

Thermogravimetric / Mass Spectrometric Characterization of the Thermal Decomposition of (4-O-Methyl-D-Glucurono)-D-Xylan

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Synopsis

A thermogravimetric/mass spectrometric (TG/MS) system was used to characterize the thermolysis reactions of (4-O-methyl-D-glucurono)-D-xylan. The mass spectrometric peaks, measured as function of time, were attributed to water, methanol, carbon monoxide, carbon dioxide, formaldehyde, formic acid, acetic acid, acetone, acrolein, 2-furaldehyde, and 3-hydroxy-2-penteno-1,5-lactone. The time derivative of the thermogravimetric curve (DTG) consisted of two partially overlapping peaks, indicating a multistep mechanism. The mass spectrometric intensities of the peaks assigned to methanol and 2-furaldehyde coincided with the first DTG peak, suggesting that the first DTG peak represents both dehydration and fragmentation pathways. Methanol, water, formyl group, and carbon dioxide contributed to both of the DTG peaks. This indicates that the dehydration, decarboxylation, and decarbonylation took place in two steps. The compounds observed only in the second DTG peak and later (acetone, formic acid, formaldehyde, acrolein, acetic acid, and 3-hydroxy-2-penteno-1,5-lactone) are probably products of reactions which occur after the collapse of the original polysaccharide structure.

INTRODUCTION

The (4-O-methyl-D-glucurono)-D-xylan is regarded as the most reactive polymer component of many plant materials toward thermal decomposition. This polysaccharide, which is similar to cellulose, consists of pyranose units linked by (1-4)- β -glycosidic bonds. One major difference between xylan and cellulose is the absence of C-6 carbons on the main chain consisting of xylopyranose units. Other differences include the presence of 4-O-methyl-D-glucuronic acid units, which are linked to the C-2 carbons of some of the xylopyranoses by α -glycosidic bonds. The noncellulose polysaccharides also possess a lower molecular weight and different supramolecular structure than cellulose.

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The thermal decomposition of (4-O-methyl-D-glucurono)-D-xylan has been intensively studied during last decade.¹⁻⁵ Although many products of thermal degradation were identified, the mechanism of their formation is still not understood. Generally the thermolysis reactions of polysaccharides can be divided to cleavage of glycosidic, C—H, C—O, and C—C bonds, dehydration, decarboxylation, decarbonylation reactions, formation of C—C, C=C, C—O bonds, as well as carbonyl and carboxyl groups.⁶⁻⁸ There are suggestions of homolytical^{9,10} as well as heterolytical bond cleavages.^{4,6}

In the present study we used a thermogravimetric/mass spectrometric (TG/MS) system to characterize thermolysis reactions of (4-O-methyl-D-glucurono)-D-xylan at atmospheric pressure in an inert environment. The advantage of this approach is the separation of the reaction pathways according to their temperature dependence.

EXPERIMENTAL

Materials

(4-O-Methyl-D-glucurono)-D-xylan was prepared from beech sawdust.¹¹ It had an optical rotation $[\alpha]_D^{22} = -70$ (c 0.5, water), and a molecular weight $\bar{M}_n = 18,610$. It contained 3.35% ash, 19.3% carboxyl, and 2.93% methoxyl groups. The neutral portion of the saccharides formed on hydrolysis contained 98% of D-xylose. The polysaccharide was recycled by mixing with 100 mL of 0.1M HCl and stirred for 12 h at 5°C. The sample was then dialysed and freeze dried. The ash content of the product was 0.47%.

Methods

Thermal degradation was studied by a Perkin-Elmer TGS-2/System 4 thermobalance coupled to a Balzers QMG 511 mass spectrometer and a DEC PDP 11/34 computer.^{12,13} An argon atmosphere, linear sample heating rates of 10 K/min or 80 K/min from 50 to 650°C, and samples of about 1 mg in open platinum crucibles were used. The furnace of the thermobalance was connected to the ion source by a heated quartz capillary. Compounds with boiling points above 150°C did not reach the ion source. At 10 K/min heating rate, all mass spectrometric intensities were measured in the range of m/z 15–150, except the highest background peaks of the argon carrier gas (m/z 20, 36, and 40). At 80 K/min heating rate, the higher reaction rate permitted measurements of only 20 preselected ions. The preselection was based on the 10 K/min experiments. After subtracting the background level and making corrections for a few well-defined fragmentation patterns, the results were plotted by a digital plotter connected to the computer. Smaller ion intensities were magnified appropriately. The actual magnitudes of the intensities are summarized in Table I. The applied software was described previously.¹³ The tentative identification of the observed mass spectrometric ions was based partly on mass spectra collections,¹⁴ and partly on chemical considerations.

