

Hexenuronic acid groups in pulping and bleaching chemistry

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THE QUEST TO IMPROVE THE efficiencies of pulping and bleaching operations has renewed interest in the fate of hemicellulose in these processes. Recent research has been focused on the modified hemicellulose, hexenuronoxylan, or 2-*O*-(4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid)-D-xylan, which is xylan containing hexenuronic acid units.

Hexenuronic acid is one of the main uronic acid constituents in kraft pulps (1-13) and in the fractions of xylan found in kraft pulping (14) and in bleaching liquors (15, 16). Consequently, the reactions of hexenuronic acid with such bleaching chemicals as chlorine dioxide and ozone are important. Our objective here is to review the current knowledge of hexenuronic acid and to summarize its effects on pulping and bleaching.

HISTORICAL BACKGROUND

In the early 1950s, the 4-*O*-methylglucuronic acid unit, or 2-*O*-(4-methyl- α -D-glucopyranosyluronic acid), was found to be the main acidic constituent of xylan in both hardwoods and softwoods. This finding led to intensive investigations into the alkaline degradation of 4-*O*-methylglucuronoxylan, or 2-*O*-(4-methyl- α -D-glucopyranosyluronic acid)-D-xylan, which is xylan that contains 4-*O*-methylglucuronic acid units.

One approach used in these investigations was to isolate the 4-*O*-methylglucuronoxylan from wood and then treat the product in a homogeneous medium. Researchers

analyzed the changes in chemical composition during these treatments, including the change in glucuronic acid content (17-24).

Another approach was to characterize the chemical compositions, including the glucuronic acid content (25-28), of residual xyans in kraft pulps produced under various pulping conditions. In these studies, the quantity of glucuronic acid was mainly determined from the carbon dioxide given off during boiling with 12% HCl.

The content of 4-*O*-methylglucuronic acid was also indirectly estimated through the determination of methoxyl content. When hot alkaline treatments were used, the amount of glucuronic acid in xylan detected by techniques based on carbon dioxide measurements was always higher than that estimated indirectly by methoxyl content (17-19, 21, 22). This observation led Clayton, in 1962, to speculate correctly that 4-*O*-methylglucuronic acid was converted to hexenuronic acid by the elimination of the 4-*O*-methoxyl group after the loss of the hydrogen atom attached to the 5th position of the glucuronic acid residue (22). **Figure 1** shows the conversion of 4-*O*-methylglucuronoxylan to hexenuronoxylan during an alkaline treatment.

Clayton's pioneering speculation led to the development of the pulping and bleaching chemistry of hexenuronoxylan. The first evidence that directly supported Clayton's speculation was reported by Johansson and Samuelson fifteen years later (29). By this time, it was widely recognized

ABSTRACT

Hexenuronic acid groups are formed in xylan chains during kraft pulping. These acid groups cause increased consumption of bleaching chemicals, decreased brightness, greater brightness reversion, and poorer metal removal. These hexenuronic acid groups can be selectively removed by an acid treatment, and bleaching chemicals can be saved as a result. This review of current knowledge of hexenuronic acid chemistry includes discussions of the structure, the stability and reactivity, the preparation and quantification, and the formation and degradation of hexenuronic acid during kraft pulping and bleaching.

Application:

Savings in bleaching chemicals can be realized when pulps undergo an acid treatment to remove hexenuronic acid groups before bleaching.

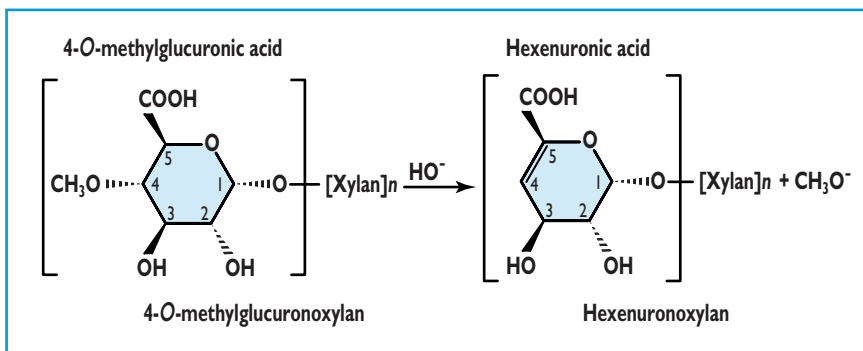
that hexenuronic acid moieties that are attached to xylan escape being detected when the techniques are based on the measurement of carbon dioxide from acid hydrolysis. The reason is that these moieties are unstable in an acid medium (29, 30).

In the ensuing years, research on the behavior of hemicellulose during pulping and bleaching was very much neglected. Most efforts in wood and pulping chemistry were focused on lignin chemistry (31). Consequently, the full identification and verification of the occurrence of hexenuronoxylan during alkaline pulping was achieved only recently through NMR spectroscopy (7, 9, 15).

