Alkaline destruction of birch xylan in the light of recent investigations of its structure

MATS H. JOHANSSON and OLOF SAMUELSON, Chalmers University of Technology, Department of Engineering Chemistry, Gothenburg, Sweden

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SUMMARY: In studies of birch xylan and its reactions in alkaline media it was found that a galacturonic acid group is present in the xylan chain adjacent to a reducing xylose end group. The galacturonic acid retards the endwise degradation (peeling). This and other xylan reactions of practical importance during alkaline cooking of wood are discussed in the light of recent investigations of xylan and model substances.

□ Undersökningar angående björkxylan och dess reaktioner främst med alkali har lett till upptäckten att en galakturonsyraenhet är inbyggd i xylankedjan närmast en reducerande xylosändgrupp. Galakturonsyran bromsar alkalisk nedbrytning av xylan från den reducerande änden. Denna och andra tekniskt betydelsefulla reaktioner i alkaliskt medium diskuteras i ljuset av nyare undersökningar av xylan och modellsubstanser.

□ Bei Untersuchungen von Birkenholzxylan und dessen Reaktionen in alkalischen Medien wurde gefunden, dass eine Galakturonsäuregruppe in der Xylankette, benachbart zur reduzierenden Xylose-Endgruppe, vorkommt. Die Galakturonsäure verzögert den Abbau vom Kettenende her (Peeling). Diese und andere Xylanreaktionen von praktischer Bedeutung beim alkalischen Holzaufschluss werden im Lichte neuerer Untersuchungen an Xylan und Modellsubstanzen diskutiert.

ADDRESS OF THE AUTHORS: Chalmers University of Technology, Department of Engineering Chemistry, Fack, S-402 20 Gothenburg, Sweden.

The structure of the reducing end has a great influence on the stability of polysaccharides in alkaline media. It is well known that xylan is more stable towards endwise alkaline degradation (peeling) than glucomannan and hydrocellulose (1). Reduction with borohydride followed by determination of alditol end groups shows that xylan in the wood contains reducing xylose end groups (2), while mannose is the predominant reducing end group in glucomannan (3). It is also well known that a blockage of OH-2 in 4-*O*-substituted reducing sugars by glycosidation or etherification increases the alkali stability dramatically. Accordingly, the higher stability of xylan has been ascribed (1) to the fact that on an average every tenth of the 1,4-linked xylose moieties carries a 4-*O*-methylglucuronic acid group linked glycosidicaliy at C-2. Recent investigations show, however, that galacturonic acid units present in the xylan molecule contribute markedly to the stability of xylan. The purpose of this paper is to review recent studies of the structure of birch xylan and of reactions responsible for a retardation of the alkaline peeling. Some unpublished results are also included. If not otherwise stated the results refer to *Betula verrucosa.*

Galacturonic acid groups in xylan

The isolation of large amounts of 4-*O*-(α-D-galactopyranosyluronic acid)-D-xylose after mild acid hydrolysis of birch xylan (4) and the observation that the galacturonic acid groups cannot be removed by fractionation showed that nonreducing galacturonic acid groups are glycosidically linked to the xylan molecule (5). A large proportion of these groups can be destroyed by alkali treatment at 100°C under such conditions that only a slight drop in viscosity occurs (6). This indicates that the galacturonic acid groups cannot be distributed randomly in the xylan chain but rather are located close to the ends of the molecules.

Reduction with borohydride of xylan samples isolated by alkaline extraction (7, 8) or treated with alkali at low temperature (9), e.g. 40°C, showed that *L*-galactonic acid end groups are formed. By several methods it was confirmed that these groups are formed by reduction of reducing galacturonic acid end groups liberated in high yield by endwise alkaline degradation starting at the reducing xylose moiety in the xylan chain (8, 9). The large proportion of reducing galacturonic acid end groups after alkali treatments, which give a hardly detectable loss in yield, shows that in the untreated xylan the galacturonic acid group must be located very close to the reducing xylose end group. The results indicate that only one xylose group is lost by peeling before the reducing galacturonic acid group is formed. Accordingly, reduction of wood meal with borohydride followed by mild acid hydrolysis gives 4-*O*-(α-D-galactopyranosyluronic acid)-D-xylitol in high yield (9). No traces of the corresponding aldobiouronic acid are formed. The results clearly show that the galacturonic acid group in the xylan present in the wood is linked directly to the terminal reducing xylose group by a 1,4-glycosidic bond.

