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Thermal synthesis and pyrolysis of a xylan*

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ABSTRACT

A xylan has been synthesized in yields up to 64% by thermal polymerization of methyl β-D-xylopyranoside, catalyzed by phosphoric acid. The polymer is highly branched, with d.p. ~20. The xylose units in the polymer are predominantly pyranose, with some furanose, and 14% of the nonreducing end groups are in the furanose form. The "reducing" end groups are at least partly in the form of methyl xylosides. Vacuum pyrolysis of the pure synthetic xylan gave a high char yield (48%, compare, for example 5% from pure cellulose), 1,4-anhydro-α-D-xylopyranose (5.7%), and 1,5-anhydro-4-deoxypent-1-en-3-ulose (2.4%). The structure of the latter compound was verified by degradation experiments and it was shown to be the compound previously isolated from pyrolysis of natural xylans and incorrectly assigned as 3-hydroxy-2-penteno-1,5-lactone. This glyculose has considerable importance as a marker compound for xylans in pyrolysis of biomass materials.

INTRODUCTION

We have recently embarked upon a series of studies of chemical mechanisms in pyrolysis of polysaccharides[1–3]. These studies have included cellulose[1], cellobiitol as a model for cellulose[2], and amylocyclodextrin as a model for starch[3]. The general thesis has been that in the pure glucans (especially when completely free from metal ions) the dominant pyrolytic reaction proceeds by a scission of glycosidic bonds to yield shortened polymer chains ending in a glucosyl cation. These cations are stabilized either by intramolecular formation of an anhydride (usually 1,6), or by intermolecular addition to a hydroxyl group of another polysaccharide molecule (transglycosylation). Subsequent scission of a glycosidic linkage adjacent to an anhydride end group yields volatile 1,6-anhydro-β-D-glucopyranose (LG) which is thus removed from the equilibria occurring in the solid and is obtained in high yield. An alternative channel for high-yield formation of LG is the scission of the glycosidic linkage of a nonreducing end group, with subsequent rapid formation of the volatile LG. The latter type of reaction channel has been shown to be especially facile with the pendant L-arabinofuranose units of arabinogalactan[4] and with single pendant D-galactopyranose units of galactoglucomannans[5]. The present study is intended to extend this type of work to xylans and also to investigate the effects of "neutral" inorganic salts on the pyrolysis.

Xylans are significant components of most plant cell walls, usually as hetero-

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polysaccharides classified as hemicelluloses. Xylan chains are commonly (1→4)-β-linked and usually carry L-arabinofuranose and uronic acid groups. Therefore, because most materials classified as biomass are derived from plant cell-walls, and because thermochemical utilization is one of the most promising methods for utilization of biomass, the pyrolysis of xylans is of some practical importance. The detailed chemistry of the field has not been extensively studied, however, because of the heterogeneous nature of natural xylans and in fact there are no prior chemical studies of pyrolysis of a pure xylan. Our approach to this system has now been motivated by a recent study of thermal polymerization of some glucopyranosides, which yielded highly branched glucans[6]. Similar polymerization of xylopyranosides was anticipated to yield an analogous, highly branched pure xylan. Admittedly the linkages in the xylan were not expected to correspond entirely to the "naturally" predominant β-(1→4), but our previous studies[1-5] have all indicated that the orientation and position of the glycosidic linkages have only limited influence on pyrolytic behavior of polysaccharides.

Xylans have previously been synthesized by the thermal polymerization of D-xylopyranose[7,8]. Shafizadeh *et al.*[9] presented thermogravimetric data suggesting that zinc chloride catalyzed the thermal polymerization of phenyl β-D-xylopyranoside, but did not isolate the polymer. In a subsequent paper, Shafizadeh *et al.*[10] reported a "polymeric tar" which condensed at room temperature in the vacuum pyrolysis of methyl β-D-xylopyranoside. A reducing end-group analysis was reported to indicate the presence of molecules of average d.p. 6. However, this analysis was based on two assumptions, namely that only oligomeric or polymeric material was present in the tar, and that all such molecules have a reducing end group. It is now possible to conclude that neither of these assumptions was valid. Thus we have recently shown[6] that polymers formed from glucosides retain the aglycon at the "reducing" end group, and furthermore our preliminary experiments associated with the present study indicated that under the experimental conditions used by the aforementioned workers a large proportion of the methyl xyloside would simply have distilled over into the tar. Both effects would have invalidated the reducing end-group analysis.