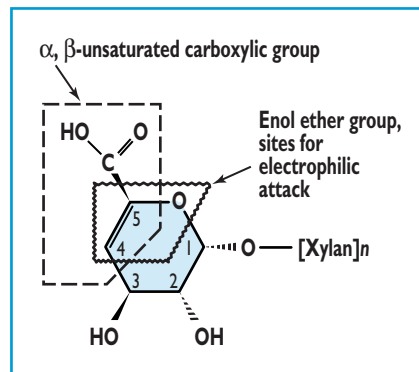
METHODOLOGY

Preparation and isolation

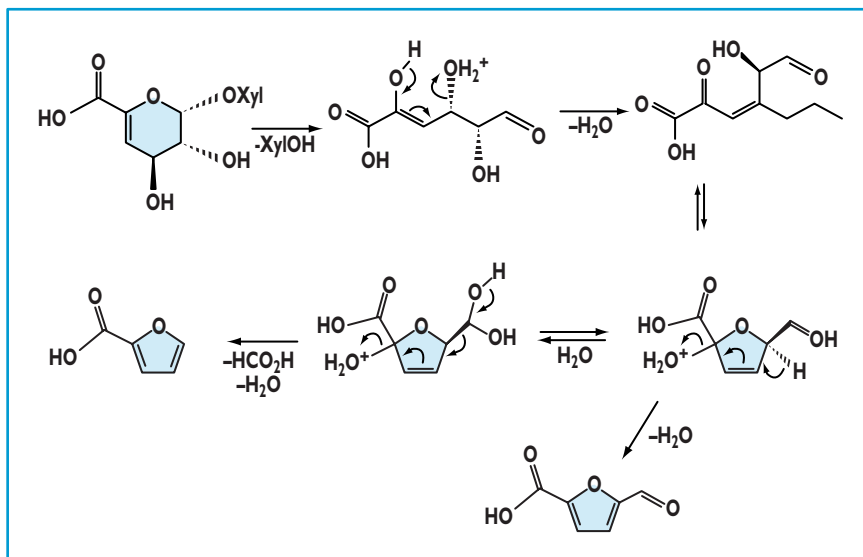
In 1960, Hamilton and coworkers described a procedure to prepare xylan "devoid" of uronic acid sub-



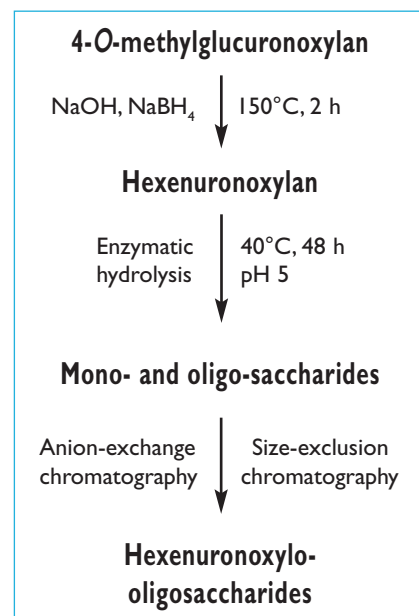
1. The conversion of 4-O-methylglucuronoxylan to hexenuronoxylan during kraft pulping, as suggested by Clayton in 1962 (22).



2. Functionality of hexenuronic acid groups attached to xylan.



3. Pathway proposed by Teleman et al. for the acid degradation of hexenuronic acid groups attached to xylan (7).



A. The procedure developed to prepare hexenuronoxylan and hexenuronoxyloligosaccharides from 4-O-methylglucuronoxylan.

stituents by the alkaline hydrolysis of 4-O-methylglucuronoxylan (24). It is clear now that the xylan produced was hexenuronoxylan rather than xylan without any uronic acid substituents. The uronic acid groups in the hexenuronic acid moieties had escaped detection because the techniques were based on the measurement of carbon dioxide.

Recently Teleman and coworkers developed an improved procedure for preparing hexenuronoxylan (7). This procedure is given in brief in **Scheme A**. The xylan resulting from their procedure contained 4.1 mol% hexenuronic groups, together with about 0.5 mol% residual 4-O-methylglucuronic acid groups (7). A further

hydrolysis of the hexenuronoxylan with an enzyme mixture containing purified endoxylanase, β -xylosidase, and α -glucuronidase, followed by separation with anion-exchange and size-exclusion chromatography, led to hexenuronoxyloligosaccharides. These saccharides are xylo-oligosaccharides that contain 4-O-methylglucuronic acid units.

This enzyme hydrolysis method, when applied to kraft pulps, allowed hexenuronoxylan to be isolated as hexenuronoxyloligosaccharides in nearly quantitative yields (2, 13). Other methods, such as solvent extraction (3, 15, 20, 26), alkaline extraction (26, 32), and mechanical peeling (33), have also been applied

to isolate hexenuronoxylan in kraft pulps.

Hexenuronoxylolose, or 2-O-(4-methyl- α -D-glucopyranosyluronic acid)-D-xylose, is one of the key model disaccharides of hexenuronoxylan. This model compound can be obtained by an alkaline treatment of 4-O-methylglucuronoxylolose, followed by anion-exchange chromatography (30). This type of conversion can also be achieved by the use of sodium methylsulfinylmethide in methyl sulfoxide (34).