During treatment of xylan with sodium hydroxide at 40°C the liberated galacturonic acid groups are epimerized to taluronic acid end groups (determined as altronic acid in reduced samples). The destruction of the uronic acid end groups is slow under these conditions. These results are in agreement with the independent observation that OH-2 in the galacturonic acid group is blocked by a glycosidic linkage.

Rhamnose groups in xylan

Like galacturonic acid, rhamnose is a constituent not only in pectic substances in the wood but also in xylan (in any case in birch xylan). Hence, attempts to remove the rhamnose groups from birch xylan by various fractionation methods have been unsuccessful (5). Enzymatic degradation of xylan from Japanese birch (*Betula platyphylla*) showed that the rhamnose units constitute a link between a sequence of at least two adjacent xylose groups and a galacturonic acid group.

The results showed that C-2 in the galacturonic acid group is linked glycosidically by an α-bond to rhamnose, which in its turn is linked to xylose by a 1,3-β-glycosidic bond (10). Analyses of acid oligomers obtained after hypochlorite treatment of xylan from *Betula verrucosa* show that the same structural elements are present (11). Among the isolated acids was [β-D-Xyl*p*-(1→4)-]$_2$-β-D-Xyl*p*-(1→3)-α-*L*-Rha*p*-(1→2)-D-GalA containing three xylose units followed by one rhamnose unit and the terminal reducing galacturonic acid group, liberated by loss of the unstable reducing xylose end group discussed above.

These results together with those referred to above

show that the structure of the reducing end in birch xylan can be written: -β-D-Xylp-(1→4)-β-D-Xylp-(1→3)-α-L-Rhap-(1→2)-α-D-GalpA-(1→4)-D-Xyl.

The 1,3-glycosidic linkages are less stable to alkaline peeling than 1,4-linkages, since a β-alkoxy elimination can occur without prior rearrangement of the terminal reducing aldose to a ketose end group. Accordingly, we have never observed any reducing rhamnose moieties in alkali treated xylan. Instead, the expected 3,6-dideoxyhexonic acids are formed in high yield from the rhamnose groups after severe treatments of birch xylan in alkaline medium (6).

Molecular size of birch xylan

If the sugar units in a polysaccharide molecule are held together exclusively by glycosidic bonds, only one reducing end group can be present per molecule. The reducing end groups can be determined by chromatography after reduction with borohydride to the corresponding alditol end groups and subsequent acid hydrolysis. It was already mentioned, that the reducing xylose end group is easily lost during alkaline extraction. In addition, it is difficult to avoid air oxidation of the terminal xylose groups to aldonic acid groups. For xylan isolated by alkali extraction the degree of polymerization (DP), defined as the number of xylose units per molecule, cannot be determined from the reducing pentose groups only (as xylitol+lyxitol). One can, however, obtain a reasonable value by calculating DP from the sum of reducing pentose groups, reducing galacturonic acid groups, and aldonic acid end groups.

If the wood meal is reduced with borohydride before the alkali extraction, both the alkaline peeling and the formation of aldonic acid end groups during the extraction are avoided. This simplifies the determination of the DP. *Table 1* shows the results obtained with three samples of xylan extracted from reduced birch meal with 10, 16 and 24% KOH. As it can be seen, the yield of xylan from reduced birch meal was high and hardly affected by the hydroxide concentration during the extraction. Likewise, the intrinsic viscosity determined in copper ethylenediamine was virtually the same, regardless of the strength of the potassium hydroxide solution.

