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# The role of deoxyhexonic acids in the hydrothermal decarboxylation of carbohydrates

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**Abstract**

Hydrothermolysis of D-glucose, cellobiose, and $\beta$-cyclodextrin leads to the formation of small amounts of 3-deoxyhexonic acids. These acids are known to be produced by the alkaline degradation of carbohydrates. The formation under neutral hydrothermal conditions of the 3-deoxyhexonic acids provides evidence for the formation of 3-deoxy-D-*erythro*-hex-2-ulose, a compound that has been reported to play a role in both alkaline and acidic conversion of carbohydrates. Hydrothermolysis of 2- and 3-deoxy-D-*arabino*-hexonic acid does not lead to significant decarboxylation, and therefore these compounds cannot be considered to play a major role in the initial hydrothermal decarboxylation of biomass.

*Keywords:* Hydrothermolysis; Glucose; Cellobiose; $\beta$-Cyclodextrin; Deoxyhexonic acids

## 1. Introduction

Upon hydrothermal treatment (300–350°C, 5–18 MPa) of phytomass the oxygen from the (hemi)cellulose is removed mainly as carbon dioxide, which makes the technique attractive for the production of a pyrolysis oil with high H/C and C/O ratios [1,2]. The chemistry behind the decarboxylation of carbohydrates under hydrothermal conditions is still obscure but some hints may be found in the literature on the

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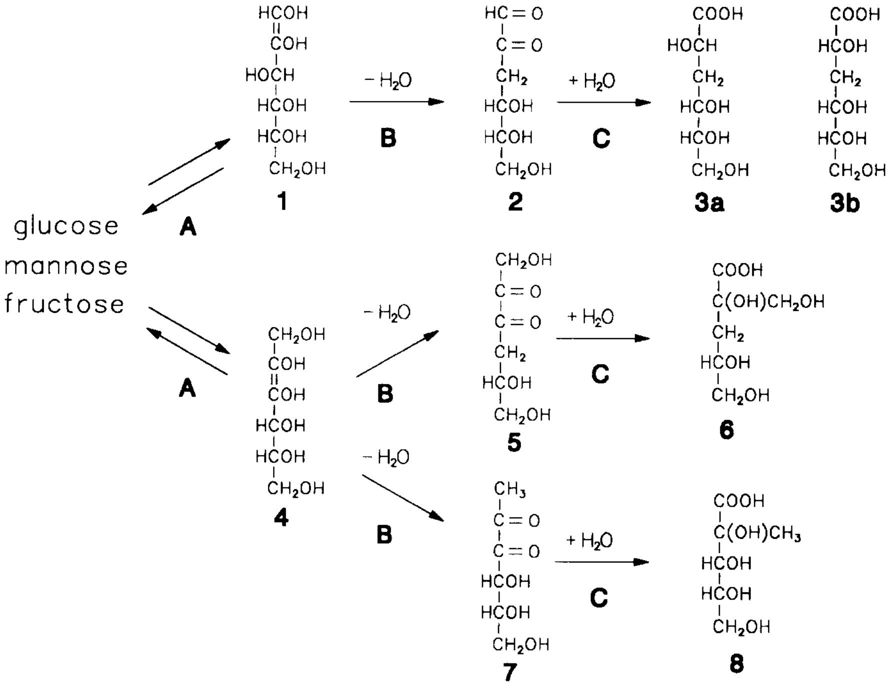
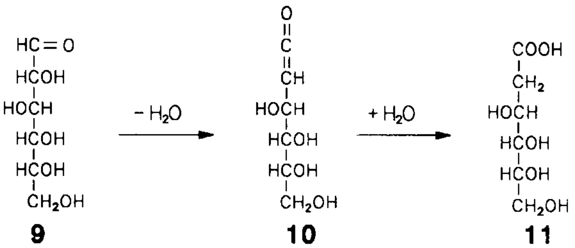


Scheme 1. Simplified scheme of the formation of hexonic acids by alkaline treatment of carbohydrates [7]: **A**, formation of 1,2-enediol (**1**) and 2,3-enediol (**4**) in the Lobry de Bruyn–Alberda van Ekenstein transformation; **B**, $\beta$-elimination; **C**, benzilic acid rearrangement.

mechanisms of dry pyrolysis, as well as acidic and alkaline degradation of saccharides.