Similarly, hexenuronic acid, as a monomer model of hexenuronoxylan, can be obtained through an alkali-catalyzed β -elimination of D-glucuronates, D-galacturonates, or L-iduronates (35, 36). The chemistry of this type of β -elimination reaction has already been reviewed (37, 38). Many crystalline derivatives of hexenuronic acid and hexenuronoxyllose have been obtained (37–39).

Quantification and identification

As explained, uronic acid analysis, which relies on methods based on carbon dioxide measurement, is not suitable for the determination of hexenuronic acid groups. Titrations can be used to quantitatively analyze the hexenuronic acid groups in pure hexenuronoxylan (40), but in kraft pulps, titrations alone will not work because the titration method determines the amount of all the acidic groups (40, 41).

We can also determine the content of hexenuronic acid groups in hexenuronoxyllose by measuring the UV absorption between 220 and 240 nm (34). Hexenuronic acid groups absorb strongly in this range. However, when this method is applied to kraft pulps, other constituents, such as lignin, may interfere (40).

Recently, Vuorinen and coworkers described a method for quantifying hexenuronic acid groups in kraft pulps (12). This method is based on a selective acid hydrolysis of hexenuronic acid groups to furan derivatives. After hydrolysis, the UV absorption is measured at 245 nm and/or 285 nm for the liberated furan derivatives in the hydrolyzate. However, the acid-soluble fraction of residual lignin in kraft pulps can also have an ultraviolet absorption in the range of 240–285 nm.

Shimizu reported in 1981 that hexenuronoxyllose reacts with thiobarbituric acid to yield a pink product that has an ultraviolet-visible absorption maximum at 550 nm (34). This concept was adopted by Gellerstedt and Li in developing a chemical degradation method to quantify hexenuronic acids in kraft pulps (42). In this degradation technique, consecutive treatments with mercuric acetate, periodate, and thiobarbituric acid are followed by chromatographic separations and UV spectroscopic analysis.

NMR spectroscopy, which is a well-established method for measuring hexenuronoxylan, has played a key role in the elucidation of the pulping and bleaching chemistry of hexenuronoxylan. The first evidence to support the occurrence of hexenuronic acid groups during kraft pulping was obtained by ^1H NMR and mass spectroscopy (29). Hexenuronic acid moieties have characteristic signals for H-4, C-4, and C-5. One- and two-dimensional ^1H and ^{13}C data of hexenuronoxyllo-oligosaccharides and hexenuronoxylan have been well documented (7, 8, 27, 29, 43). NMR spectroscopy is also one of the main tools used to study the conformation of hexenuronic acid derivatives (44).

	Acid degradation rate constant $\times 100, \text{h}^{-1}$		
	80°C	90°C	100°C
4-O-Methylglucuronoxyllose	0.43	1.58	4.57
Hexenuronoxyllose	35.6	91.8	311

Reactions in 0.5M sulfuric acid.

1. Effect of temperature on the acid hydrolysis rate of hexenuronoxyllose

Other analytical techniques have also been used, combined with enzymatic hydrolysis, to characterize hexenuronic acid groups in kraft pulps. These techniques include capillary zone electrophoresis (45) and anion-exchange chromatography with a pulsed amperometric detector (2, 13).

REACTIONS DURING PULPING AND BLEACHING

Stability and reactivity

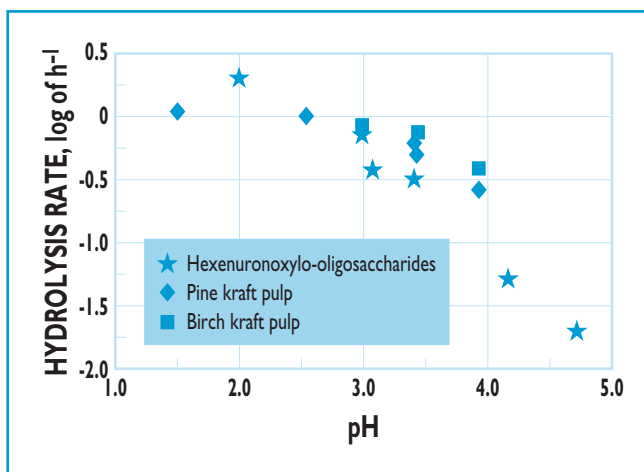
Hexenuronic acid belongs to a class of compounds that contain enol ether or unsaturated carboxylic acid groups (Fig. 2). These functional groups strongly influence the stability and reactivity of hexenuronic acid.

In general, both enol ether and unsaturated carboxylic acid groups are rather inert under mild conditions. The derivatives of hexenuronic acid can be stored for several years at room temperature without decomposing (39). However, hexenuronic acid moieties are the targets of both electrophilic and nucleophilic attack (46). The pKa values for hexenuronic acid and 4-O-methylglucuronic acid attached (1 $\rightarrow$ 2) to xylose are 3.03 and 3.13, respectively, as determined from pH-dependent NMR chemical shifts (8).

In solutions of strong alkalinity at high temperatures, hexenuronic acid decomposes slowly (29). For example, the decomposition reaction of the model dimer, hexenuronoxyllose, in 1M NaOH at 150°C has a low rate constant of 0.52 h $^{-1}$.