Analysis of alditols after hydrolysis showed that only xylitol was present. Large amounts of 4-*O*-(α-D-galactopyranosyluronic acid)-D-xylitol are, as already mentioned, obtained after a very mild acid hydrolysis of reduced birch meal. After the more severe hydrolysis used in the present work, only small amounts of this acid were recorded. These are included in the amounts of xylitol reported in the table.

The number average degree of polymerisation, DP, was calculated on the assumption that after reduction every xylan molecule contained one xylitol end group. In the calculation of the number of xylose groups per unit mass of xylan a correction was applied for the presence of 4-*O*-methylglucuronic acid substitutents (1 per 10 xylose groups). In agreement with the viscosity determinations the calculated degree of polymerisation was almost the same for the three xylan samples (DP_X= =156—158).

To check if all of the reducing groups in the wood meal were accessible during the reduction of the wood meal, a sample of the xylan isolated in 24% potassium hydroxide was again treated with borohydride for 1 day. Hydrolysis followed by alditol analysis showed no difference compared to the original xylan. The results indicate that all reducing groups of the xylan in the wood meal are accessible for borohydride reduction.

No detectable amounts of aldonic acid groups were present. It is therefore concluded that the DP values 156—158 are representative of the samples of reduced and subsequently alkali extracted birch xylan.

Sugar analysis showed that xylose predominated. An appreciable amount of rhamnose was also present. According to the structure of the reducing end given above, one rhamnose group should be present per reducing xylose end group. The observed number of rhamnose moieties (table 1) was only slightly higher, indicating that practically all rhamnose units in the reduced and subsequently extracted xylan were glycosidically linked

Table 1. Yield and analysis of xylan from birch meal reduced with 0.2 M KBH_4 for 4 days at room temperature isolated by extraction for 3 hours at room temperature.[1]

	Yield %	Intrinsic viscosity dm^3/kg	Xylitol		Rhamnose		4-*O*-methylglucose[2]	4-*O*-methylglucose
			mmol/100 g	DP_x	mmol/100 g	DP_r	mmol/100 g	xylitol
10% KOH	22.4	94.2	4.24	156	4.52	147	20.2	4.8
16% KOH	22.9	94.4	4.21	157	4.55	146	20.3	4.8
24% KOH	22.9	94.6	4.19	158	4.58	145	20.0	4.8
			4.20	158				
F1	15.8	101.6	4.01	165	4.23	157	18.3	4.6
F2	55.2	97.0	4.12	161	4.42	150	18.6	4.5
F3	22.1	87.8	4.25	156	4.61	144	21.0	4.9
F4	6.9	61.3	4.90	135	5.82	114	23.3	4.8

[1] Birch meal (0.125—0.375 mm) extracted with acetone (one day), water (two days), 0.5% ammonium oxalate (one day), rinsed with water and air dried at 28°C before reduction. Loss in yield during reduction 10%.

[2] Determined by GC of cyclic $(CH_3)_2Si$-derivatives and GC and GC-MS of oxime-$(CH_3)_3Si$-derivatives (13).

to the xylan. Consequently, the number average degree of polymerisation calculated from the rhamnose contents (DP_r), was for all samples somewhat lower than that calculated from the xylitol determinations.

The molecular size distribution was studied by fractional precipitation (12) of reduced and subsequently alkali extracted xylan. The results included in table 1 show that the fraction (F1) most easily precipitated with ethanol exhibited the highest intrinsic viscosity and the highest DP, determined both by the xylitol and by the rhamnose methods. The corresponding values for the second fraction (F2), which constituted 55% of the xylan, were only slightly lower than those obtained for the first fraction. Somewhat lower values were obtained for the third fraction, but still the differences between the fractions were modest. The last fraction, which was much smaller than the earlier fractions, exhibited a larger decrease, but still DP_X was about 82% of that of the first fraction. No precipitation occurred on addition of acetic acid. Hence, we conclude that the molecular size distribution in reduced and extracted xylan is very uniform.