RESULTS

Figure 1(a) displays the DTG curve (thick line) of the substrate heated at 10 K/min heating rate, and four abundance curves (thin lines) of ions m/z 31,

TABLE I
Tentative Assignments and Normed Intensity Maxima of the Observed Mass Spectrometric Ions

m/z	Tentative assignment of ions	Contribution to DTG peak	Maximum at 10 K/min [nanoampere]	Maximum at 80 K/min [nanoampere]
15	Methyl group	Both	2.2	8.9
16	Ammonia [M - 1] ⁺	Both	2.3	11
18	Water	Both	103	377
27	Acrolein fragment	2	0.9	—
28	CO	2	21	81
29	Formyl group	Both	5.5	22
30	CH ₂ O	2	1.6	7.4
31	Methoxyl group	1	4.3	17
32	Methanol	1	3.6	—
43	Acetyl group	2	0.9	3.0
44	CO ₂	Both	15	68
46	HCOOH	2	0.2	0.4
58	Acetone	2	0.2	0.7
95	2-furaldehyde [M - 1] ⁺	1	0.7	1.3
96	2-furaldehyde	1	0.7	1.4
114	C ₅ H ₆ O ₃	2	0.1	—

32, 95, and 96. Weight loss began at 200°C and reached a maximum DTG value of 0.188%/s at 272°C. The DTG curve appears to be composed of two partially overlapping peaks. The ion intensities displayed in Figure 1(a) strictly follow the first peak.

In Figure 1(b), ions with m/z 15, 16, 18, and 44 are compared to the DTG peak. Note that all these ions show the same double peak as the DTG.

In Figure 1(c) ions whose intensity-time dependance followed the second DTG peak are shown: m/z 27, 30, and 46 (295°C). The ions in Figure 1(d) (m/z 43, 58, and 114) appeared after the second maximum of the DTG curve.

The same behaviors were observed at 80 K/min rate [see Figures 2(a)–2(c)]. The higher decomposition temperatures displayed in these figures are due to the higher sample heating rate. The maximum of the DTG curve is 1.6%/s, which is more than eight times higher than the value at 10 K/min. This large increase in DTG peak is a signature of competing reactions.¹⁵ However, the increase of the intensity maxima was considerably less, indicating that the amount of the nondetected high molecular weight compounds is higher at 80 K/min.

DISCUSSION

The ions observed to overlap the first DTG peak were assigned to methanol (m/z 31 and 32) and 2-furaldehyde (m/z 95 and 96). These compounds were identified previously⁴ and that is why we did not supply any additional evidence. They indicate the demethoxylation of 4-O-methyl-D-glucuronic units and dehydration of pyranose units. The reactions producing these compounds are probably related to each other since the α -glycosidic bonds are more sensitive to thermal degradation than the β -glycosidic ones.⁵ As it was observed on model compounds the formation of 2-furaldehyde in the region of