Because enol ethers are acid labile, hexenuronic acid groups are not stable in acidic solutions. As early as 1973, it was suggested that a mild acid hydrolysis of hexenuronic acid moieties would yield furan derivatives (30). Such furan derivatives were recently identified (47, 48). Structural analysis of the acidic degradation products of hexenuronoxylan led to the proposed pathway shown in Fig. 3 for the acid degradation of hexenuronoxylan (7). Kinetic data seem to support a bimolecular reaction mechanism (12).

The acid degradation reaction is strongly influenced by the reaction temperature and pH. Table I shows comparisons of kinetic data for the hydrolysis of hexenuronoxyllose and 4-O-methylglucuronoxyllose in 0.5M sulfuric acid at various temperatures (34). Hexenuronoxyllose, because of its double bond at C-4 and C-5, degrades 70 times faster than does 4-O-methylglu-



4. The effect of pH at 95°C on the rate of hydrolysis of hexenuronic acid groups in hexenuronoxylo-oligosaccharides, in a pine kraft pulp, and in a birch kraft pulp.

cunonoxylose. If the reaction temperature is increased from 80°C to 100°C, the rate of degradation increases by about nine fold.

Figure 4 shows the effects of pH on the rates at which hexenuronic acid groups hydrolyze in a softwood kraft pulp, in a hardwood kraft pulp, and in an isolated hexenuronoxylo-oligosaccharide compound, each at 95°C (12). In general, the hydrolysis rate increases as the pH decreases (12). The half-life (which is the time by which hexenuronic acid groups have decreased to half the initial concentration) of the acid hydrolysis reaction at pH 3 is about 45 min, with a rate constant of 0.95 h⁻¹ (12).

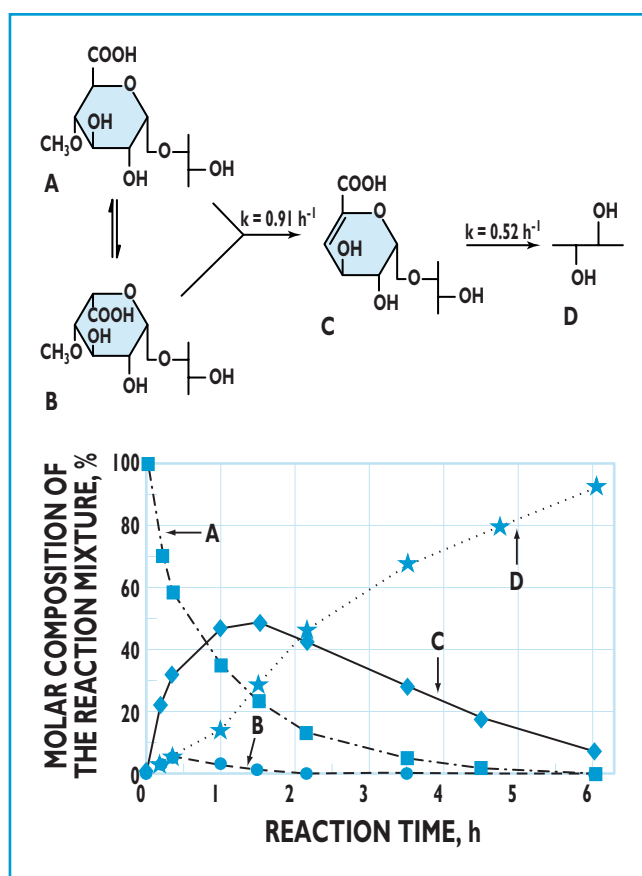
Formation and degradation during kraft pulping

The possible conversion of 4-O-methylglucuronoxylan to hexenuronoxyloxy during kraft pulping was clearly demonstrated in 1977 by Johansson and Samuelson (29) in experiments with the model dimer, 4-O-methylglucuronoxylan. As Fig. 5 shows, 4-O-methylglucuronoxylan converts rapidly to hexenuronoxylose in 1M

Pulping process	Kappa no.	Hexenuronic acid, μmol/g
Conventional	25.5	22.7
Lo-Solids®	21.0	15.3
Soda	25.0	0.5
Soda-AQ	21.0	3.7
Polysulfide	24.2	4.6

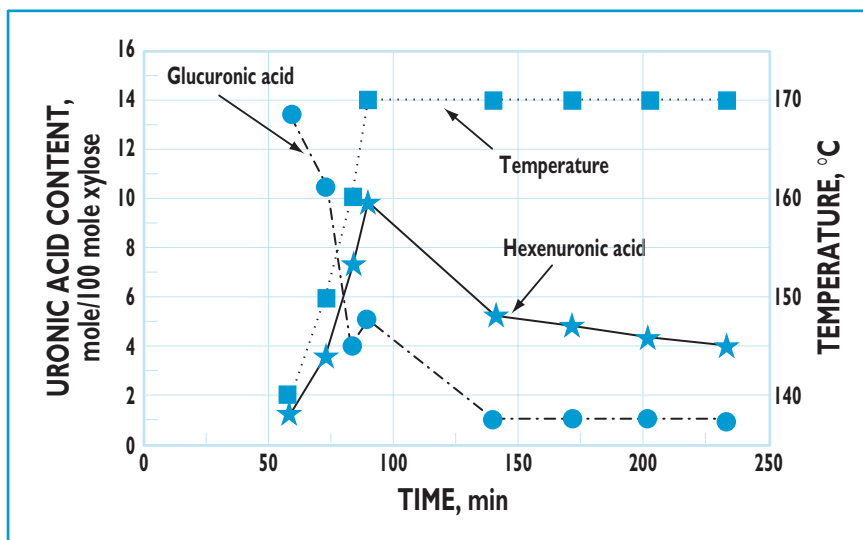
Lo-Solids is a registered trademark of Ahlstrom Machinery Inc.