Some reactions which take place under hydrothermal conditions are quite similar to acid-catalyzed reactions at lower temperatures (e.g., formation of HMF from fructose [3,4]), but other hydrothermal reactions (e.g., the formation of hydroxylated benzenes via an intramolecular aldol condensation reaction [4,5]) have a base-catalyzed counterpart at ambient temperatures [5]. For that reason it seems plausible that other compounds which are characteristic for alkaline degradation of carbohydrates, such as 3-deoxy-D-hexonic acids, may also appear in the hydrothermal conversion of carbohydrates. 3-Deoxy-D-*arabino*-hexonic acid (**3a**) and 3-deoxy-D-*ribo*-hexonic acid (**3b**), together known as metasaccharinic acid (**3**), are well-known as products of aqueous alkaline degradation of monosaccharides [6–8] (Scheme 1) as well as of di- and poly-saccharides [9]. Besides **3** many other products of alkaline degradation have been identified, including isosaccharinic (**6**) and saccharinic acids (**8**). Compounds **3** are formed under these conditions via the benzilic acid rearrangement of 3-deoxy-D-*erythro*-hexos-2-ulose [10] (3-deoxy-D-glycosulose or 3-deoxy-D-glucosone, **2**) which is the dehydration product of the 1,2-enediol **1**. Inter alia, both **1** and **2** have also been mentioned as intermediates in the acid-catalyzed formation of 5-hydroxymethyl-2-furaldehyde (HMF) [11], although recent work points towards a different reaction pathway [3].

In this context it is relevant to note that the formation of large amounts of carbon



Scheme 2. Proposed formation of 2-deoxy-D-*arabino*-hexonic acid (**11**) from D-glucose by a dehydration/rehydration pathway [13].

dioxide is observed in the dry pyrolysis of carbohydrates [12], which originates mainly from C-1 and C-2 in the carbohydrate [13]. It was argued that the decarboxylation might be attributed to **3**. Decarboxylation of **3** might be more effective under hydrothermal conditions, because the presence of water would inhibit the dehydration reactions which predominate under pyrolytic conditions.

Literature on the decarboxylation of α-hydroxycarboxylic acids such as **3** is scarce. Antal and co-workers [14] reported the hydrothermal dehydration of lactic acid to acrylic acid (350–400°C, 25–34 MPa) which was accompanied by both a decarbonylation and a decarboxylation reaction. The decarboxylation pathway, which afforded acetaldehyde and hydrogen, was inhibited by increasing the pressure, which points to a free-radical reaction mechanism. Goudriaan and Peferoen [1] submitted 2-hydroxyoctanoic acid (2-hydroxycaprylic acid) to pyrolysis as well as to hydrothermolysis. Decarbonylation predominated during pyrolysis, whereas decarboxylation was found to be favored under hydrothermal conditions. The decarboxylation products included heptene as well as heptanol.

2-Deoxy-D-*arabino*-hexonic acid (2-deoxy-D-gluconic acid, **11**) might also be involved in the decarboxylation of saccharides, as indicated by Shafizadeh and Lai [13]. Formation of **11** from saccharides under pyrolytic as well as hydrothermal conditions via dehydration and rehydration (Scheme 2) is quite plausible. Compound **11** has been found in the thermal degradation of chitin [15] and in radiolysis products of aqueous D-glucose [16], where it is formed by the reaction of D-glucose with hydroxyl radicals. Decarboxylation of β-hydroxycarboxylic acids and the related β-lactones with concomitant dehydration is a well-known reaction, and is known to proceed under anhydrous thermal conditions as well as in aqueous solution under acid catalysis [17]. Decarboxylation of **11** might therefore take place under hydrothermal conditions. Indeed, some decarboxylation of **11** and of the lactone of 3-deoxy-D-*ribo*-hexonic acid (**3b**) was observed in pyrolysis experiments, but it was accompanied by significant dehydration [18].

In this work we focused on the possible hydrothermal formation of deoxy-D-hexonic acids from carbohydrates, to quantify the contribution of the typical 'alkaline' degradation reactions in hydrothermolysis of carbohydrates. As model compounds for (1 → 4)-α- and -β-D-glucans, β-cyclodextrin and cellobiose were subjected to hydrothermolysis. The hydrothermolysis of both 3-deoxy-D-*arabino*-hexonic acid (**3a**, 3-deoxy-D-mannonic acid) and 2-deoxy-D-*arabino*-hexonic acid (**11**) was also studied in order to determine the contribution of these acids to the hydrothermal decarboxylation of carbohydrates.