Ester linkages

Table 1 shows that acid hydrolysis of the xylan samples obtained by borohydride reduction of wood meal and subsequent alkaline extraction yielded appreciable amounts of 4-*O*-methylglucose. This sugar is not obtained upon hydrolysis of non-reduced xylan. Evidently, 4-*O*-methylglucose groups are formed by reduction of 4-*O*-methylglucuronic acid substituents linked to the xylan. It can therefore be concluded that a large proportion of these substitutents are esterified. The reduction led to approximately five 4-*O*-methylglucose groups per one xylitol end group (i.e. per molecule of the subsequently alkali extracted xylan). Since ester linkages are only partially reduced under the applied conditions, the results show that in the wood a very great proportion of the 4-*O*-methylglucuronic acid groups is esterified.

The wood meal had not been in contact with any alcohol before the borohydride reduction. Hence, hydroxyl groups present in the wood must be involved in the ester formation. The location of these hydroxyl groups has not been investigated. Attempts to produce ester linkages of similar properties in non-reduced xylan (isolated by alkali extraction) by treating the samples with mineral acid at room temperature or drying at elevated temperature after removal of the metal cations have failed. This may be taken as an indication that each xylan unit (which after alkali extraction is a discrete molecule) in the wood is a block in a block polymer. These blocks are linked together by ester linkages.

Retardation of the alkaline peeling

The most important retarding ("stopping") reaction which competes with the alkaline peeling in cellulose is the formation of 3-deoxyhexonic (metasaccharinic) acid end groups. Since 1,4-linked sugar units constitute the backbone of both cellulose and xylan, it can be assumed

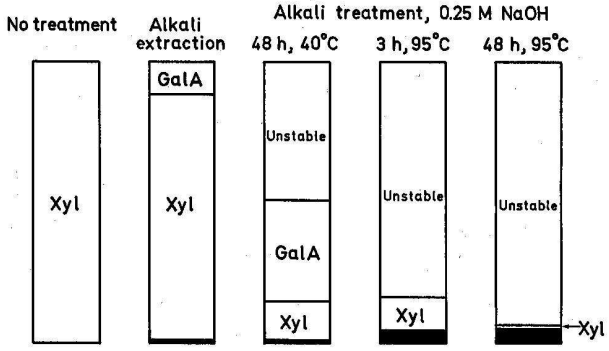

Fig. 1. Proportions of end groups at the reducing end of xylan after alkaline treatments.
Xyl=reducing xylose (incl. isomerized species); GalA=reducing galacturonic (incl. taluronic) acid; Unstable=unstable during acid hydrolysis.
Filled rectangles=3-deoxypentonic acids. Aldonic acid groups formed by air oxidation during alkali extraction are disregarded.

that analogous reactions would give 3-deoxypentonic acid end groups in xylan. The existence of this reaction has been eagerly disputed. A recent investigation shows, however, that significant amounts of both the *erythro* and *threo* forms are produced during alkali treatment. Compared with other retarding reactions (9) this reaction is of little importance (*fig. 1*). A higher rate of peeling of an unsubstituted xylan chain suggested by model experiments with 1,4-linked oligomeric sugars (14) cannot solely explain the very great difference compared with cellulose. The main explanation is the retarding effect of the 2-substituted galacturonic acid unit directly linked to the reducing xylose end group and the presence of 4-*O*-methylglucuronic acid substituents along the xylan chain.

It was shown in fig. 1, that an appreciable proportion of the reducing xylose end groups present in the xylan in wood is lost already during the alkali extraction used for the isolation of the xylan. Isomerization to a xylulose end group followed by β-elimination explains the liberation of reducing galacturonic acid end groups (*fig. 2*). These are in part epimerized to taluronic acid groups already at 40°C. A very large number of both types of reducing uronic acid groups are present after treatment for 48 hours at 40°C, which leads to a loss of xylan of only about 1% by weight. In addition, new retarding groups are formed from the galacturonic acid end groups. The new end groups are unstable in acid and therefore not determined by the applied technique. After alkali treatment at 95°C for 3 hours (loss in yield 12%), all reducing uronic acid end groups have reacted, i.e. either been converted into other retarding groups or lost. The latter reaction leads to new reducing xylose end groups as intermediates during the endwise degradation under these conditions. This is confirmed by the decrease in rhamnose content. End groups unstable in acid predominate under these conditions. Even after 48 hours at