II. Hexenuronic acid content in various softwood kraft pulps

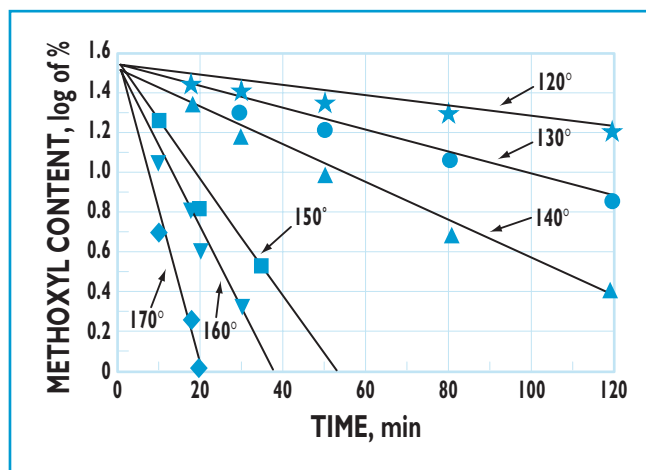


5. Isomerization and degradation of 4-O-methylglucuronoxylan in 1M NaOH for various times at 150°C, where (A) refers to 4-O-methylglucuronoxylan, (B) to 4-O-methylpyranoxylan, (C) to hexenuronoxylose, and (D) to xylitol.

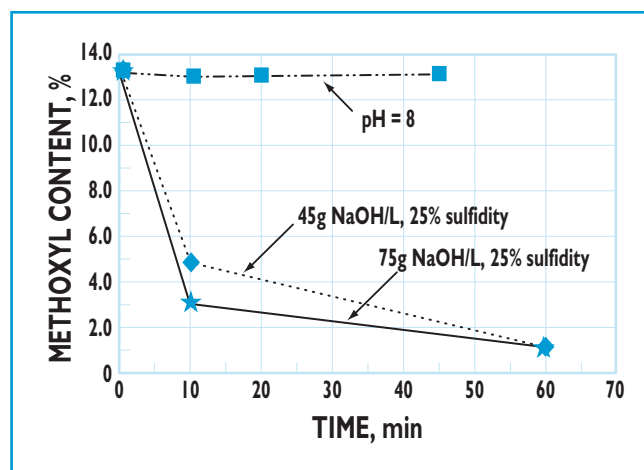
NaOH at 150°C, directly or through its epimer, 4-O-methylpyranoxylan, or 2-O-(4-methyl-β-L-idopyranosyluronic acid)-D-xylose. The formation of hexenuronoxy-



6. The amounts of hexenuronic acid groups formed during the kraft pulping of pine. The temperature profile during the kraft cook is also indicated.



7. The effect of reaction temperature ($^{\circ}\text{C}$) on the degradation of methoxyl groups of 4-O-methylglucuronoxylan in 1.55M NaOH at different temperatures.



8. The effect of reaction pH on the degradation of methoxyl groups of 4-O-methylglucuronoxylan.

lose (with a pseudo-first-order rate constant of 0.91 h^{-1}) reaches a maximum after about 1.5 h and then decreases as a result of its decomposition into xylitol (with a rate constant of 0.52 h^{-1}).

The formation of hexenuronic acid units during kraft pulping was verified by research groups in Finland (2, 9, 13). Figure 6 shows the amount of hexenuronic acid units formed during the progression of a kraft cook (2, 9). Hexenuronic acid forms rapidly during the rise-to-temperature. As the cooking continues at 170°C , the hexenuronic acid group content decreases.

As described earlier, the behavior of isolated 4-O-methylglucuronoxylan in a hot alkaline treatment was intensively studied in the fifties and sixties. Although data related to the main reaction product, hexenuronoxylan, were neglected in those studies, we can derive some conclusions by reinterpreting the early data.

Figure 7 shows the losses of methoxyl in 4-O-methylglucuronoxylan in 1.55N NaOH at different temperatures (18). Apparently, the hexenuronoxylan is not formed in significant amounts at lower temperatures ($<130^{\circ}\text{C}$), as evident in the limited loss of methoxyl groups. Similarly, the formation of hexenuronoxylan is insignificant at pH 8 (17), as Fig. 8 shows. Increasing the reaction temperature and/or active alkali increases the loss of methoxyl groups and increases the formation of hexenuronoxylan (Figs. 7 and 8).