## 2. Experimental

*Chemicals.*—2-Deoxy-D-*arabino*-hexonic acid (**11**) was prepared as the Ca salt by air oxidation of 2-deoxyglucose (Janssen Chimica, Beerse, Belgium) (4 g) in $H_2O$, (70 mL), in a thermostated stirred vessel [19] catalyzed by 10% Pd/C (1 g) at 60°C, analogous to the oxidation of D-glucose to D-gluconic acid [20]. The pH was kept constant at pH 9 by addition of aqueous NaOH. The oxidation was stopped after base addition slowed down. After removal of the catalyst by filtration, Na ions were removed from the solution by addition of an excess of Dowex 50-X8-100 ion-exchange resin in the $H^+$-form. $Ca(OH)_2$ was added to the solution until pH 9 and $CO_2$ was passed through the solution to give pH 6–7. The solution was concentrated in vacuo to ca. 40 mL and the $CaCO_3$ was removed by filtration. The remaining solution was evaporated in vacuo and this was repeated several times with the addition of dry EtOH until solid calcium 2-deoxy-D-gluconate was obtained (yield: 87%); Karl Fisher titration showed this calcium salt to be the dihydrate; $[\alpha]_D^{25}$ + 4.1° (*c* 4, $H_2O$); $^{13}C$ NMR data ($D_2O$): $\delta$ 43.02 (C-2), 64.67 (C-6), 69.41, 72.83, 74.39 (C-3,4,5), 181.71 (C-1); purity > 98% (as determined by HPLC, CarboPAC PA 1 column, described in the analysis section).

Calcium 3-deoxy-D-*arabino*-hexonate was prepared from D-glucono-1,5-lactone according to Bock et al. [21] and was purified as described by Wood and Fletcher [22] to yield the 3-deoxy-D-*arabino*-hexonic acid (**3a**) calcium salt dihydrate; mp 160–161°C (reported [19] mp 161–162°C); $[\alpha]_D^{20}$ – 22.2° (*c* 2, $H_2O$) (reported [19] $[\alpha]_D^{20}$ – 22°); $^{13}C$ NMR data were in accordance with the literature [19]. Aqueous solutions of the carboxylic acids were prepared by passing a deaerated aqueous solution of the calcium salts over an ion-exchange resin in the $H^+$-form which was washed subsequently with some additional deaerated water.

Anhydrous D-glucose z.a. was obtained from J.T. Baker, Deventer, The Netherlands, cellobiose (crystalline) from Sigma-Aldrich, Bornem, Belgium, and $\beta$-cyclodextrin (99%) from Janssen Chimica. All solutions for hydrothermolysis were prepared with deaerated demineralized water, and these feed solutions were kept under a helium atmosphere during hydrothermolysis.

*Hydrothermolysis.*—Hydrothermal conversions at 340°C and 27.5 MPa were performed in a continuous tubular reactor as described previously [4] for residence times of 1 to 3 min. For residence times of 5 to 75 s the reactor set-up of the Hawaii Natural Energy Institute at the University of Hawaii at Manoa was used. This reactor set-up was designed and built by Antal and co-workers [3], and consists of a high-pressure solvent delivery system and a sampling valve and pressure release unit, to which several tubular reactors can be connected. The annular reactor (i.d. 3.2 mm, length 50 cm) was used for residence times of ca. 75 s, while a small tubular reactor (i.d. 0.76 mm, length 27 cm) was used to reach very short residence times of 5 to 7 s. This reactor set-up enabled the sampling and quantification of small amounts of gas formed during the reactions.

*Analyses.*—Gas analyses were performed on a 1.83 m × 3.2 mm SS Alltech Carbosphere column, 80/100 mesh, using a Hewlett–Packard 5890 GC with TCD and FID detection which is described elsewere [14].