RESULTS AND DISCUSSION

A thermogravimetric study of methyl β-D-xylopyranoside (MeXyl) was conducted in order to determine the optimum polymerization and catalyst conditions. Fig. 1 shows thermogravimetric (t.g.) curves and the corresponding differential thermogravimetric (d.t.g.) curves for the heating of MeXyl with and without the addition of an acid catalyst. The horizontal line near the top of Fig. 1 corresponds to the theoretical weight-loss resulting from scission of all glycosidic bonds and loss of methanol. The d.t.g. curve of pure MeXyl shows a maximum at 270° with a shoulder at 238°. We interpret the shoulder as due to loss of methanol to form polymer and the peak maximum as due to subsequent pyrolysis of the polymer to form char and volatiles. A catalyst was sought that would optimize the separation of these two events. Among the several acid catalysts investigated, all resulted in lowering the temperatures of both

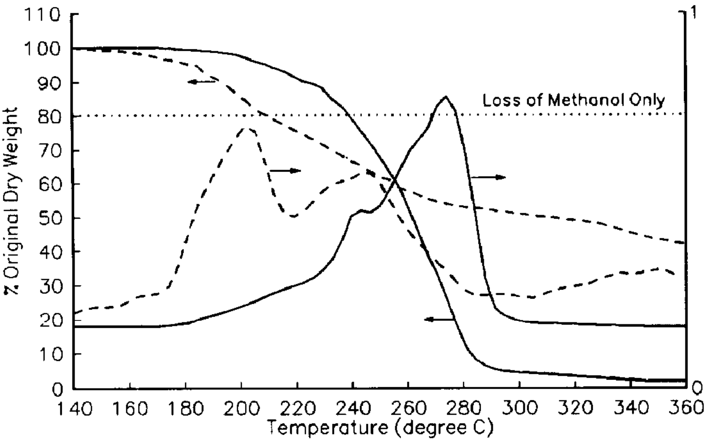


Fig. 1. Thermal analysis of methyl β-D-xylopyranoside: (—) neat; (---) with 1% phosphoric acid. Arrows indicate applicable axes.

polymerization and pyrolysis. However only phosphoric acid was non-volatile under the conditions used and also effective in increasing the temperature range separating these two events, as shown in Fig. 1.

Preparative polymerizations were carried out with MeXyl containing 1% phosphoric acid at temperatures between 160 and 170°, and results are shown in Table I. After experiment 2, improved homogeneity of the initial reaction mixture was achieved by grinding the xyloside/acid mixture obtained by evaporation at <35° from a 95% ethanol solution. Experiments 1–3 were conducted with 1-g samples in flat-bottom vials in a thermostatically controlled oven, but subsequent experiments were conducted using a 1–10 g sample as a thin layer with occasional stirring in an open Erlenmeyer flask in a thermostatically controlled oil bath. This procedure was critical for obtaining good heat distribution to the melt in the later stages of the polymerization when the melt became more viscous and the escaping methanol generated a voluminous semi-solid foam. Argon plasma spectrometry of polymer 6 revealed that the phosphorus from the catalyst was becoming incorporated into the polymer, presumably as phosphate esters. To minimize this, subsequent polymerizations were conducted with less acid. The polymers were precipitated from aqueous solutions of the melts with ethanol. Polymers and ethanol-soluble fractions were analyzed for carbohydrate content (expressed as apparent anhydroxylose content) by phenol–sulfuric acid analysis[11], and unchanged MeXyl and its anomer, (see below) were determined by trimethylsilylation and g.l.c. of the ethanol-soluble fractions. The results are shown in Table I.

The Me_3Si/g.l.c. analysis showed that the recovered starting material had undergone anomerization, the ratio of α to β anomer ranging from 1.2 to 0.5. This result demonstrates the reversibility of the first step (formation of a xylosyl cation, **1**) in the polymerization. The mechanism of polymerization is regarded as general for all glycosides and has previously been detailed for glucoside polymerization[6]. Formation of the xylosyl cation **1** has previously been invoked to explain the anomerization of ethyl xylosides[12].

