

# Thermal Degradation of Model Compounds with Blocked Hemiacetal Group Related to (4-O-Methyl-D-Glucurono)-D-Xylan

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## Synopsis

Reduced (4-O-methyl-D-glucurono)-D-xylan and nine methylglycosides related to this polysaccharide were studied by dynamic and isothermal thermogravimetry. It could be stated from the results that the thermal stability of saccharides is increasing with increasing number of pyranose units. The models related to (4-O-methyl-D-glucurono)-D-xylan are more thermally stable than the corresponding hexoglycanic models. Rates of gasification of models containing uronic acid methylesters are higher than those of neutral methylglycosides. The rate of polysaccharide gasification was the highest one from all models studied. The supramolecular structure of polysaccharide is dramatically influencing the course of thermal degradation.

## INTRODUCTION

The most abundant hemicellulose component of beach wood is (4-O-methyl-D-glucurono)-D-xylan. Although thermal degradation of (4-O-methyl-D-glucurono)-D-xylan was less intensively studied,<sup>1-6</sup> some results from thermal degradation of other acidic polysaccharides<sup>7</sup> could be used for the interpretation of thermolysis of uronic acid units. Thermolysis of uronic acid component of the polysaccharide was studied only rarely.

In our previous work the thermal stability of models related to cellulose was studied.<sup>8</sup> In this paper ten models related to (4-O-methyl-D-glucurono)-D-xylan were analyzed with the help of dynamic and isothermal thermogravimetry (TG).

## EXPERIMENTAL

**Materials.** Synthesis of methyl  $\beta$ -D-xylopyranoside (1), methyl  $\beta$ -D-xylobioside (2), methyl  $\beta$ -D-xylotrioside (3), methyl  $\beta$ -D-xylotetraoside (4), methyl  $\beta$ -D-xylopentaoside (5), methyl  $\beta$ -D-xylohexaoside (6), methyl 2-O-(methyl- $\alpha$ -D-glucopyranosyluronate)- $\beta$ -D-xylopyranoside (7), methyl 4-O-[2-O-(methyl 4-O-methyl- $\alpha$ -D-glucopyranosyluronate)- $\beta$ -D-xylopyranosyl]- $\beta$ -D-xylopyranoside (8), and methyl 2-O-(methyl 4-O-methyl- $\alpha$ -D-glucopyranosyluronate)-4-O-( $\beta$ -D-xylopyranosyl)- $\beta$ -D-xylopyranoside (9), has been described previously.<sup>9-15</sup> The (4-O-Methyl-D-glucurono)-D-xylan prepared from beech sawdust<sup>16</sup> contained 19.3% of uronic acids, 2.93% of methoxyl,  $[\alpha]_D^{22} = -70^\circ$  ( $c = 0.53$  g/dL,  $H_2O$ ), and the neutral portion of saccharides contained 98% of D-xylose after acid hydrolysis. Molecular weight was determined osmotically ( $M_n =$

18610). The ash content of this sample was 2.73%. Polysaccharide (**10**) was prepared from (4-O-methyl-D-glucurono)-D-xylan by reduction with NaBH<sub>4</sub>. To 1 g of substrate in 100 mL of water, 0.5 g of powdered NaBH<sub>4</sub> (Fluka AG) was added. The sample was left to stand at room temperature for several days; then it was dialyzed and lyophilized; the ash content of **10** was 4.91%.

**Methods.** TG Measurements were performed in inert atmosphere on TGS-1 (Perkin-Elmer) instrument as described previously.<sup>17</sup> The method for determination of rate constants as the first-order constants and activation energies was a numerical method of linear regression using programmable calculators and was also described previously.<sup>17</sup> In the case of isothermal measurements only the values measured during the first 5 min of thermolysis were used to exclude the disturbing influence of consecutive reactions. The obtained rate constants were considered as the initial rates of gasification.

## RESULTS AND DISCUSSION

The results of dynamic TG measurements of the models used are given in Table I. The thermal stability was judged on the basis of the quantity of residue left at a certain temperature. Thermal degradation of these nonreducing models includes a variety of reactions such as volatilization, dehydration, transglycosylation, cleavage of glycosidic bonds, decarboxylation, demethoxylation, deesterification, fragmentation, etc.

Methyl  $\beta$ -D-xylopyranoside (**1**) is not a suitable model for thermolysis study of (4-O-methyl-D-glucurono)-D-xylan because under TG measurement conditions it is volatilized without degradation.<sup>18</sup> At 275°C the whole sample **1** was volatilized. Methyl  $\beta$ -D-glucopyranoside is less volatile than **1** and undergoes also transglycosylation.<sup>17</sup> Methyl  $\beta$ -D-xylobioside (**2**) is thermally more stable than **1**. When we compare the thermal stability of **2** and methyl  $\beta$ -D-cellobioside in the temperature interval from 250 to 350°C, we can find a slightly higher quantity of residue for the hexoglycanic model.<sup>8</sup> The same trend is observed for methyl  $\beta$ -D-xylotrioside (**3**) when it is compared with methyl  $\beta$ -D-cellotrioside. The quantity of residue at 350°C is higher for **2** and **3** in comparison with the corresponding hexoglycanic models. From these results it