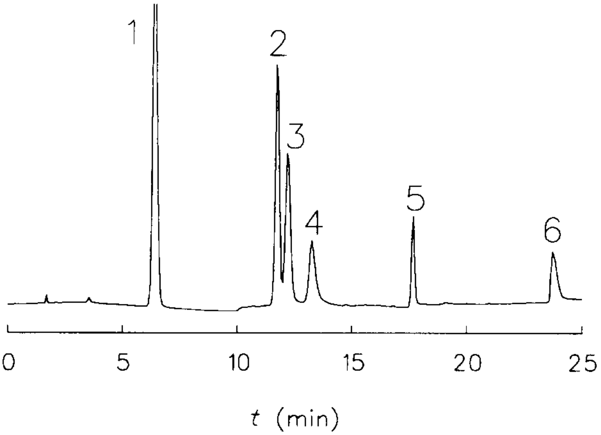


Fig. 1. HPLC chromatogram (CarboPac PA 1) of D-glucose, two deoxyhexonic acids, and some D-glucose oligomers: 1, D-glucose; 2, cellobiose; 3, 3-deoxy-D-*arabino*-hexonic acid (**3a**); 4, 2-deoxy-D-*arabino*-hexonic acid (**11**); 5, α-cyclodextrin (used as an internal standard, added after the reaction); 6, β-cyclodextrin.

HPLC analyses of the liquid-phase products were performed on Rezex Organic Acid or Bio-Rad HPX87H columns; 60°C or room temperature; eluent, 0.01 M aq $CF_3CO_2H$ at 0.6 mL/min; RI detection. For identification of the products this HPLC set-up was coupled to a mass spectrometer (VG 70-Se operating in the plasma spray mode).

Quantitative HPLC analyses of 2-deoxy- and 3-deoxy-D-hexonic acids were achieved using a Dionex CarboPac PA 1 column; eluent, 0.1 M NaOH at 1 mL/min, with an NaOAc gradient from 0 to 0.25 M in 25 min; pulsed amperometric detection. α-Cyclodextrin was used as an internal standard and was added to the samples after hydrothermolysis. This analysis enabled quantitative determination of cellobiose, β-cyclodextrin, and deoxyhexonic acids in one run (Fig. 1). Any lactones formed during hydrothermolysis of the deoxyhexonic acids will be detected as the original (ionized) acids in this set-up, because of the fast hydrolysis of the lactones at high pH as was experimentally proved. The described HPLC set-up is able to separate isosaccharinic (**3**) and metasaccharinic (**6**) acid.

Some samples were freeze-dried to enable trimethylsilylation [shaking for 30 min at 30°C in a solution of 18% (v/v) *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (98%, Janssen Chimica) and 9% (v/v) chlorotrimethylsilane (98%, Janssen Chimica) in dry pyridine z.a. (J.T. Baker)]. These trimethylsilylated samples were analyzed by GC-MS (Hewlett–Packard 5890 Series II GC, equipped with a 50 m × 0.25 mm Chrompack CP Sil 5 CB column, He carrier, attached to a VG 70-Se mass spectrometer using EI).

## 3. Results and discussion

*Hydrothermal formation of 3-deoxy-D-hexonic acids.*—In the hydrothermolysis products of D-glucose, cellobiose, and β-cyclodextrin small amounts of 3-deoxy-D-hexonic

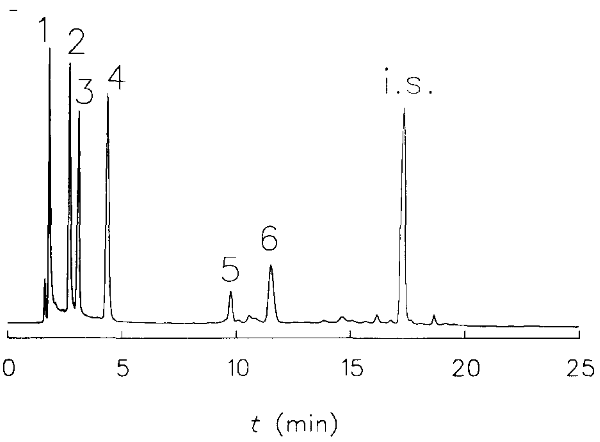


Fig. 2. HPLC chromatogram (CarboPac PA 1) of the hydrothermolysis mixture of β-cyclodextrin at 340°C, 27.5 MPa, 60 s, after addition of internal standard (α-cyclodextrin): 1, several overlapping compounds; 2, 2-furaldehyde (**13**); 3, unidentified; 4, 5-hydroxymethyl-2-furaldehyde (**12**); 5, unidentified; 6, 3-deoxy-D-hexonic acids (**3**); i.s., internal standard [small peaks between 14 and 20 min are due to very small amounts of oligomeric saccharides; β-cyclodextrin (retention time 24 min) is completely converted].