TABLE I

Thermal polymerization of methyl β-D-xylopyranoside

Conditions (acid)	*Wt. loss*[a] *(%)*	*Isolated yield, % (aXyl*[b]*)*		*Recovered MeXyl (α/β), %*
		polymer[c]	*EtOH sol.*[d]	
1. 165°, 1 h (1%)	18.1	15 (92%)	63 (88)	15 (0.5)
2. 170°, 1 h (1%)	19.7	31 (89%)	49 (81)	4 (0.9)
3. 170°, 1.5 h (1%)	19.6	55 (88%)	26 (81)	1 (1.1)
4. 165°, 1 h (1%)	20.2	64	n.d.[e]	n.d.
5. 160°, 1 h (1%)	18.5	50	n.d.	n.d.
6. 165°, 1 h (1%)	19.7	53	27	3 (1.2)
7. 180°, 2 h (0.1%)	23.0	29	34	3 (0.5)
8. 170°, 1 h (0.5%)	20.0	57	n.d.	n.d.
9. 180°, 1 h (0.1%)	23.0	38	n.d.	n.d.
10. 180°, 1 h (0.1%)	19.4	47	n.d.	n.d.

[a] Theoretical weight loss: 19.4%. [b] Apparent anhydroxylose content. [c] Polymer is fraction insoluble in 95% ethanol; percent yield based on theoretical maximum yield. [d] Ethanol-soluble fraction; percent yield based on starting material. [e] Not determined.

Experiments 1–3 heated in air oven; 4–10 heated in an oil bath.

An ^{1}H-n.m.r. spectrum of polymer 2 showed a methoxyl singlet at 3.5 p.p.m. which we assign to methyl xyloside end groups. Polymer 2 was subjected to hydrolysis, the released methanol was determined by g.l.c., and the number-average molecular weight corresponded to d.p. 26, assuming one xyloside end group per molecule in the polymer. Gel chromatography on Sephadex G-50 (Fig. 2) indicated a range of molecular weights, with average d.p.$_w$ ~22 using gel calibration values provided by the gel manufacturer and based on dextrans[13]. A similar analysis for polymer 7 indicated d.p.$_w$ ~17. The synthetic xylans are thus somewhat larger than the glucans from methyl glucoside (d.p.$_n$ 13, d.p.$_w$ ~12)[6].

Polymer 7 was subjected to methylation analysis[14], and the results are shown in Table II. Reduction with sodium borodeuteride was utilized separately to distinguish between the 2-monomethyl and 4-monomethyl derivatives as well as between the 2,3-dimethyl and 3,4-dimethyl derivatives. Retention times and molar ratios are relative to the 2,3,4-trimethyl derivative and the ratios have been corrected for carbon response[15]. The predominant 2,3-dimethyl derivative originates from (1→4)-linked pyranose and/or (1→5)-linked furanose in-chain units. The least abundant in-chain pyranose unit gives rise to the 3,4-dimethyl derivative and is thus (1→2)-linked, suggesting that the 2-hydroxyl is the least sterically accessible of the secondary hydroxyl groups. Our synthetic xylan is thus a heavily branched polysaccharide whose relatively random linkages are controlled by statistical and steric factors.

It is noteworthy that 14% of the trimethyl derivatives derive from furanose nonreducing end groups. Dutton and Unrau[16] found that such furanose rings constitute 38% of the nonreducing end groups in xylans synthesized from the thermal polymerization of xylose. Furanose end groups have also been detected in the glucans from

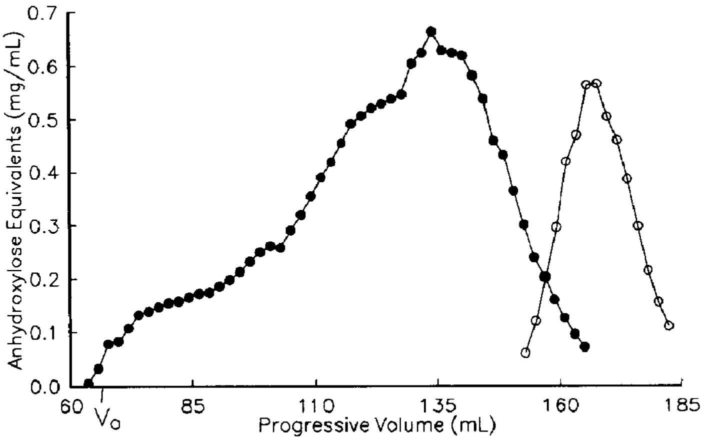


Fig. 2. Gel chromatography on Sephadex G-50: (●) MeXyl polymer; (○) glucose.

thermal polymerization of glucopyranosides[6]. A mechanism whereby such furanose units can derive from glycopyranosyl cations has been proposed by Mowery *et al.*[17] to account for the isomer distribution in glycosidation reactions. An analogous reaction presumably occurs with the xylopyranosyl cation prior to polymerization. The resultant xylofuranosyl cation, when added to the growing xylan polymer, would carry a primary hydroxyl group at C-5, which would then present a favored position for addition of further xylosyl cations. On this basis it is probable that a significant proportion of the 2,3-dimethyl derivatives listed in Table II are derived from (1→5)-linked in-chain furanose rings. The major portion of the in-chain units however are pyranose, since the 3,4- and 2,4-dimethyl derivatives could not form from furanose units.

