# Influence of Cations and Borate on the Alkaline Extraction of Xylan and Glucomannan from Pine Pulps

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## Synopsis

Southern pine pulp fibers were extracted with Na, K, and Li hydroxides at several concentrations from 0.5 to 4.0 *m* (molal). The amounts of extracted xylan and glucomannan increased with the swelling of the cellulose structure up to 2.0–2.5 *m*. The addition of $H_3BO_3$ to alkaline solutions produced the $B(OH)_4^-$ anion, which had less swelling power than $OH^-$. It was not effective for removal of xylan except for some very accessible xylan of holocellulose. Removal of xylan from chemical pulps depended upon $OH^-$ in molar excess over $H_3BO_3$. In the same extractions, glucomannan removal was enhanced by $B(OH)_4^-$ alone and further increased by additional $OH^-$. The formation of anions (carboxylate in xylan and borate complex of glucomannan) appeared to be important for the release of polymer from within the cellulose structure. Some glucomannan was more accessible in oxygen pulp than in holocellulose. The resorbed xylan of kraft pulp was less accessible than the xylans of either holocellulose or oxygen pulp.

## INTRODUCTION

Glucomannan and xylan are quantitatively important polymers in pine wood. The amounts that remain in pulped fibers have led to much discussion concerning their influence on fiber properties. In attempts to increase bleachable pulp yields, a primary concern is retention during pulping, particularly of glucomannan. In other cases, removal is important, as in the manufacture of cellulose products. The degree of integration of the two polymers into the cellulose structure influences both their removal from pulp fibers and the pulp properties. It was expected that an investigation of the mechanism of alkaline extraction of the hemicelluloses would increase understanding of the cellulose–hemicellulose relationship.

It has been shown that small-scale alkaline extractions of pulp fibers can be standardized to yield repeatable quantitative data.[1] This standardization was necessary in the present research for determining the amounts of xylan and glucomannan removed under various extraction conditions. Data from very brief extractions with 6% NaOH showed that the polymers were located primarily within the fiber pore structure.[1]

Subsequent experiments were an effort to relate extraction results to the degree of cellulose swelling by using a series of increasing NaOH concentrations. Each pulp sample was treated at room temperature for 1 h in a single

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TABLE I
Composition[a] of Materials before Alkaline Extraction

| Component | Loblolly pine holocellulose (%) | Slash pine oxygen pulp (%) | Loblolly pine kraft pulp (%) |
|---|---|---|---|
| Glucose | 55.8 | 72.5 | 78.5 |
| Mannose | 16.2 | 14.4 | 8.3 |
| Xylose | 9.0 | 6.0 | 7.7 |
| Galactose | 2.3 | 0.3 | 0.6 |
| Arabinose | 1.8 | 0.5 | 0.6 |
| Uronic acid | 2.7 | 1.2 | 0.3 |
| Acetyl | 1.7 | — | < 0.1 |
| Total | 89.5 | 94.9 | 96.0 |
| Cellulose | 50.4 | 67.7 | 75.7 |
| Glucomannan | 23.9 | 19.5 | 11.7 |
| Xylan | 13.5 | 7.7 | 8.6 |
| Acetyl | 1.7 | — | — |

[a] Data are percentages of components as anhydrides. Methoxyl on uronic acid is not included.

NaOH concentration. Each 1-h extract was characteristic of a single alkaline concentration because no water wash was used. The results suggest that hemicellulose molecules located in any particular pore in the cellulose structure are not released until the NaOH concentration is high enough to expand that pore sufficiently to permit egress of the molecules. An example of high accessibility was water-washed pine holocellulose which released 25% of its xylan together with pectin and soluble lignin when extracted by only 0.1-*m* NaOH; these very accessible fractions were lost in chemical pulping. In general, smaller proportions of glucomannan were accessible to NaOH, suggesting that a greater proportion of the glucomannan may have been in the small pores. Because the total content of glucomannan was greater (Table I), the actual amounts of the two polymers released were similar.

This report contains measurements of the effects of three cations and borate on alkali extractions. The results supplement previous reports that KOH is much less effective than NaOH in glucomannan extraction[2] and that borate additions to the alkali increase glucomannan extraction.[3] Also, the results suggest modes of hemicellulose distribution. Oxygen pulps were used because of their large glucomannan content. A kraft pulp provided a chemical pulp containing resorbed xylan. Holocellulose was used for comparison because its hemicellulose is the least disturbed and, indeed, is almost intact.