acids (**3**, metasaccharinic acid) were found by HPLC analysis (Fig. 2, Table 1). Metasaccharinic acid was identified by comparison of the retention time with that of an authentic sample of **3a** on the CarboPac PA 1 column, and by comparison of the spectra

Table 1

Yields (mol% per mole glucose units used) of 3-deoxy-D-hexonic acids (**3**) by hydrothermolysis of carbohydrates at 340°C and 27.5 MPa

| Compound | Initial concn [a] (mM) | Catalyst | Residence time (s) | Conversion (%) | Yield of **3** (%) |
|---|---|---|---|---|---|
| D-Glucose | 50 | — | 5.7 | 99 | 2.5 |
| | 50 | 10 mM NaOH | 5.6 | 100 | 5.7 |
| | 10 | — | 46 | 100 | 2.3 |
| | 10 | — | 60 | 100 | 2.8 |
| | 10 | — | 90 | 100 | 3.6 |
| Cellobiose | 50 | — | 5.1 | 100 | 1.3 |
| | 50 | 10 mM NaOH | 6.4 | 98.9 | 1.6 |
| | 20 | — | 46 | 99 | 0.8 |
| | 20 | — | 60 | 100 | 1.2 |
| | 20 | — | 90 | 100 | 1.2 |
| β-Cyclodextrin | 43.6 | — | 6.2 | 100 | 1.1 |
| | 43.6 | 10 mM NaOH | 6.5 | ca. 10 [b] | n.o. [c] |
| | 9.6 | — | 46 | 100 | 4.8 |
| | 9.6 | — | 60 | 100 | 5.7 |
| | 9.6 | — | 90 | 100 | 5.4 |
| | 9.6 | — | 177 | 100 | 3.4 |

[a] Given in moles glucose units.

[b] Conversion could not be determined with accuracy because of interference of some hydrolyzed cyclodextrin fragments with the internal standard.

[c] Not observed.

with HPLC-MS using an organic acids column. HPLC analysis of samples of metasaccharinic acid (containing both **3a** and **3b**) which were prepared from 2-deoxy-D-*erythro*-pentose (2-deoxyribose) via the Kiliani synthesis [20] or by the alkaline degradation of 3-*O*-methyl-D-glucose [23], showed that **3a** and **3b** are not separated on the CarboPac PA1 column. A final positive identification of **3** was established by GC-MS analysis of the trimethylsilylated products and comparison with an authentic sample. MS-data: 378 (3), 363 (3), 322 (5), 292 (14), 273 (22), 258 (5), 246 (29), 231 (6), 219 (10), 205 (34), 189 (14), 155 (26), 147 (58), 129 (72), 117 (20), 103 (41), 73 (100).

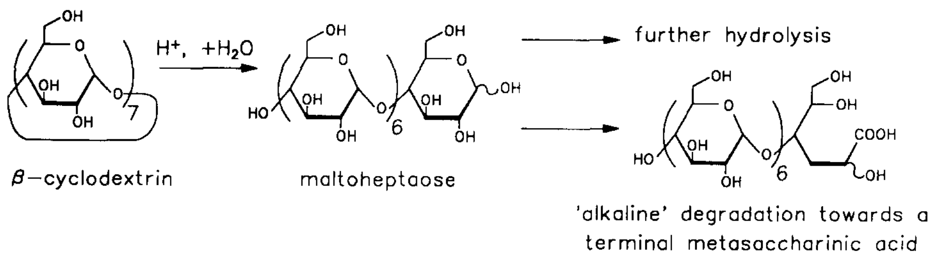
Hydrothermolysis of D-fructose (0.05 M, 340°C, 90-s residence time) gave **3** in 3.3% yield, comparable with its formation from D-glucose.

We regard the formation of **3** as evidence for the formation of 3-deoxy-D-*erythro*-hex-2-ulose under neutral hydrothermal conditions. The reaction temperature seems to exert a definite effect on the reaction pathway, because at 250°C hydrothermolysis of D-fructose gave hardly any **3**, which is in accordance with results published by Antal and co-workers [3]. This observation indicates that, upon increasing the temperature, reaction patterns emerge which are commonly linked with alkaline reaction conditions.

