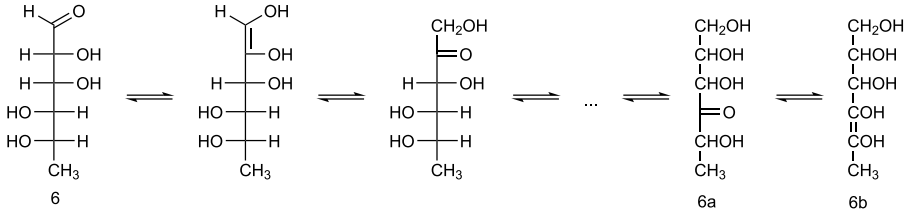
An industrial condensate sample from the steam explosion of Nordic softwood (Norway spruce, *Picea abies*) was received from the Arbaflame biofuel pellet plant at Grasmo, Norway. The conditions during the steam explosion were 20 bar steam pressure (~200 °C) and 500 s cooking time with no acid catalyst added to the system. Two condensate samples from laboratory steam explosion of Norway spruce (*Picea abies*) were produced in a 4 L laboratory steam explosion reactor. The conditions were 24 bar steam pressure (223 °C) and 20 bar steam pressure (210 °C), respectively. The cooking time was 8 min, and no acid catalyst was added to the system.

4.2. Model compound experiments

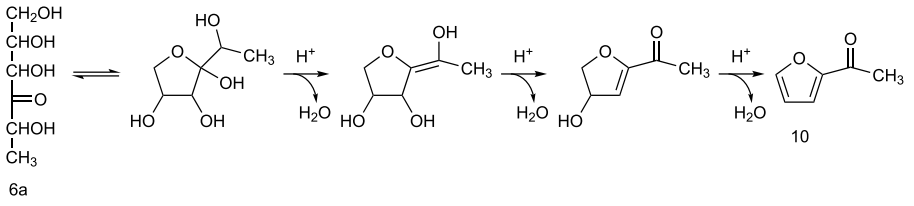
L-rhamnose monohydrate (6-deoxy-L-mannose, CAS 10030-85-0, ≥99%), L-fucose (6-deoxy-L-galactose, CAS 2438-80-4, ≥99%), sulfuric acid (CAS 7664-93-9, Titripur), furfural (CAS 98-01-1, 99%), 5-methylfurfural (CAS 620-02-0, ≥98%), 2-acetylfuran (CAS 1192-62-7, 99%) and chromium(III) chloride hexahydrate (CAS 10060-12-5, p.a.) were purchased from Sigma-Aldrich. All chemicals were used as received. 50 mM solutions of rhamnose and fucose were prepared with the addition of 2 mM sulfuric acid or 2 mM sulfuric acid +6 mM $CrCl_3$. 50 mM



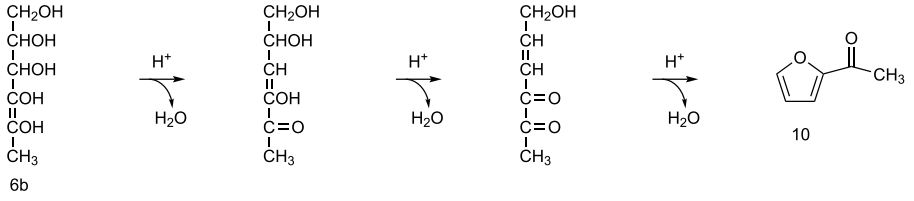
Scheme 2. Formation of 2-acetylfuran **10** from rhamnose **6** and from fucose **11** via a route analogous to the route proposed by van Putten et al. [41] for the formation of 2-hydroxyacetylfuran from D-sorbose.



Scheme 3. Multiple keto-enol tautomerizations forming a 4-keto isomer **6a** and a 4,5-enediol isomer **6b** from rhamnose **6**.



Scheme 4. Formation of 2-acetylfuran via a cyclic route analogous to the route proposed by Ahmad et al. [36] for furfural formation.



Scheme 5. Formation of 2-acetylfuran via an open-chain route analogous to the route proposed by Feather and Harris [35] for furfural formation.

solutions of the sugars in deionized water were also prepared, as reference samples. The solutions (50 mL sample size) were transferred to 100 mL Duran bottles equipped with a screw cap. The bottles were placed in a benchtop autoclave (Certoclav Multicontrol, 18 L) and heated for 120 min at 135 °C. After pressure relief of the autoclave, the reaction vessels were cooled in an ice bath and stored at 4 °C before analysis.

4.3. HPLC analyses

Standards, condensate samples and model experiment samples were analyzed on a Shimadzu Prominence HPLC system in isocratic mode. The system consisted of an LC-20AD pump with a DGU20A5R degassing unit, a SIL20AC autoinjector, a CTO-20A column oven, an SPD-M20A photodiode array (PDA) detector and an RID-20A refractive index detector. Furans were separated on an Agilent Hi-Plex H column (300 mm × 7.8 mm) using 5 mM H_2SO_4 in deionized water as mobile phase at 60 °C, with a flow rate of 0.6 mL/min. Each sample was analyzed thrice with an injection volume of 2 μL, 10 μL and 100 μL, respectively, to ensure that the detector signal was within the linear range of the calibration curve. Carbohydrates were separated on an Agilent Hi-Plex Pb column (300 mm × 7.8 mm) using deionized water as mobile phase at 50 °C, with a flow rate of 0.6 mL/min. Injection volume was 100 μL to ensure a sufficient signal-to-noise ratio in the RI detector. Samples and standards were filtered through a syringe filter (Millex LCR, 0.45 μm)

directly into the autoinjector vials. For all UV-absorbing peaks with a retention time equal to the retention time of a known reference compound, the UV spectra were extracted from the chromatography file and compared to the UV spectrum of the reference compound, recorded on the same instrument.

4.4. NMR analyses

The NMR analyses were performed as described by Løhre et al. [44]: The sample was mixed 1:1 with a solution of 0.010 M Na_2HPO_4 buffer and 20% deuterium oxide, giving the analyzed sample a 10% (V/V) content of D_2O. NMR spectra were recorded on a 600 MHz Bruker AVANCE NEO NMR-spectrometer equipped with a QCI CryoProbe with four RF channels. For quantification, 1H 1D NOESY with water suppression using presaturation, *noesygppr1d*, was used. The spectra were acquired at 298 K using a spectral width of 30 ppm, a time domain data size of 128k, 2 dummy scans, and 8 scans. The relaxation delay, d1, was set to 50 s. The compounds were identified from NMR spectra of reference compounds and from online spectral databases.

4.5. Steric energy calculations

MM2 energy minimizations were performed using commercial software (Chem3D v.19.0.1.8, PerkinElmer) with a minimum RMS gradient of 0.01.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2022.108672.

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