Since temperature and alkaline profiles are different for different cooking methods, it is not surprising to find that different kraft pulps can have considerably different uronic acid profiles (2, 4, 11, 13). Table II shows the hexenuronic acid content in various softwood kraft pulps. Hardwood kraft pulps contain more hexenuronic acid groups than do softwood kraft pulps similarly cooked, as Table III shows, because hardwoods contain more 4-O-methylglucuronoxylan (49).

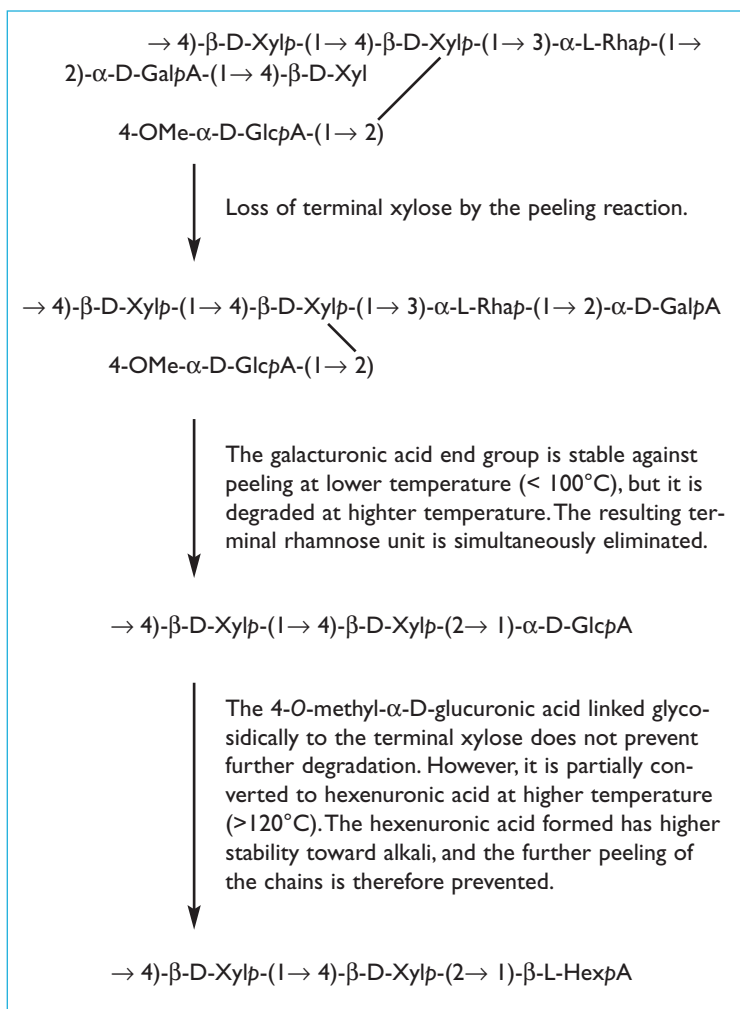
	Hardwood (birch)	Softwood (pine)
Kappa no.	18.2	25.9
Uronic acid content, $\mu\text{mol/g}$		
4-O-Methylglucuronic acid	42	14
Hexenuronic acid	76	54
Total	118	68

III. Comparison of the uronic acid content in conventional batch hardwood and softwood kraft pulps

Xylan is widely recognized to be more stable toward alkaline peeling degradation than are glucomannan and hydrocellulose, but the cause of its stability has been disputed. Some researchers at first thought the reason to be that 4-O-methylglucuronic acid is linked glycosidically at C-2 at every tenth (on average) 1,4-linked xylose unit (29, 50, 51). However, 4-O-methylglucuronic acid groups attached to a terminal xylose unit are clearly sensitive to alkaline degradation even at 100°C (52). The 4-O-methylglucuronic acid groups in xylan therefore do not prevent the peeling degradation in kraft pulping.

Along a similar line of research, it was found that while galacturonic acid groups in the xylan prevent the peeling degradation of xylan chains at lower temperatures ($<100^{\circ}\text{C}$), they do not offer protection at higher temperatures, because they decompose as a result of isomerization (29, 49). Therefore, no explanation has been accepted generally to account for the protection of xylan chains at temperatures higher than 100°C .

In view of the formation and degradation of hexenuronoxylan during kraft pulping, we conclude that the xylan chains are protected by the conversion of 4-O-methylglucuronic acid groups to hexenuronic acid groups at temperatures higher than 120°C , with hexenuronic acid groups being more stable toward alkali.