Compound **3** was formed in the first seconds of the hydrothermolysis of the carbohydrates studied, and its concentration hardly changed at residence times up to 90 s (Table 1). The amount of 3-deoxy-D-hexonic acids from D-glucose was found to be about twice the amount formed by hydrothermolysis of cellobiose. First we reasoned that this might be due to the formation of an isosaccharinic acid (3-deoxy-2-*C*-hydroxymethyl-D-pentonic acid, **6** Scheme 1) instead of **3** as the former compound is also observed in the alkaline degradation of cellobiose at ambient temperature [9]. An isosaccharinic acid is a typical product of the alkaline 'peeling reaction' of 4-*O*-substituted di- and poly-saccharides such as cellobiose [24,25]. In the hydrothermolysis mixtures, however, no isosaccharinic acid could be detected by HPLC. In the GC chromatogram only trace amounts (yields less than 0.2%) of isosaccharinic acid (**6**) and saccharinic acid (**8**) could be detected. Hydrothermolysis of a sample of isosaccharinic acid (**6**), isolated from the alkaline degradation of lactose [26], showed it to be relatively stable under hydrothermal conditions (35% conversion at 340°C, 27.5 MPa, 60 s). We therefore conclude that an isosaccharinic acid is not involved in the hydrothermolysis of D-glucose, cellobiose, and $\beta$-cyclodextrin. This indicates that the 1,2-enediol **1** is preferred over the 2,3-enediol **4** under the present conditions. Peaks 3 and 5 in the HPLC chromatogram (Fig. 2) are presently subjected to further identification by HPLC-MS and GC-MS of the trimethylsilylated products.

$\beta$-Cyclodextrin gave rather large amounts of 3-deoxy-D-hexonic acids compared to D-glucose and cellobiose. In the alkaline degradation of (1 → 4)-linked polysaccharides metasaccharinic acids are mainly formed via the 'stopping' reaction at the reducing end of the polysaccharide chain [22] (Scheme 3). It would seem that this 'stopping' reaction also plays a role at our reaction conditions, in competition with hydrolysis of the saccharide chain. Removal of the terminal metasaccharinic acid by hydrolysis exposes the chain again for the alkaline 'stopping' reaction. In this way the $\beta$-(1 → 4)-linked glucan cellulose might also produce relatively large amounts of metasaccharinic acids, assuming a minor effect, if any, of the anomeric linkage.

Although hydrothermolysis under basic conditions (10 mM NaOH) resulted in a



Scheme 3. Hydrolysis of β-cyclodextrin to maltoheptaose and the formation of a terminal metasaccharinic acid.

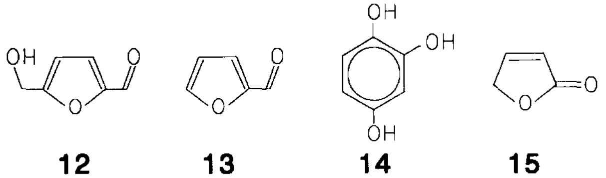
substantial increase of the amount of 3-deoxy-D-hexonic acids formed from D-glucose, the yield of **3** stayed below 6%. This might be an indication that the intermediate **2** is not formed in large amounts upon hydrothermolysis of sugars, because **2** would be quickly converted into **3** by alkali [11]. β-Cyclodextrin reacted slowly in the presence of a base. We ascribe this effect to the inhibition of the (acid-catalyzed) hydrolytic ring-opening reaction (Scheme 3), which makes the latter process rate-limiting.

Table 2 lists the major products identified and quantified in the hydrothermolysis of D-glucose, cellobiose, and β-cyclodextrin. Major products are glycolic acid, dihydroxyacetone, hydroxyacetone, formic acid, and acetic acid. Other products quantified in the

Table 2
Yields (mol% per mole glucose units used) of major products in the hydrothermolysis (340°C, 27.5 MPa) of 50 mM aqueous D-glucose, cellobiose, and β-cyclodextrin at short residence times