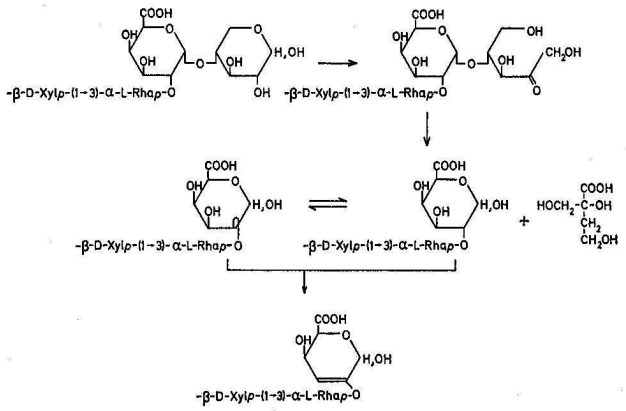

Fig. 2. Initial stages during endwise alkaline degradation of birch xylan. Reactions from top left and down:

Isomerization of the xylose end groups;

β-elimination leading to the liberation of a reducing galacturonic acid end group and the loss of the xylose end group as 3-deoxy-2-*C*-(hydroxymethyl)tetronic acid;

Reversible formation of a reducing taluronic acid end group;

β-hydroxyelimination of OH-3 in reducing uronic acid end groups leading to unsaturated end groups unstable in acid medium.

95°C (loss in yield 27%) an appreciable proportion of the rhamnose moieties remained in the xylan. In these xylan molecules only one xylose unit had been lost. Evidently, end groups formed from the liberated 1,2-linked reducing galacturonic acid moiety are so stable that an appreciable proportion was still present even after this severe alkali treatment. Model experiments permit the conclusion that an important primary reaction is a loss of OH-3 in the reducing galacturonic acid group by β-elimination. This reaction leads to the formation of a 3-deoxy-2-*O*-(α-*L*-rhamnopyranosyl)-D-*threo*-hex-2-enuronic acid end group (fig. 2). Compounds of this type retard the alkaline peeling effectively. Rearrangement of this compound to its isomer with a C3-C4 double bond will lead to a β-elimination, resulting in the formation of a reducing rhamnose moiety. This is linked to xylose by a 1,3-glycosidic bond. The molecule is therefore directly subjected to β-elimination which leads to the liberation of a reducing xylose end group. Benzilic acid rearrangement of the 3,6-dideoxypentosulose, derived from the rhamnose moiety yields the expected diastereomeric 3,6-dideoxyhexonic acids.

The loss of rhamnose groups shows that more than 50% of the end groups derived from the galacturonic acid group were lost by the alkaline peeling after 48 hours at 95°C. As expected from kinetic calculations (14) the number of reducing xylose end groups was very small after severe alkaline treatments (fig. 1). Evidently, the peeling proceeds rapidly until a reducing xylose end group with a 4-*O*-methylglucuronic acid substituent at OH-2 is reached.

The retarding effect of this substituent has previously been postulated by many authors (1). Model experiments show that a fairly slow β-hydroxy elimination of OH-3 in the xylose moiety occurs (9). This reaction gives rise to a terminal 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-3-deoxy-D-*glycero*-pent-2-enose group, which is decomposed slowly in alkaline medium but is extremely sensitive to acids. It therefore escapes observation in determinations of end groups after acid hydrolysis. After isomerization the terminal moiety will lose the 4-*O*-methylglucuronic acid substituent by β-elimination. The liberated 4-*O*-methylglucuronic acid is in alkaline medium rapidly converted into 3-deoxy-2-*C*-(hydroxymethyl)-pentaric acids (15). This reaction explains the presence of both isomers of this acid in kraft black liquor (16).

It is evident that the 4-*O*-methylglucuronic acid substituents are to a great extent responsible for the high stability of birch xylan at the high temperature prevailing towards the end of a kraft cook. During an early stage and during alkali treatments under milder conditions the galacturonic acid groups contribute markedly to the retardation of the alkaline peeling.