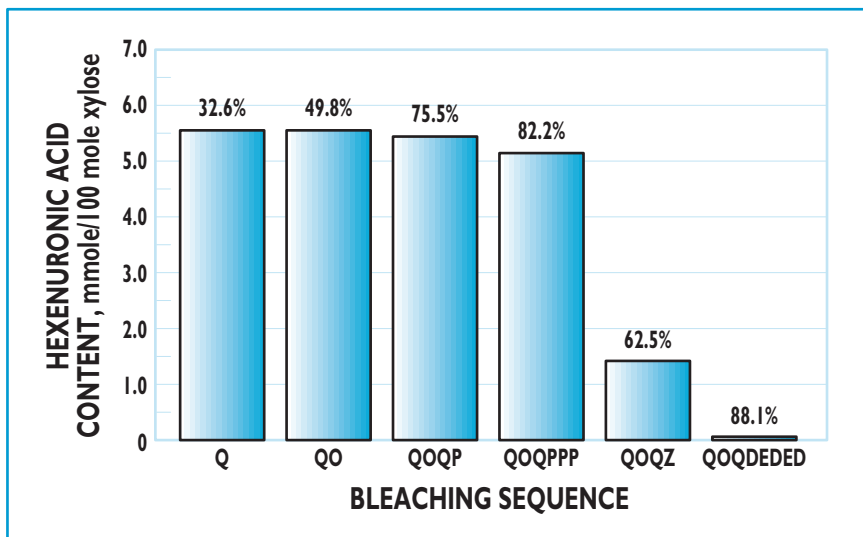
B. A proposed mechanism for end-group degradation and the stabilization of hardwood xylan during kraft pulping. Theoretically, the conversion of 4-O-methyl-D-glucuronic acid to hexenuronic acid would be responsible for the protection of xylan chains during kraft pulping.

This proposed mechanism is presented in **Scheme B**. This conclusion leads to the further consideration that yield losses may be expected if hexenuronic acid groups are removed before the pulp enters alkaline stages run under severe conditions.

Behavior during bleaching

Figure 9 shows how various bleaching stages affect the hexenuronic acid content of kraft pulp (9). These results indicate that hexenuronic acid groups are unreactive in alkaline oxygen and peroxide bleaching but that they react with chlorine dioxide and ozone, which are electrophilic bleaching chemicals (12). Hexenuronic acid has been found to be as reactive as lignin is toward electrophilic bleaching chemicals (1). The main products of the reactions between chlorine dioxide and hexenuronic acid are unchlorinated and chlorinated dicarboxylic acids. For ozone, there are two different pathways by which hexenuronic acid is oxidized to form oxalic acid, dialdose, and uronic acid products (1).

Dahlman and coworkers recently studied the composition of xylan fractions dissolved during pulp bleaching and during the dimethyl sulfoxide extraction of bleached pulps (3, 15). According to their results, the xylan fraction dissolved from kraft pulp during hydrogen peroxide bleaching contains significant amounts of hexenuronic acid groups (4–6 mol per 100 mol xylose). This finding confirmed that hexenuronic acid is stable toward oxygen delignification and toward hydrogen peroxide bleaching.



9. The effect of bleaching stages on the hexenuronic acid content. The ISO % brightness after each sequence is given above the appropriate column.

Under the conditions of the kappa number test, potassium permanganate reacts with the hexenuronic acid groups (12, 32, 42, 53, 54). Therefore, the presence of hexenuronic acid groups can contribute significantly to the measured value of the kappa number: 3–6 kappa number units for hardwood kraft pulp and 1–3 kappa number units for softwood kraft pulps (42).

Removal of hexenuronic acid groups before bleaching

Since hexenuronic acid groups consume bleaching chemicals, procedures have been developed to remove hexenuronic acid groups from kraft pulps selectively. According to Vuorinen and coworkers (12),

Reference	Typical condition			Main objective	Effect on pulp strength
	pH	Temp., °C	Time, h		
Perolle <i>et al.</i> (55)	~3	ambient	0.3–1	Enhance the efficiency of oxygen delignification	No effect
Bouchard <i>et al.</i> (56)	1.0–3.0	50	0.5	Acid wash step to remove transition metal ions	No effect
Hosoya <i>et al.</i> (58)	1.2–1.4	100	1	Acid hydrolysis step for delignification	Decreased viscosity
Buchert <i>et al.</i> (12)	3.0–4.0	85–115	0.1–24	Acid hydrolysis to remove hexenuronic acid groups	Little or no effect

IV.A summary of conditions used in various approaches for an acid treatment in bleaching processes applied to kraft pulps

a mild acid treatment can remove most of the hexenuronic acid groups from kraft pulps.

Acid treatment of kraft pulp has been of interest for various reasons. An acid treatment before oxygen delignification, for example, could increase brightness by 2–6 points (55). An acid treatment before delignification could be used to enhance the degree of delignification without excessive degradation of polysaccharides (47). Furthermore, acid treatment could be used in total chlorine-free bleaching sequences to remove transition metals and improve the efficiency of peroxide bleaching (56, 57).

An acid treatment has also been examined as a delignification stage in nonchlorine bleaching sequences (5, 58, 59), based on two assumptions: (a) that residual lignins in kraft pulps are linked to carbohydrates through ether bonds and (b) that these linkages, together with other ether-type structures in residual lignin, are more or less labile toward acid hydrolysis. The existence of covalent bonding between residual lignin and carbohydrates in kraft pulps has been proposed as being at least partially responsible for the slow rate of delignification encountered in the final kraft delignification phase (53, 60, 61). Acid conditions used in different approaches are compared in Table IV, along with comparisons of other pertinent conditions and effects.

Content of hexenuronic acid groups in unbleached conventional birch kraft pulp	5.5 mmol per 100 g pulp (42)
Consumption of chlorine dioxide by each mole of hexenuronic acid	~2 mole (12)
Total consumption of chlorine dioxide by hexenuronic acid in 100 g pulp	$2 \times 5.5 = 11 \text{ mmol}^*$

*11 mmol in 100 g of pulp is approximately equal to 7.5 kg per ton of pulp.