For the pyrolysis of MeXyl polymer, a temperature of 280° was suggested by the results of thermogravimetric experiments. Two vacuum pyrolyses were conducted on two samples of polymer 7 for 30 min at 280°, one of the samples having been mixed with 1% sodium chloride, in order to determine whether catalysis by a "neutral" salt significantly influenced the pyrolysis products as previously observed with cellulose[1]. The results are shown in Table III.

The distillate fractions (namely, −50° condensates, after removal of room-temperature condensates) are predominantly water. ^{1}H-N.m.r. spectra of these fractions after dilution with deuterium oxide showed the presence of the other components listed in Table III. The sodium chloride-catalyzed pyrolysis gave rise to glycolaldehyde (GA) in significant yield. GA is also a significant product (with simultaneous reduction in levoglucosan yield) when cellulose is pyrolyzed in presence of small amounts of sodium chloride, and we have previously speculated on a possible mechanism for this conversion[18]. Pyrolysis of the xylan containing added sodium chloride also resulted in increased yields of the one-, two-, and three-carbon compounds shown in Table III in the distillate at the expense of anhydro sugar yield in the tar fraction. These products are the same as those favored by the presence of sodium chloride in the pyrolysis of cellulose[1].

TABLE II

Methylation analysis of MeXyl polymer

OMe Positions of methylated xylitol acetates	*Molar ratio*	*G.l.c. retention time*[a]
2,3,5	0.16	0.92
2,3,4	1.00	1.00
2,4	0.70	1.32
2,3	1.07	1.40
3,4	0.32	1.40
3	0.26	1.71
2	0.50	1.72
4	0.14	1.72
Xylitol	0.15	2.00

[a] SP-2330 capillary column.

TABLE III

Vacuum pyrolyses of MeXyl polymer

Added NaCl	*Yield*[a] *(%)*		*Me_3Si/g.l.c. retention time of tar components*[b]
	0	*1*	
Distillate[c]	25.2	30.3	
glycolaldehyde	n.d.[d]	1.5	
hydroxyacetone	n.d.	0.4	
acetic acid	n.d.	0.2	
2-furaldehyde	0.2	0.2	
formic acid	n.d.	trace	
1,5-anhydro-4-deoxy-pent-1-en-3-ulose	2.4	n.d.	
Tar[e]	21.8	22.3	
1,4-anhydro-α-D-xylopyranose	5.7	0.3	0.34
unknown			0.37
3-deoxypentono-1,4-lactones	trace	3.0	0.42 and 0.44
Me α-Xyl	0.3	0.3	0.62
Me β-Xyl	0.5	0.5	0.64
probable dimers			1.3 to 1.5
Char[f]	48.2	43.1	

[a] Based on starting material. [b] Relative to glucitol; HP-1 capillary column. —50°condensate. [d] Not detected. [e] Room temperature condensate. [f] Non-volatile pyrolysis remainder.

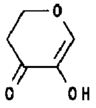
The 2-furaldehyde is formed by xylan pyrolysis with or without sodium chloride. A mechanism whereby 2-furaldehyde can arise in the acid degradation of xylose has been proposed by M. J. Antal *et al.*[19], and can be extrapolated to the pyrolysis of a xylan. This mechanism is only likely to apply to free xylopyranosyl cations derived from nonreducing end groups and to in-chain scission products which are (1→4)-linked and/or (1→3)-linked, since the formation of the O-2 to C-5 bond required by this mechanism is sterically unlikely for a xylosyl cation linked at position 2.