Model experiments

Most terminal groups in polysaccharides, previously identified and determined in studies of pulping processes, can be split off by acid hydrolysis and determined chromatographically. Unsaturated compounds of the types formed from 2-*O*-substituted reducing end groups are, as already mentioned, sensitive to acid and are rapidly decomposed. The conclusions regarding the structure of these end groups are therefore mainly based on model experiments.

Fig. 3 shows that 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose (A2) is epimerized rapidly in sodium

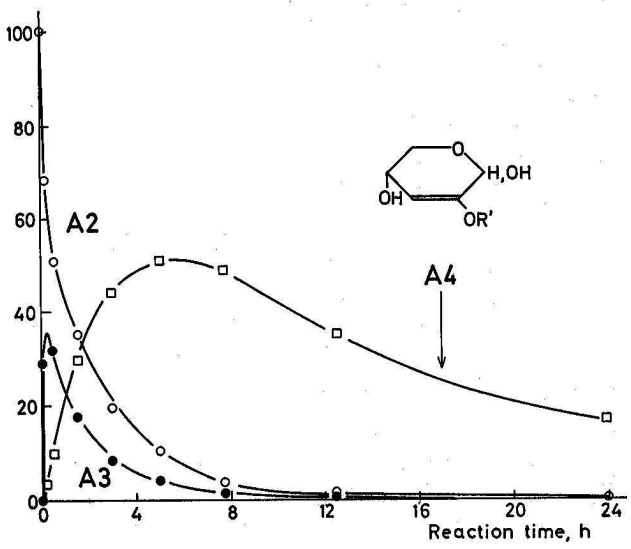

Fig. 3. Epimerization of 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose (45 mg, A2) to 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-lyxose (A3) and the formation and destruction of 3-deoxy-2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-pent-2-enose (A4) in 0.1 M NaOH (50 ml) at 70°C. The ordinate represents the composition of the reaction mixture given as number of moles per 100 moles of the starting material. R'=4-*O*-methylglucuronic acid substituent.

hydroxide at 70°C. Already after 10 min the concentration of the epimer (A3) passed through a maximum. The formation of the unsaturated compound, A4, by β-elimination of OH-3 in the xylose moiety was observed already in the first sample drawn after 5 min. After about 6 hours the concentration of this acid passed through a maximum. Two minor, overlapping peaks, one before A2 and one after A4, were recorded on the chromatograms.

The rate of destruction of the aldobiouronic acids can be approximately represented by the equation

$$d([A2]+[A3])/dt = -0.38\ ([A2]+[A3])h^{-1}.$$

The consecutive decomposition of the unsaturated acid A4 can be approximately calculated from $d[A4]/dt = -0.08[A4]$. The experiments indicated that although the main destruction of the aldobiouronic acids occurs via A4, side reactions cannot be disregarded.

Analogously, 3-deoxy-2-*O*-methyl-D-*erythro*-hex-2-enose is formed in an appreciable amount during alkali treatment of 2-*O*-methylglucose (17). This was confirmed by our experiments with 2-*O*-methylglucose. In addition, small amounts of 2-*C*-methylglyceric and 3-deoxytetronic acids were formed in these experiments. This indicates that a reverse aldol reaction leading to a cleavage between C2 and C3 occurs. Erythrose formed in this reaction is rapidly converted into these acids. It is likely that this reaction path is of some importance also for the destruction of the aldobiouronic acids. An analogous cleavage of the xylan moiety will give rise to glyceraldehyde, which is converted into lactic acid found in the experiments.