TABLE I  
Results of Dynamic TG Measurements (%) of Model Compounds Related  
to (4-O-Methyl-D-Glucurono)-D-Xylan

Model	Temperature (°C)							
	105	250	275	300	325	350	375	400
1	99.7	15.6	0	—	—	—	—	—
2	97.0	94.3	91.5	76.3	36.0	17.7	14.7	12.9
3	98.8	97.1	96.8	82.3	26.4	22.6	20.6	18.7
4	97.4	95.7	94.4	79.1	30.9	21.7	19.8	17.7
5	98.6	98.1	97.5	95.7	75.6	43.6	36.5	31.1
6	99.1	98.0	96.3	90.5	64.7	38.5	32.1	28.1
7	99.7	84.8	79.8	75.3	64.9	50.0	40.1	35.4
8	97.2	94.2	90.9	79.1	41.0	32.3	29.1	26.6
9	98.1	95.9	93.5	86.1	50.9	24.3	20.2	18.1
10	98.8	95.3	83.7	53.5	36.0	29.7	25.0	20.5

may be concluded that the volatilization effect plays an important role up to 350°C. Above this temperature, however, also some other reactions take part. When we compare the thermal stability of methyl  $\beta$ -D-xylo-tetraoside (4), methyl  $\beta$ -D-xylo-pentaoside (5), and methyl  $\beta$ -D-xylo-hexaoside (6) together with models 2 and 3 it turns out that the thermal stability of the used models is increasing with increasing number of pyranose units.

Three models containing uronic acids in the form of methylester were studied also. Methyl 2-O-(methyl 4-O-methyl- $\alpha$ -D-glucopyranosyluronate)- $\beta$ -D-xylopyranoside (7) has been studied already previously and it was found to be more thermally stable than 2.<sup>5</sup> This is inconsistent with our results. The residue of 7 at 250°C is about 10% smaller than for 2, but at 300°C the residues are on the same level of magnitude. So it is very important to determine the temperature interval in which we compare the thermal stability. Model 7 has two methyl groups more in comparison with 2; therefore, it volatilizes easier. In the interval from 300 to 400°C, 7 exhibits a greater residue than 2. It is known that the uronic residues are not decarboxylated quantitatively, and some acidic derivatives of furan with low volatility are formed.<sup>7</sup> That is why the residue of model 7 is greater than that of model 2. When methyl 4-O-[2-O-(methyl 4-O-methyl- $\alpha$ -D-glucopyranosyluronate)- $\beta$ -D-xylopyranosyl]- $\beta$ -D-xylopyranoside (8) is decomposed under the same conditions, the formed residue is higher than for 7 up to 300°C. For temperatures higher than 325°C the residue is smaller for 8 than for 7. We propose that this is due to the smaller ratio of glucuronic acid units to xylose in the molecule of 8 in comparison with 7. Methyl 2-O-(methyl 4-O-methyl- $\alpha$ -D-glucopyranosyluronate)-4-O-( $\beta$ -D-xylopyranosyl)- $\beta$ -D-xylopyranoside (9), which differs from 8 in the xylose unit on which the glucuronic acid methylester is linked, is more stable than 8 up to 325°C but at 350°C the residue is the smallest one in comparison with the models 7 and 8.

Reduced (4-O-methyl-D-glucurono)-D-xylan (10) contains uronic acid residue in the form of sodium salt but no reducing groups. It is known that at temperatures lower than 200°C the cleavage of  $\beta$ -glycosidic linkages as well as dehydration reactions takes place.<sup>3</sup> Also it is known that the presence of small amounts of acids or bases influences the course of thermal degradation.<sup>2,5</sup> So it is probable that the presence of sodium salt also influences the thermal degradation. The ratio between xylose and glucuronic acid units in polysaccharide 10 is higher than for models from 7 to 9. This is thought to be one of the reasons for its lower stability (at 300°C the residue is the lowest one in comparison for all oligosaccharides). So, according to the dynamic TG measurements, the thermal stability decreases in following sequence: xylooligosaccharides > xylooligouronides > reduced (4-O-methyl-D-glucurono)-D-xylan.