| | D-Glucose | | Cellobiose | | β-Cyclodextrin | |
|---|---|---|---|---|---|---|
| | Water | 10 mM NaOH | Water | 10 mM NaOH | Water | 10 mM NaOH |
| Residence time (s) | 5.7 | 5.6 | 5.1 | 6.4 | 6.2 | 6.5 |
| Conversion (%) | 99 | 100 | 100 | 98.9 | 100 | ca. 10 |
| D-Glucose | 0.8 | — | 4.5 | — | 1.0 | — |
| 3-Deoxy-D-hexonic acids (**3**) | 2.5 | 5.7 | 1.3 | 1.6 | 1.1 | — |
| HMF | 7.0 | — | 9.9 | — | 6.9 | — |
| 2-Furaldehyde | 3.2 | — | 6.7 | — | 5.4 | — |
| 1,2,4-Benzenetriol | 2.6 | — | 2.1 | — | 2.3 | — |
| Glycolic acid | 49.7 | 40.7 | 52.8 | 40.8 | 45.9 | 2.9 |
| Dihydroxyacetone | 29.1 | 36.7 | 19.6 | 21.0 | 22.0 | 4.1 |
| Hydroxyacetone | 15.9 | 33.3 | 8.0 | 29.7 | 13.5 | 5.2 |
| Formic acid | 16.1 | 11.8 | 16.7 | 20.5 | 9.2 | 13.6 |
| Acetic acid | 6.7 | 11.6 | 2.3 | 10.5 | 2.0 | 9.3 |
| Gases [a] | | | | | | |
| $H_2$ | 4.1 | 5.0 | 3.1 | 8.1 | [b] | [b] |
| CO | 4.7 | 9.1 | 4.4 | 15.1 | | |
| $CO_2$ | 6.9 | 17.6 | 5.0 | 13.6 | | |
| $CH_4$ | 0.1 | 0.1 | 0.1 | 0.0 | | |
| Carbon balance (%) | 61.5 | 64.7 | 60.0 | 52.3 | 51.1 | |

[a] Some light hydrocarbons could also be detected but their yield was always below 0.1%.
[b] Not quantified.



Scheme 4. Some compounds (**12**, **13**, **14**) formed by hydrothermolysis of saccharides, and 2-(5*H*)-furanone (**15**) formed from 2-deoxy-D-*arabino*-hexonic acid.

reaction mixtures include the typical acid-catalyzed dehydration products HMF (**12**), 2-furaldehyde (**13**), and the HMF-related 1,2,4-benzenetriol (**14**) [4] (Scheme 4).

The addition of 10 mM NaOH inhibited the formation of these products, and increased the formation of hydroxyacetone (acetol) substantially. The latter also holds for acetic acid. The formation of the major products glycolic acid and dihydroxyacetone was less profoundly affected by the addition of NaOH. The formation of formic acid was also little affected by base addition.

*Initial gas formation.*—The formation of gases in the initial stage of hydrothermolysis of D-glucose and cellobiose was monitored (Table 2). The gas analyses show that in the initial stage of hydrothermolysis of D-glucose and cellobiose there is no predominant formation of carbon dioxide. Addition of NaOH increases gas formation but it does not seem to favor much the formation of carbon dioxide compared to the formation of carbon monoxide.

*Hydrothermal conversion of 2- and 3-deoxy-D-hexonic acids.*—3-Deoxy-D-*arabino*-hexonic acid (**3a**, 3-deoxy-D-mannonic acid) was used to study the hydrothermolysis of 3-deoxy-D-hexonic acids (which consist of both the *ribo*- and *arabino*-hexonic acid), and 2-deoxy-D-*arabino*-hexonic acid (**11**, 2-deoxy-D-gluconic acid) was used to find out whether this $\beta$-hydroxy-carboxylic acid would be a better intermediate for decarboxylation as was indicated by Shafizadeh and Lai [13].

The deoxyhexonic acids were slowly converted under hydrothermal conditions, with half-lives of ca. 20 and 100 s (Fig. 3). This makes them sufficiently reactive to be fully converted during the hydrothermolysis of biomass which takes at least 5–10 min, although they react much slower than glucose.

Using HPLC-MS, some degradation products could be identified (Table 3). Among the products of **11**, 2-(5*H*)-furanone (**15**) could be positively identified. Compound **15** could be a product of the dehydration of the lactone of **11** followed by retroaldolisation to **15** and glycolaldehyde. It may be mentioned that in the dry pyrolysis of **11**, 5-(2-hydroxyethylidene)-2-(5*H*)-furanone was detected [18].

No direct decarboxylation products such as "2-deoxyribitol" from **3** or 1-deoxy-D-arabinitol from **11** could be detected. When formed, these compounds would probably react rapidly under the conditions applied here, because they are susceptible to dehydration reactions [27].