The structure of the unsaturated acid A4 was deduced from the observation that reduction with borohydride gave an acid which in contrast to A4 yielded formaldehyde on periodate oxidation and from analyses of the hydrolysis products (9). Additional experiments confirm the postulated structure. Hence, the reaction mixture (fig. 3) obtained after 6 hours was neutralized to pH 8.2 and separated by anion exchange chromatography in 0.04 M sodium acetate. The fraction containing A4 was divided into two parts. One of these was reduced with sodium borohydride and then hydrolysed in 0.01 M sulphuric acid for 47 days at room temperature. Gas chromatography of the oxime-$(CH_3)_3$Si-derivatives showed that 4-*O*-methylglucuronic acid and 3-deoxypentulose were formed in equimolar amounts. No appreciable amounts of other compounds were recorded under these working conditions. When the reduced A4 was hydrolysed at about 100°C, 4-*O*-methylglucuronic acid and a number of minor compounds were recorded.

The other part of the fraction containing A4 was hydrolysed at room temperature, without prior reduction, by the sample being passed through a column packed with the free-acid form of a cation exchanger of sulphonic acid type (Dowex 50-X8). Reduction with borohydride followed by gas chromatography of the $(CH_3)_3$Si-derivatives showed that the expected reduction products (3-*O*-methylgulonic acid and the *erythro* and *threo* forms of 3-deoxypentitol) were formed in high yield. Direct analysis of the hydrolysis products as oxime-$(CH_3)_3$Si-derivatives without reduction showed that 4-*O*-methylglucuronic acid and 3-deoxypentosulose were formed during acid hydrolysis of A4.

Epimerization and removal of 4-O-methylglucuronic acid substituents at high temperature

The reactions already discussed are of great interest much below 100°C. Additional reactions become important under the more severe conditions prevailing during a kraft cook. Among these is the loss of 4-*O*-methylglucuronic acid groups (18). The presence of 4-*O*-methylliduronic acid in kraft pulp shows that an epimerization of the 4-*O*-methylglucuronic acid occurs during the cooking (19). Model experiments with 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol show that this reaction occurs with an appreciable rate in 1 M NaOH at 150°C (20). A more important reaction is the transformation of the uronic acid moieties to 4-deoxy-β-*L-threo*-hex-4-enopyranosyluronic acid by β-elimination of CH_3O-4 following loss of H-5 (see *fig. 4*). This unsaturated acid moiety is further decomposed and gives rise to a loss of the substituent and the liberation of OH-2 in the xylan as illustrated by the model experiments, which gave xylitol as the stable end product (together with fragmentation acids such as formic acid and condensation products derived from the acid moiety). In the model experiments the pseudo-first-order reaction rate for the formation of the unsaturated compound ($k_3 = 0.91\ h^{-1}$) was significantly higher than that for its decomposition ($k_x = 0.52\ h^{-1}$). This suggests that an appreciable number of 4-deoxy-β-*L-threo*-hex-4-enopyranosyluronic acid moieties are present in kraft pulp. Their instability in an acid medium explains why these groups escape observation in analyses of the acid groups in kraft pulp by techniques based on acid hydrolysis. This reaction path earlier postulated by Clayton (21) has been disputed. The model experiments strongly indicate that the reaction path given in the figure is responsible for the loss of 4-*O*-methylglucuronic acid groups in xylan during a kraft cook.

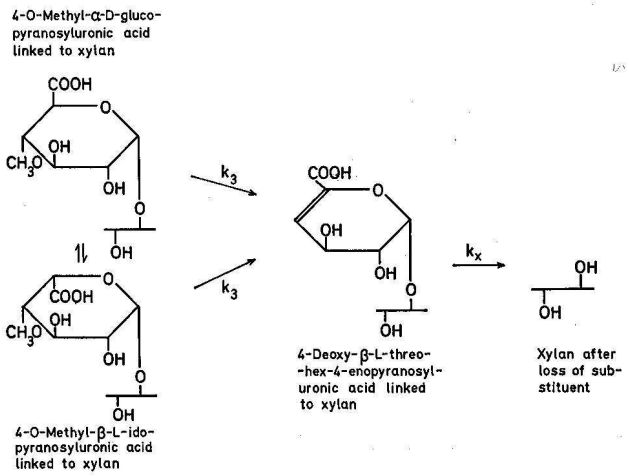

Fig. 4. Isomerization and loss of 4-*O*-methylglucuronic acid groups linked to OH-2 in xylan.

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