## EXPERIMENTAL

### Pulps

Oxygen pulp of slash pine (*P. elliottii* Engelmann) was previously obtained by a 16-h cook at 135°C.[4] It was prepared in a 59% yield but screened to a 53% yield, air-dried, and stored until used for extractions. Unbleached kraft

pulp of loblolly pine (*P. taeda*, yield 44%) was air-dried. Holocellulose was prepared by extraction of loblolly pine tangential slices with $CH_2Cl_2$:95% ethanol (1:1, v:v), followed by extended soaking at room temperature in sodium chlorite as described by Thompson and Kaustinen.[5] The slices were washed after delignification, mechanically fiberized in a Valley beater, and air-dried. Table I shows the chemical composition of the three materials for extraction. The difference between 100 and each sum in Table I is the approximate lignin content. The differences matched Klason lignin analyses except for the more soluble lignin of the holocellulose in which Klason lignin was only 0.6% instead of about 10.5%. (About 90% of the holocellulose lignin was removed by 0.1-*m* NaOH.)

## Extractions

A pulp sample (0.5-g) was placed in a 3-cm-diameter, coarse, ground-glass filter funnel. It was then partially dispersed in 20 mL of water by tamping with the flattened end of a glass rod. Three water washes were sucked through the glass funnel as the fibers were pressed with the rod. Weight losses during washing were less than 1%.

The first two extractions after washing were two dispersals in alkali each for 15 s. To minimize dilution of alkali by the 1–1.3 mL of wash water remaining in the fibers, the first dispersal was in 20–25 mL of alkali; the second was in 15 mL. Like the water washes, each dispersal was followed by suction and pressing, but after the second extraction a further 5 mL of alkaline solution was passed through the fiber mat while maintaining suction.

The next extraction was 1 h. The sample was (1) transferred to a small beaker and soaked in 15 mL of solution for 1 h, (2) returned to the funnel for suction and pressing, and (3) dispersed with another 15 mL for about a minute followed by suction and a 5-mL alkaline wash as before.

The two 15-s extracts and the subsequent 1-h extract were combined for analysis. (After 1 h, extraction rates for xylan and glucomannan are very low.[1]) Concentrations of alkali expressed in molarity (*m*) are about equivalent to molarity (*M*) in the concentrations used.

## Analyses

Glucose, mannose, and xylose were determined simultaneously by spectrophotometry.[6] In this method the xylose result includes part of the arabinose and uronic acid. Because all three constituents are in xylan, spectrophotometric analyses of an extract and the starting pulp can provide the percentage extraction of xylan. Mannose results suffice for calculating the percentage glucomannan extracted. Uronic acid was analyzed by a colorimetric method.[7]

The galactose and arabinose of the pulps in Table I were determined by HPLC.[8] The approximate polysaccharide compositions in Table I were calculated by assuming (1) galactose to be in the glucomannan, (2) a glucose to mannose ratio of 1:3 in the glucomannan, and (3) arabinose and uronic acid to be in the xylan.

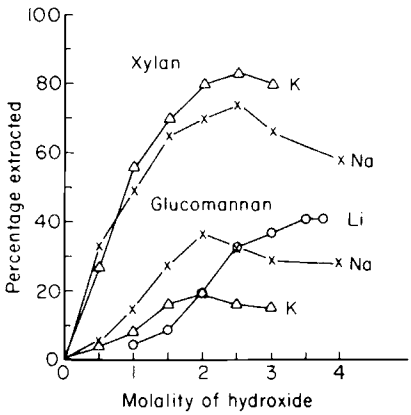


Fig. 1. Comparison of extractabilities of xylan and glucomannan by three hydroxides during 1 h at room temperature (20°C). The unextracted oxygen pulp contained 8.9% xylose anhydride and 14.5% mannose anhydride (ML875396).

## RESULTS AND DISCUSSION

### Cation Effects

It was previously found that the quantities of xylan and glucomannan extracted from pine pulp fibers increased almost linearly as concentrations of NaOH increased from 0 to 1.5 *m*. Extractions by NaOH and KOH increased, as shown in Figure 1 for this concentration range, then increased more gradually to maxima at concentrations of 2–2.5 *m*. This behavior parallels the swelling changes reported for some forms of cellulose in similar concentrations of alkalis.[9,10] In addition to the obvious importance of swelling and mercerization, the shapes of the extraction curves in Figure 1 are influenced by changes in hemicellulose solubility, conformation, and diffusibility. Extractabilities below 2- to 2.5-*m* alkali relate more to cellulose swelling than to cellulose mercerization or to decreased polymer solubility at high ionic strength.