The 1,5-anhydro-4-deoxy-pent-1-en-3-ulose (**22**) has not previously been reported as a polysaccharide pyrolysis product. It is however the five-carbon analogue of 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**3**) which has been shown to be a product of cellulose pyrolysis[20]. A mechanism whereby **3** arises in the pyrolysis of cellulose has been proposed by Shafizadeh *et al.*[20], and an analogous mechanism would explain the formation of **2** from a xylan. The ^{1}H-n.m.r. spectrum of **2** was derived from the spectrum of the distillate fraction from the pyrolysis of the pure xylan after deduction of the spectra of water and 2-furaldehyde and shows a 1-H singlet at δ 7.46, and a 2-H doublet of doublets at δ 2.66 coupled with a 2-H doublet of doublets at δ 4.40, the relative simplicity of the latter signals arising from the magnetic equivalency of the protons in each of the two methylene groups. We believe that a compound previously reported as a product of xylan pyrolysis by Miyazaki[21] and subsequently accepted by later workers[22-25] as 3-hydroxy-2-penteno-1,5-lactone (**4**) was in fact **2**. The reported mass spectrum and ^{1}H-n.m.r. spectrum are the same as our compound, and the ^{1}H-n.m.r. spectrum does not show the singlet near δ 5 that would be anticipated[26] for H-2 in **4**.

This product has considerable importance as a marker compound for xylans in pyrolysis of biomass materials. Thus the relevant molecular ion (*m/z* 114) observed in molecular-beam mass spectrometry studies of biomass pyrolysis has been described as a "characteristic hemicellulose indicator species"[27] and must be due (at least partly) to our compound **2**. Similarly, this ion has been listed[28] as a "polysaccharide marker compound" in the pyrolysis–m.s. of biomass, with a "proposed identification" as 4-hydroxy-5,6-dihydro-(2*H*)-furan-2-one (presumably intended as 4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one, which was the name given to **4** by Miyazaki[21]). In view of these apparent uncertainties we have taken further steps to confirm the identity of **2** as a significant pyrolysis product from xylans.

The ^{13}C-n.m.r. spectrum of the distillate, after deduction of the 2-furaldehyde spectrum, showed a singlet at 153 p.p.m. in the completely decoupled spectrum, converting to a doublet in the off-resonance decoupled spectrum. This chemical shift is the same as that for C-1 of an authentic sample of **3**, the structure of which has been confirmed by X-ray crystallography[29].

The structure of **2** was further verified by the following sequence of reactions. Reduction of the distillate with sodium borohydride yielded **5** (presumably four isomers) and also converted the 2-furaldehyde into 2-furanmethanol, which was removed during evaporation of the aqueous solution. Compound **5** was oxidized with periodate and then further reduced with sodium borohydride to yield 2-hydroxyethyl 3-hydroxypropyl ether (**6**), which showed an appropriate ^{1}H-n.m.r. spectrum. Further support for the identity of **6** was provided by g.l.c.–m.s. of its methylated and acetylated derivatives (entries 2 and 4 in Table IV). In each case, comparable data were obtained for a closely related authentic compound (entries 1 and 3). Finally, it is noteworthy that there is no likely mechanism whereby the pyrolysis of a xylan could give rise to **4**,



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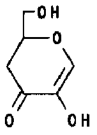

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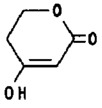

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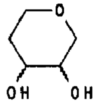

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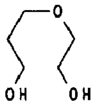

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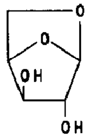

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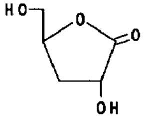

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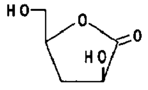

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TABLE IV

G.l.c.–m.s. data for derivatives of **6** and for closely related authentic compounds

Compound	*Retention time*[a]	m/z *(relative intensity)*
Bis(2-methoxyethyl) ether (diglyme)	1.0	31 (51), 43 (15), 45 (41), 58 (47), 59 (100), 89 (12)
2-Methoxyethyl 3-methoxypropyl ether	1.5	31 (19), 41 (19), 43 (10), 45 (100), 58 (19), 59 (25), 71 (11), 72 (19), 73 (17), 89 (5), 103 (6)
Bis(2-acetoxyethyl) ether	3.8	43 (100), 87 (50)
2-Acetoxyethyl 3-acetoxypropyl ether	4.6	43 (100), 73 (10), 87 (25), 101 (33)

[a] Relative to diglyme; HP-1 capillary column.