The results of isothermal TG measurements in the temperature range from 270 to 310°C are given in Table II. All the calculated rate constants were first-order rate constants (with regression coefficients from 0.95 to 0.99) and were considered as the starting rates of gasification (formation of degradation products such as CO, CO<sub>2</sub>, H<sub>2</sub>O, etc., as well as volatilization of the substrate). Model 1 was not studied by this method because it is volatilized without degradation under these conditions.<sup>18</sup> The rate constant values for 2 are smaller than for methyl  $\beta$ -D-cellobioside,<sup>8</sup> so that the thermal stability of 2 is higher in comparison with methyl  $\beta$ -D-cellobioside. Activation energy for 2 is

TABLE II  
Results of Isothermal TG Measurements of Model Compounds Related  
to (4-O-Methyl-D-Glucurono)-D-Xylan at Temperature Interval 270–310°C

Model	Rate constants (min <sup>-1</sup> )					Activation energies (kJ mol <sup>-1</sup> )
	<i>k</i> <sub>270</sub>	<i>k</i> <sub>280</sub>	<i>k</i> <sub>290</sub>	<i>k</i> <sub>300</sub>	<i>k</i> <sub>310</sub>	
2	0.0065	0.0133	0.0206	0.0421	0.0782	161.6
3	0.0015	0.0021	0.0045	0.0069	0.0114	138.3
4	0.0157	0.0164	0.0491	0.0967	0.2066	182.1
5	0.0025	0.0053	0.0209	0.0523	0.1378	271.6
6	0.0014	0.0056	0.0107	0.0774	0.1443	315.2
7	0.0214	0.0333	0.0473	0.0892	0.1272	119.8
8	0.0256	0.0374	0.0666	0.1615	0.2421	156.7
9	0.0132	0.0221	0.0327	0.0606	0.1202	142.9
10	0.0461	0.0667	0.1407	0.2994	0.3332	144.1

greater than for the corresponding hexoglycanic model.<sup>8</sup> So we propose that the reactivity toward transglycosylation or dehydration is decreased due to absence of primary hydroxyl groups. Also in the case of **3** the rate constants of gasification in the temperature interval from 270 to 310°C are more than one order smaller than for methyl β-D-celotrioside.<sup>8</sup> We suppose that the dehydration or condensation reactions are playing a more important role during isothermal degradation where at higher temperatures the reaction is completed in a much shorter time in comparison to dynamic TG measurements. Rate constants for the trimers are smaller than for the dimers for both the hexoglycanic and pentoglycanic models, respectively. Activation energy of **3** is approximately equal to the value of methyl β-D-celotrioside gasification but smaller than for **2**. Model **4** exhibits the highest rate constant values among all studied neutral oligosaccharides. Also, the activation energy is higher than for **2** or **3**. Models **5** and **6** are thermally stable, their rate constants are smaller in comparison to model **4**, and the activation energies are higher than for models from **2** to **4**. It could be concluded that the thermal stability of pentoglycanic-type methylglycosides increases with the increasing of the quantity of pyranose units.

The rate constants for uronide **7** are higher than for **2** and the value of activation energy is smaller than in the case of **2**. Also the rate constants for models **8** and **9** are higher than for **2** and the activation energies are smaller. All the three uronides are more volatile than **2**. The two xylouronides **8** and **9** are less thermally stable under these conditions than neutral trimer **3**. This confirms also the better volatilization of models **8** and **9** in comparison to **3**. The rate constants of **8** are higher than for **9**. This could be due to the lower thermal stability of β-glycosidic linkages of the xylose units compared to the α-glycosidic linkages of the 4-O-methyl-D-glucuronic acid unit.<sup>19</sup>

When a β-glycosidic linkage is split in the model **8** compound **1** is formed but when the same linkage is split in **9**, model **7** is formed. Thus, in this way a higher quantity of residue is formed during isothermal degradation of **9** than in the case of **8**. Activation energies of trimers **8** and **9** are higher than for dimer **7**. The values of polysaccharide **10** rate constants are the highest ones for all studied models. The activation energy is lower than for most of the linear pentoglycanic oligosaccharides. When we compare the rate constants of

reduced microcrystalline cellulose<sup>8</sup> to the values of the reduced xylan, it can be seen that the values of the latter one are higher by more than 1 order of magnitude. On the other hand, its activation energy of gasification is higher than that of reduced microcrystalline cellulose.<sup>8</sup>

This could be explained by the differences in the supramolecular structure of these two polysaccharides.

The values of kinetic parameters obtained on unmodified beach xylan degraded in vacuum<sup>1</sup> at temperatures from 204 to 221°C were lower than for model 10. These results cannot be compared with the results of our work because of the different conditions used. It could be supposed, however, that the thermal stability of unmodified (4-O-methyl-D-glucurono)-D-xylan is lower in comparison with the reduced polysaccharide for the same reason as was stated for models related to cellulose.<sup>8</sup> On the other hand, we came to the same conclusion as the Japanese authors<sup>1</sup> in that the thermal degradation of (4-O-methyl-D-glucurono)-D-xylan is more complex in comparison to cellulose.

### CONCLUSIONS

The thermal stability of methylglycosides related to (4-O-methyl-D-glucurono)-D-xylan increases with the increasing number of pyranose units. The pentoglycanic models related to (4-O-methyl-D-glucurono)-D-xylan are more thermally stable than the corresponding hexoglycanic models of cellulose. Rates of xylouronide gasification are higher than those of the neutral models. The rate of polysaccharide gasification was the highest one from all studied models. The supramolecular structure of polysaccharide dramatically influences the course of thermal degradation.

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