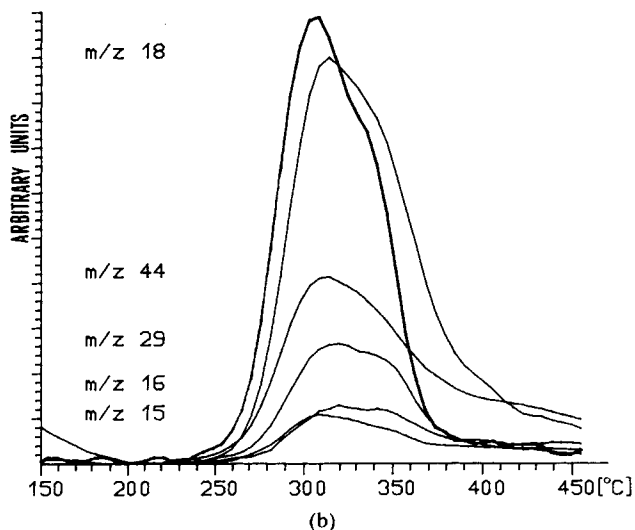
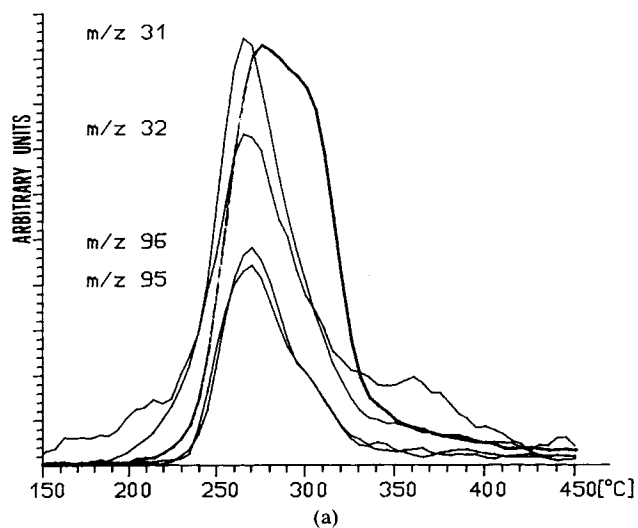


Fig. 1. Comparison of the DTG curve (thick line) and the ion intensities (thin lines) at 10 K/min heating rate. The m/z values are indicated at the level of the corresponding intensity maxima. The smaller intensities are magnified for a better view. The tentative assignment of the ions and the numerical values of the intensity maxima are given in Table I. (a) Intensities having maxima at the first overlapping DTG peak. (b) Intensities of the ions contributing to both overlapping DTG peaks. (c) Intensities having maxima at the second overlapping DTG peak. (d) Intensities having maxima after the second overlapping DTG peak.

the first DTG peak is related to the dehydration of glucuronic units.¹ Figures 1(b)–2(b) show those ions formed from compounds which contributed to both overlapping weight loss processes. They were identified as water (m/z 18), carbon dioxide (m/z 44), formaldehyde (m/z 29), ammonia (m/z 16), and various compounds containing the methyl group (m/z 15).¹⁴ Note that the intensity of m/z 16, shown on Figure 2 was corrected by subtracting the

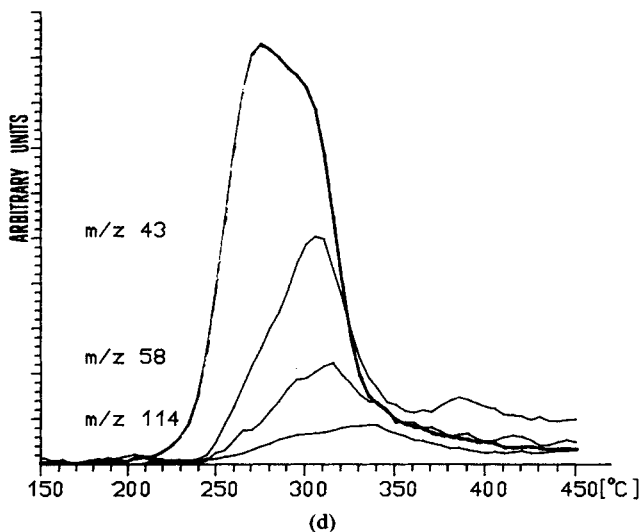
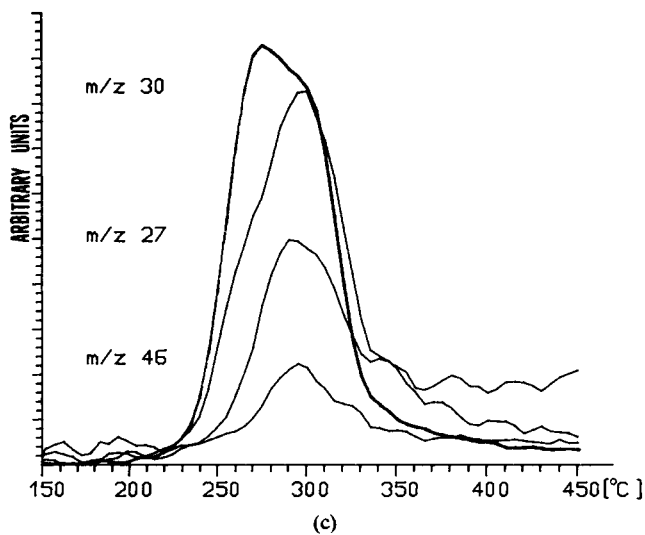