V.A theoretical estimate of ClO_2 consumption by hexenuronic acid groups

As the calculation in Table V illustrates, hexenuronic acid groups are present in hardwood kraft pulps in large enough quantities to consume an appreciable amount of chlorine dioxide. Therefore, the removal of hexenuronic acid groups in hardwood kraft pulps prior to bleaching can provide substantial savings in chlorine dioxide. Because softwood kraft pulps contain fewer hexenuronic acid groups, the savings are less substantial for softwood pulps.

As Fig. 10 shows, the selective removal of hexenuronic acid groups in a hardwood kraft pulp by an acid treatment under the conditions of Buchert *et al.* (12) decreased the chlorine dioxide consumption by 6.8 kg/ton of pulp. These actual savings are close to the theoretical savings estimated in Table V.

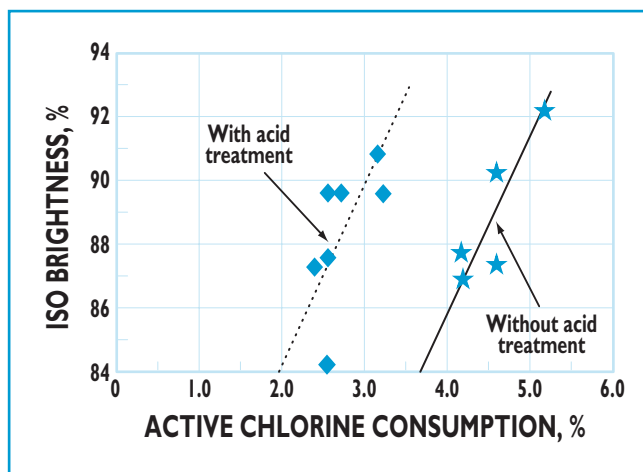
As Fig. 11 shows, such an acid treatment removes metal ions more effectively than does a milder acid washing step (12). This result suggests that metal ions in kraft pulps

are mainly bound to uronic, especially hexenuronic, acid groups (12, 62). Reportedly, an acid treatment also improves the brightness stability of bleached kraft pulps (12), which is consistent with the general influence of uronic acids on the brightness stability of pulp (63, 64).

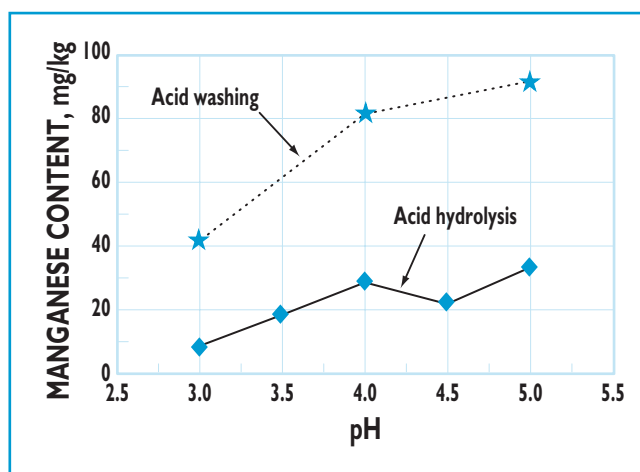
CONCLUDING REMARKS

During kraft pulping, 4-O-methylglucuronic acid groups attached to xylan are partially converted to hexenuronic acid groups, forming hexenuronoxylan. The resulting hexenuronic acid groups are relatively stable toward an alkali treatment. Therefore, these groups may prevent the peeling degradation of xylan chains at higher temperatures during kraft pulping.

Hexenuronic acid groups react with electrophilic bleaching chemicals such as chlorine dioxide and ozone. If an acid treatment is used to selectively remove these hexenuronic acid groups, bleaching chemi-



10. The effect of acid hydrolysis on the consumption of active chlorine in elemental-chlorine-free bleaching of a hardwood kraft pulp. The acid hydrolysis was applied before or after oxygen delignification in the ODED bleaching sequence.



11. A comparison of the efficiency of acid washing (at 70°C) and acid hydrolysis (at 95°C) on the removal of manganese from an unbleached birch kraft pulp at various levels of pH.

cals can be saved. The savings are more substantial for hardwood kraft pulps than for softwood kraft pulps because the hardwood pulps contain more hexenuronic acid groups.

An added benefit of an acid treatment is that the brightness stability

of bleached kraft pulps is improved. The reason for this improvement is the removal of metal ions, which are believed to be bound to uronic acid groups, especially hexenuronic acid groups. **TJ**

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Received for review May 14, 1998.

Accepted May 18, 1999.

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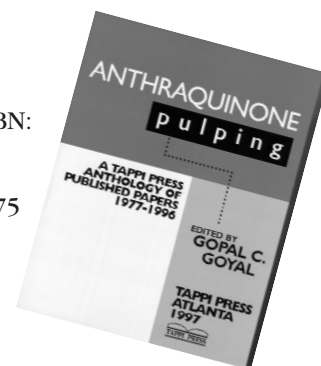
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