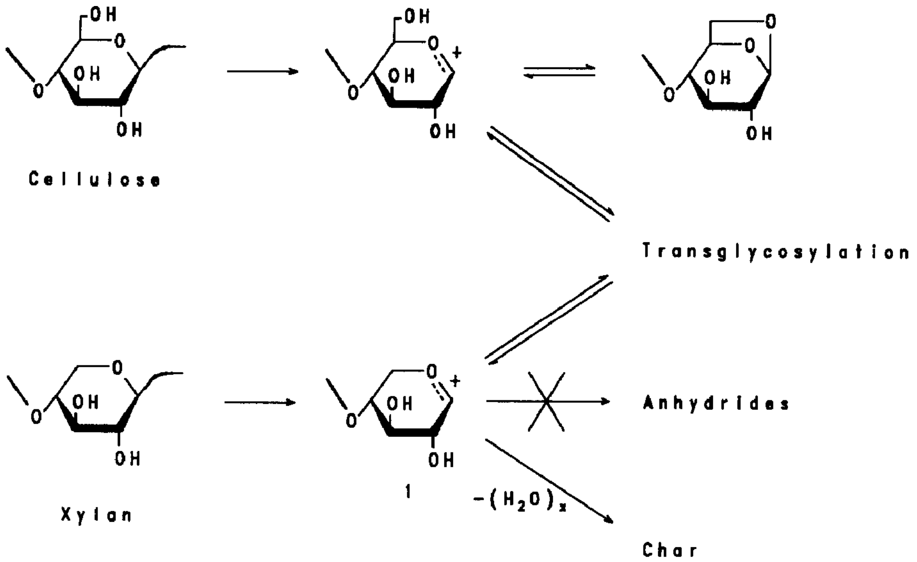
whereas the pyrolytic formation of **2** from a xylan has a direct precedent in the formation of **3** from cellulose.

The tar fractions (namely, room-temperature condensates) from the pyrolyses were analyzed by Me$_3$Si/g.l.c./m.s. as shown in Table III. The 1,4-anhydro-α-D-xylopyranose (**7**) has been previously detected in the products of pyrolysis of naturally occurring xylans[25,27,28,30] and of xylose[31,32]. Our identification of the Me$_3$Si derivative of this anhydro sugar was based on the fact that its mass spectrum was virtually identical with the derivative of authentic 1,5-anhydro-β-L-arabinofuranose[4]. The addition of 1% sodium chloride to the xylan resulted in a 19-fold decrease in the yield of **7** (Table III), analogous to a 50-fold decrease in the yield of levoglucosan from cellulose pyrolyzed with 1% sodium chloride[1].

The presence of both pyranose and furanose rings in the MeXyl polymer allows for two possible mechanisms for the formation of **7**, one involving O-5 to C-1 ring closure of the xylofuranosyl cation, and the other involving O-4 to C-1 ring closure of the xylopyranosyl cation. Such a closure could occur when the cation is present at the "reducing" end of a chain following a chain scission, provided that the cation is not substituted at O-4 for pyranose or at O-5 for furanose. The resulting anhydroxylose end group could then be liberated by an adjacent glycosidic scission to form the volatile anhydro sugar. This is analogous to the mechanism previously postulated for pyrolytic formation of levoglucosan in high yield from cellulose[1]. An additional channel for formation of the anhydroxylose involves scission of the glycosidic bond of a non-reducing end group followed by subsequent ring closure of the liberated cation. Xylofuranosyl end groups would follow this channel to yield the anhydride with high efficiency by analogy with pendant L-arabinofuranosyl end groups in polysaccharides, which have been shown to yield 75% pyrolytic conversion into the anhydride[4]. The low yield of **7** from MeXyl polymer, relative to the yield (up to 66%) of levoglucosan from cellulose, may be explained in part by assuming that, in forming the anhydride, the addition of O-4 to C-1 in a xylopyranosyl cation has a higher activation energy than the addition of O-5 to C-1 in a glucopyranosyl cation.

The D-*erythro* and D-*threo* epimers of 3-deoxypentono-1,4-lactone (**8** and **9**, respectively) were tentatively identified in the tar from the sodium chloride-catalyzed pyrolysis, these identifications being based on a match with g.l.c. retention times and mass spectra determined for the authentic compounds[33]. These compounds are the five-carbon analogues of "glucometasaccharinolactones" (D-*ribo* and D-*arabino* epimers of 3-deoxyhexono-1,4-lactone), which have been shown to be pyrolysis products of (1→3)-linked glucans[34]. Evidently the corresponding pentonolactones can arise by an analogous mechanism from a xylan. This mechanism involves formation of a 3-linked xylosyl cation by chain scission in the xylan and subsequent reaction of the cation with water to form a reducing end group. The water is provided by competing, nonspecific, thermal-elimination reactions such as those that produce char. The open-chain form of this end group then undergoes a β-alkoxycarbonyl elimination and subsequent rearrangements analogous to those known to occur in alkaline degradation of (1→3)-linked polysaccharides[35]. The resultant "xylometasaccharinic" acids lactonize and volatilize in the pyrolysis experiment. Sodium chloride catalyzes the formation of these lactones at the expense of the anhydro sugar. This has also been shown to occur[34] with a (1→3)-β-D-glucan in which the addition of 1.5% sodium chloride increased the pyrolytic yield of "metasaccharinolactones" from an undetectable amount to 37% while decreasing the levoglucosan yield from 49% to <1%.