Fig. 1. (Continued from the previous page.)

intensity arising from fragments m/z 16 of H_2O and CO_2 . The ion m/z 16 can be a molecular ion of methane or $[M - 1]^+$ fragment of ammonia. However while fixed gases were observed as pyrolysis products of xylan at $300^\circ C$,⁴ we also know that ammonium was used for isolation of polysaccharide from wood.¹¹

The double peak of the m/z 18 ion intensities assigned to water is due to different dehydration reactions. At lower temperatures, 2-furaldehyde is probably formed mainly by dehydration of pentose units, which were formed from uronic acid units by decarboxylation. DeGroot et al.¹⁶ observed decarboxylation by TG-FTIR (Fourier transform infrared) analysis of wood material at the region of 250 – $300^\circ C$. Hence it is possible that CO_2 formation is related to

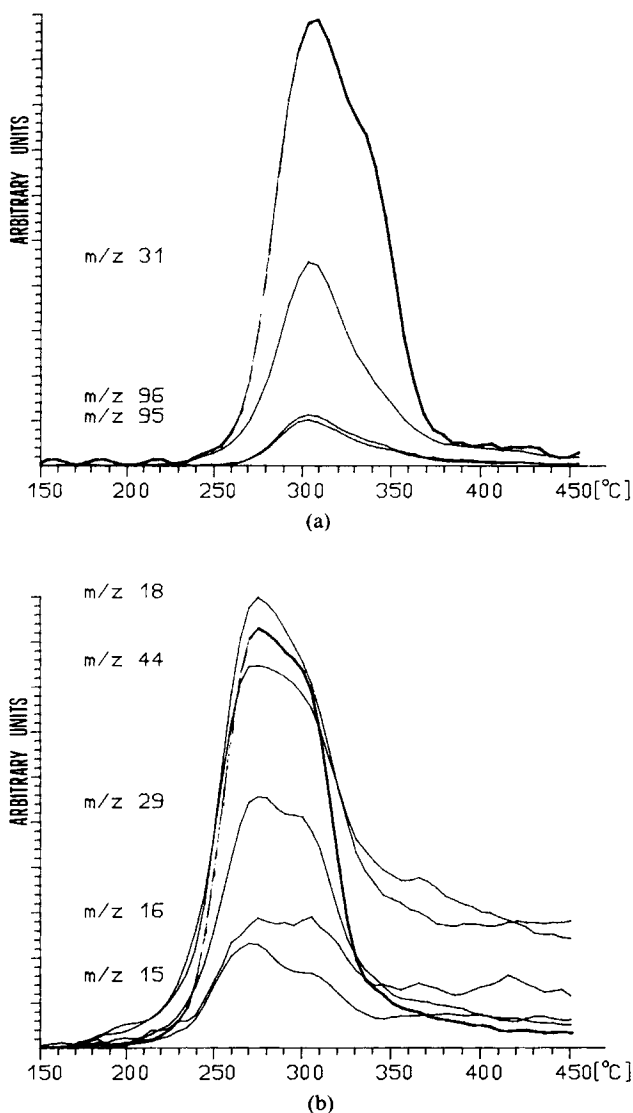


Fig. 2. Comparison of the DTG curve (thick line) and the ion intensities at 80 K/min heating rate. The tentative assignment of the ions and the numerical values at the intensity maxima are given in Table I. (a) Intensities having maxima at the first overlapping DTG peak. (b) Intensities contributing to both overlapping DTG peaks. (c) Intensities having maxima near to the second overlapping DTG peak.

the degradation of uronic acid units, although carbon dioxide was also observed in degradation of polysaccharides not originally containing carboxylic groups but formed by oxidation.⁶ At higher temperatures the D-xylose units of the main chain undergo dehydration. The relation between decarboxylation (m/z 44) and dehydration of uronic acid units was observed previously.³ The ion intensity belonging to the water was much higher than the other intensities (see Table I), indicating that the dehydration products were transformed in char and tar as well.