Gas formation from these deoxyhexonic acids was also monitored (Table 3). It was found that **11** produces two to four times as much $CO_2$ as glucose itself. In water, the selectivity for $CO_2$ formation from **3a** is ca. 17.8% (mole $CO_2$ per mole **3a** converted),

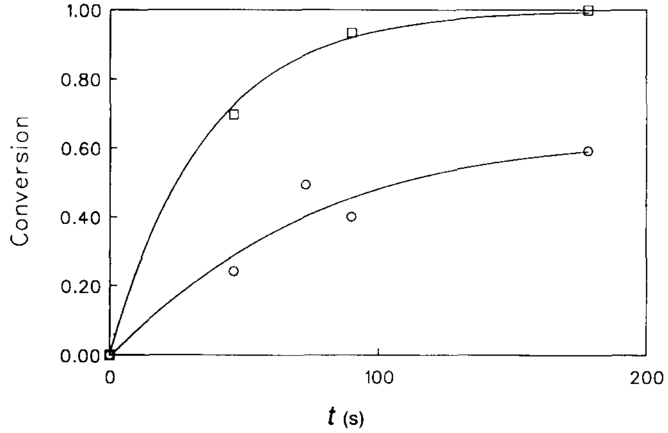


Fig. 3. Conversion of deoxyhexonic acids during hydrothermolysis (at 340°C, 27.5 MPa) versus reaction time: ○, 3-deoxy-D-*arabino*-hexonic acid (**3a**); □, 2-deoxy-D-*arabino*-hexonic acid (**11**).

which is more than twice the amount formed by glucose. In 10 mM aq NaOH, however, the selectivity of **3a** towards $CO_2$ (15.5%) is even slightly less than the amount of $CO_2$ produced by glucose.

The hydrothermal decarboxylation of **3a** and **11** is certainly not quantitative (i.e., 1 mole $CO_2$ per mole acid), and it is also accompanied by the formation of hydrogen,

Table 3
Yields (mol% per mole hexonic acid used) of identified products in the hydrothermolysis of deoxyhexonic acids at 340°C, 27.5 MPa, and 73 s residence time

| | 3-Deoxy-D-mannonic acid (**3a**) | | 2-Deoxy-D-gluconic acid (**11**) | |
|---|---|---|---|---|
| | Water | 10 mM NaOH | Water | 10 mM NaOH |
| Conversion (%) | 49.3 | 68.2 | n.d. [a] | n.d. [a] |
| 2-Deoxyribose | [b] | [b] | | |
| Lactic acid | [b] | [b] | | |
| Unknown (*m*/*z* 114) | [b] | [b] | | |
| Acetic acid | 7.6 | 14.3 | | |
| Glycolic acid | | | 9.5 | 21.4 |
| Hydroxyacetone | | | 4.8 | 5.3 |
| 3-Hydroxy-2-butanone | | | 23.6 | 16.0 |
| Butanedione | | | [b] | [b] |
| Acetone | | | 5.3 | |
| 2-(5*H*)-Furanone (**15**) | | | 4.8 | |
| Unknown (*m*/*z* 102) | | | [b] | [b] |
| Gases | | | | |
| $H_2$ | 4.6 | 14.6 | 17.9 | 28.7 |
| CO | 0.5 | 1.2 | 3.9 | 0.7 |
| $CO_2$ | 8.8 | 10.6 | 26.5 | 30.6 |
| $CH_4$ | 0.1 | 0 | 0.1 | 0 |

[a] Could not be determined because of degradation of **11** during mailing of the samples from Hawaii to Delft.
[b] Compound was identified with HPLC-MS but not quantified.

similar to the decarboxylation of lactic acid [14]. This might be an indication of the formation of formic acid, as this acid quickly decomposes to hydrogen and carbon dioxide under hydrothermal conditions, especially in the presence of oxides of stainless steel components [28] (here, the wall of the tubular reactor).

## 4. Conclusions

The detection of 3-deoxyhexonic acids in the hydrothermolysis mixtures of D-glucose and its oligomers shows that reaction patterns which are characteristic of alkaline degradation, as well as the specific acid-catalyzed degradations, can occur under these conditions. Only small amounts of 3-deoxy-D-hexonic acids (metasaccharinic acids) were observed, but other more reactive alkaline degradation products might also be transiently formed. Although the hydrothermolysis of 3- and 2-deoxyhexonic acids results in considerable decarboxylation, $CO_2$ formation from these compounds is far from equimolar. Therefore these compounds will contribute to the hydrothermal decarboxylation of carbohydrates, but, considering the small amounts of deoxyhexonic acids formed, this contribution will be limited.

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