The tar components listed in Table III account for less than one third of the total tar, and t.l.c. analysis suggested the presence of a variety of oligomers. In agreement with this, a group of late-running peaks in the Me_3Si/g.l.c. analysis of the tar indicated the possible presence of xylosylanhydroxyloses. The Me α- and β-Xyl found in the tar (Table III) evidently originate from the "reducing" ends of the polymer molecules. A significant but unidentified component (Me_3Si/g.l.c./m.s.; presumed M^+, 258) was also observed in both tar samples. A major singlet at 2.44 p.p.m. in the ^{1}H-n.m.r. spectra of the tar fractions may be associated with this unknown.



Scheme 1

The high char yield (as compared with ~5% from pure cellulose) shown in Table III is typical of xylan pyrolyses and is reflected also in the t.g. results. A probable cause of this difference is that scission of the common glucans generally yields a glucosyl cation carrying a free primary hydroxyl group at C-6 which can readily form a stable 1,6-anhydride, and which on further scission yields the volatile levoglucosan[1]. On the other hand, the pyrolytic scission of a xylan is most likely to yield a xylopyranosyl cation that will often be substituted at O-4; thus there is no feasible mechanism for intramolecular "stabilization" of such a cation *via* anhydride formation. The xylosyl cation may be "stabilized" by intramolecular addition of a hydroxyl group from another xylan molecule (transglycosylation). The overall effect however, is that the xylosyl cation from a xylan is much less likely to be "stabilized" than the glycosyl cation from a glucan, and hence the former is more likely to enter the non-specific dehydration pathways that lead to char formation rather than volatiles (tar). These effects are of obvious relevance to thermochemical processing of biomass and are summarized in Scheme 1.

EXPERIMENTAL

General methods. — Except where otherwise stated, analytical methods were employed as described previously[6]. Vacuum pyrolyses were conducted on a 0.25-g scale under a nitrogen flow as described previously[36]. The sample containing 1% (w/w) NaCl was mixed by dissolution in a minimum amount of water followed by freeze-drying. All ^{13}C- and ^{1}H-n.m.r. spectra were recorded at room temperature at 22.5 and 270 MHz, respectively, using D_2O as solvent, and 2-methyl-2-propanol as internal standard (δ 30.9 and 1.20 p.p.m.). For g.l.c.–m.s. analysis of the partially methylated xylitol acetates, a Supelco SP-2330 fused-silica capillary column (30 m, 0.25 mm i.d.) was used on a temperature program of 80° isothermal for 2 min followed by a rate of 30°/min up to 170°, and then 2°/min up to 240°. The column used for g.l.c.–m.s. analyses of pyrolysis fractions and of the compounds listed in Table IV was a Hewlett–Packard HP-1 crosslinked methyl silicone gum capillary (12 m, 0.2 mm i.d.); two temperature programs were used: (*1*) for the derivatized tar fractions from the pyrolyses: 60° isothermal for 1.5 min followed by a rate of 30°/min up to 110° and then 4°/min up to 200°; (*2*) for the compounds listed in Table IV: 50° followed by a rate of 5°/min up to 125°. Yields of "tar" components were determined by f.i.d. response relative to D-glucitol added as the internal standard, using response factors measured with authentic compounds for the xylosides, with the L-arabinose isomer for the anhydroxylose and with 3-deoxy-D-*arabino*-hexono-1,4-lactone for the analogous pentonolactones.

Thermal polymerizations of methyl β-D-xylopyranoside. — Acid-treated xyloside samples were prepared by adding a small volume of aq. H_3PO_4 to a 95% ethanol solution of the xyloside, followed by rotary evaporation in vacuo at <35°, grinding to a fine powder, and drying at 40°/1 torr. The product was a fine powder that melted rapidly under the polymerization conditions used. Polymerization was effected by isothermal heating of a 1–5 g sample in an open, conical flask in a thermostatically controlled oil bath ($\pm$0.1°). During heating, the contents of the flask went from a clear, colorless bubbling melt to a highly viscous red-brown foam which hardened upon cooling. The mass was occasionally stirred with a nickel spatula and the flask was removed at 20–30 min intervals and weighed, so that the heating could be stopped near to the theoretical weight loss. The final melt was dissolved in water (5–7.5 mL) and added dropwise to abs. EtOH (100–150 mL) with stirring. Vigorous shaking was sometimes required to induce flocculation of the precipitated polymer. The polymer was subsequently washed by centrifugation twice with 95% EtOH and twice with acetone, then dried as a light-tan colored powder at 40°/1 torr (MeXyl polymer).