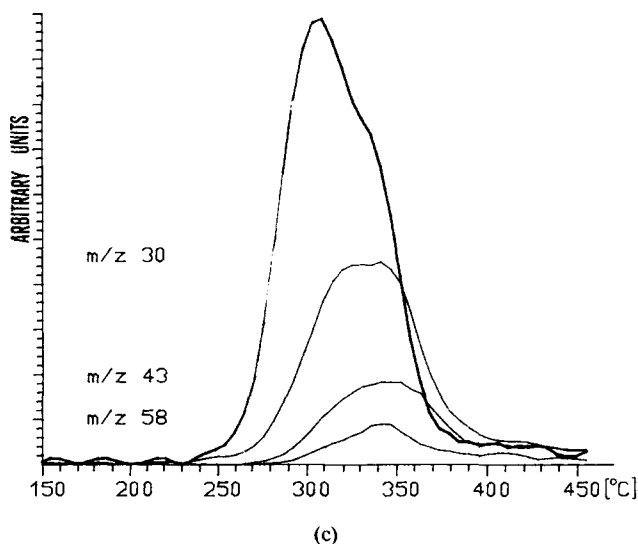


Fig. 2. (Continued from the previous page.)

The second dehydration peak, which is not associated with 2-furaldehyde formation, must result from the dehydration of the D-xylose units of the linear D-xylan chains which were not cleaved from macromolecule fragments. This dehydration is random and is accompanied by double bond and carbonyl group formation.¹⁷ The carbonyl groups, which are reflected by the m/z 29 (formyl) ion may also result from the cleavage of glycosidic bonds. The dehydration of the main chain of (4-O-methyl-D-glucurono)-D-xylan is more complex and many of the dehydration products remain in the residue.¹⁷

The ions close to the second maximum of the DTG curve (CH_2O , m/z 30; C_2H_3 , m/z 27; and CH_2O_2 , m/z 46) represent secondary products of thermolysis. Retroaldolization is characterized by the appearance of the formaldehyde ion.³ The m/z 27 (C_2H_3) ion is the base peak for acrolein,¹⁴ while m/z 46 is the next most intensive ion for formic acid (after m/z 29), which was also observed in relation to the second DTG peak. Formic acid is a known product of xylan thermolysis.⁴

The ions having maximal intensity after the second DTG peak were tentatively assigned to acetyl groups (m/z 43), acetone, (m/z 58), and 3-hydroxy-2-penteno-1,5-lactone (m/z 114) ions. The presence of ketene (CH_2CO , m/z 42) could not be associated with m/z 43. It is known that ketene becomes detectable at 400°C and reaches its maximum at 700°C.¹⁹ The intensity of m/z 43 reaches its maximum at 300°C and then decreases [Fig. 1(d)].

The (4-O-methyl-D-glucurono)-D-xylan used in this study did not contain acetyl groups in quantity detectable by ^{13}C -NMR (nuclear magnetic resonance) spectroscopy.¹⁸ Consequently, we presume that acetyl ions (m/z 43) did not result from the acetyl groups of the polysaccharide. Acetic acid and acetone are known products of xylan,⁴ and cellulose thermolysis.^{6,20} 3-Hydroxy-2-penteno-1,5-lactone has also been reported several times.¹⁻³ The ion m/z 132 was not observed under TG/MS conditions, probably because

the temperature of degradation was much lower than those employed previously.^{3,21}

CONCLUSIONS

The TG/MS studies point to the role of dehydration, demethoxylation and fragmentation reactions during the early stages of (4-O-methyl-D-glucurono)-D-xylan thermolysis. These reactions are observed in two steps. Although the dehydration reactions continue at higher temperatures. 2-furaldehyde is formed only in the first dehydration step. In addition the dehydration reactions also form moieties having double bonds, carbonyl groups, and conjugated double bond-carbonyl groups. These moieties rearrange, condense, and fragment to generate CO, CO₂, formaldehyde and other products, which continue to evolve at higher temperatures.

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