Identification of 1,5-anhydro-4-deoxy-pent-1-en-3-ulose (**2**). — The ^{1}H-n.m.r. spectrum of the distillate fraction from pyrolysis of the MeXyl polymer showed the spectra of water and 2-furaldehyde, plus three other major signals: δ 7.46 (s, 1 H, H-1), 2.66 (dd, 2 H, $J_{4,5}$ 7.0, $J_{4',5'}$ 7.5 Hz, H-4), and 4.40 (dd, 2 H, H-5). The coupling of the H-4 protons with the H-5 protons was confirmed by a decoupling experiment. ^{13}C-N.m.r. spectra, both completely decoupled and off-resonance decoupled, were also obtained, and these showed three major signals, in addition to those for 2-furaldehyde: 153.2 (d, C-1), 36.3 (t, C-4), and 69.4 p.p.m. (t, C-5). Signals for C-2 and C-3 were not observed because of the low concentration of the sample. For purposes of comparison, the corresponding ^{13}C-n.m.r. data for authentic 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**3**) were obtained: 152.5 (d, C-1), 135.9 (s, C-2), 192.4 (s, C-3), 37.5 (t, C-4), 80.8 (d, C-5), and 63.6 p.p.m. (t, C-6).

Reduction of **2** was effected by adding $NaBH_4$ (30 mg) in water (2.5 mL) to an aliquot of distillate fraction (0.5 mL) containing ~15 mg of **2** (as indicated by ^{1}H-n.m.r.

integration relative to the internal standard). After 1 h, the mixture was neutralized with Amerlite IR-120 (H^+), evaporated under vacuum, and MeOH was distilled 4 times from the residue to remove borate esters. Oxidation was effected by adding $NaIO_4$ (43 mg) in water (0.5 mL) to an aq. solution of the reduced distillate fraction (0.5 mL). After 2 h, ethylene glycol (0.05 mmol) in water (1 mL) was added to the mixture. After 1 h, final reduction was effected by adding $NaBH_4$ (1.3 mmol) in water (1 mL). After 1 h, the mixture was deionized with Dowex 50 (H^+) and AG1-X8 (OH^-) (1.5 mL each). After evaporation of the final solution to dryness and dissolving the residue in D_2O, the ^{1}H-n.m.r. spectrum showed only water and signals consistent with the ether product **6**: δ 1.79 (quintuplet, 2 H, $J = 6.4$ Hz) and 3.28–3.73 (apparently four overlapping triplets, 8 H). Two aliquots of this solution corresponding to 1 mg each of **6** were removed for methylation and acetylation. Methylation was performed in Me_2SO (1 mL) with NaOH powder (30 mg) and MeI (100 μL) while stirring for 30 min in a cold bath (10°). The methylated product was separated by partitioning with $CHCl_3$ (1 mL), which was subsequently washed with water (1 mL) three times and evaporated. Acetone was then added in preparation for g.l.c.–m.s. analysis. Acetylation of the other aliquot was performed with Ac_2O (100 μL) in pyridine (100 μL) for 45 min at 100°. After evaporation to dryness, the product was extracted with EtOAc, which was subsequently evaporated and replaced with acetone for g.l.c.–m.s. analysis.

Identification of 3-deoxypentono-1,4-lactones (**8** *and* **9**). — An epimeric mixture containing approximately equal proportions of the brucine salts of 3-deoxy-D-*erythro*-pentonic acid and 3-deoxy-D-*threo*-pentonic acid[33] was treated with IR-120 (H^+) ion-exchange resin, and the resulting acids were lactonized by drying under vacuum to give authentic **8** and **9**. Me_3Si/g.l.c. retention times and mass spectra of these epimers matched those of the two tar components eluting at 0.42 and 0.44 (see Table III). No conclusions were made regarding which of these elution times correspond to a specific epimer. Major *m*/*z* signals (and relative intensities corresponding to the two epimers) are as follows: 59 (25, 25), 73 (100, 100), 75 (35, 44), 117 (99, 99), 129 (25, 25), 143 (50, 70), 147 (50, 70), 233 (25, 28), 261 (6, 6), and 276 (6, 0.3).

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