In Figure 1, the greatest difference shown between extractabilities of xylan and glucomannan occurs at the lower concentrations of LiOH, where even less glucomannan is removed than at the same concentrations of KOH. In contrast, the curve of xylan extractabilities with LiOH falls so close to the NaOH curve in Figure 1 that it is omitted for clarity. Extraction of glucomannan by LiOH is exceptional in that a much higher concentration of LiOH than of NaOH or KOH is necessary for maximum extraction.

No single explanation accounts for the differences in Figure 1. In comparing extractive capabilities of cations, Hamilton and Quimby[2] pointed to different ratios of ions to ion pairs and to a different hydration, especially of $K^+$. Westman and Lindstrom[11] found differences when measuring the effects of cations on the swelling of a specially prepared crosslinked cellulose gel. Swelling maxima were at 3.25*M* LiOH and 2.75*M* NaOH, but no maximum was found for KOH. The different concentrations at maximum swelling, they suggested, could be caused by greater ion pair formation by LiOH. The glucomannan extractions by LiOH in Figure 1 do conform to the suggested decreased $OH^-$ concentration caused by LiOH ion pair formation. The ab-

sence of a similar effect on xylan extraction by LiOH, however, indicates that the $OH^-$ concentration is sufficient for cellulose swelling and xylan extraction. It may be that the $OH^-$ concentration provided by LiOH below 2 m ionizes the xylan carboxyl groups but not the glucomannan hydroxyl groups. It may also be that for some reason KOH is less able than NaOH to form glucomannan alcoholate.

## Borate Effects

The extraction tests with borate by Jones et al.[3] and by Ward and Murray[12] utilized higher alkali concentrations than those reported here, high enough for mercerization to be a major factor. Furthermore, in their work, hydroxide molality appreciably exceeded boric acid molality. The borate stimulation of glucomannan extraction is demonstrable at nonmercerizing concentrations of alkali. Figure 2 shows the consequences of partial neutralization of 1.5-*m* NaOH by $H_3BO_3$ and, for comparison, the results of using lower NaOH concentrations in the absence of boric acid. It is assumed that $H_3BO_3$ acts as a monobasic acid in removing $OH^-$. The decreases of extracted xylan in the presence of $H_3BO_3$ are seen to be exactly those given by equivalent reductions in NaOH down to 0.25 *m*. The extractions of glucomannan, in contrast, are increased by additions of $H_3BO_3$.

When the NaOH is neutralized with acetic acid, the glucomannan extractions follow exactly the line of extraction with NaOH alone in Figure 2. This comparison between the effects of acetic and boric acids points out the unique effect of $H_3BO_3$ on glucomannan.

In Figure 3 the variable is the amount of NaOH or KOH in a fixed $H_3BO_3$ concentration, a reversal of the order in Figure 2. Although an oxygen pulp replaces the holocellulose of Figure 2, the effects of $H_3BO_3$ are in the same direction. The top graphs demonstrate again the decreased xylan extraction produced by the neutralization of $OH^-$ with $H_3BO_3$. Only if the added $OH^-$ molality exceeds the 1.0 molality of $H_3BO_3$ do the xylan extractions proceed appreciably. If the graphs were plotted on the basis of actual $OH^-$ concentration, the $H_3BO_3$ curves would be translated to the left by 1.0-*m* units. The

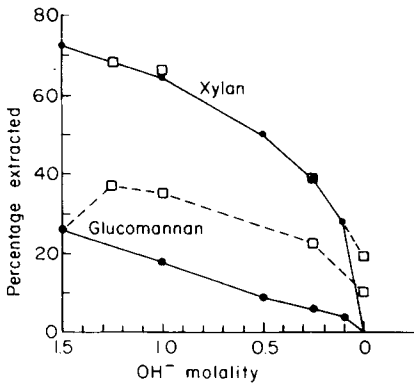


Fig. 2. Influence of $H_3BO_3$ on extractions of xylan and glucomannan by NaOH. One-hour extractions from holocellulose by NaOH alone (—) and by 1.5*m* NaOH plus increasing amounts of $H_3BO_3$ (□). Neutralization of $OH^-$ by $H_3BO_3$ is calculated on a 1:1 basis (ML875397).

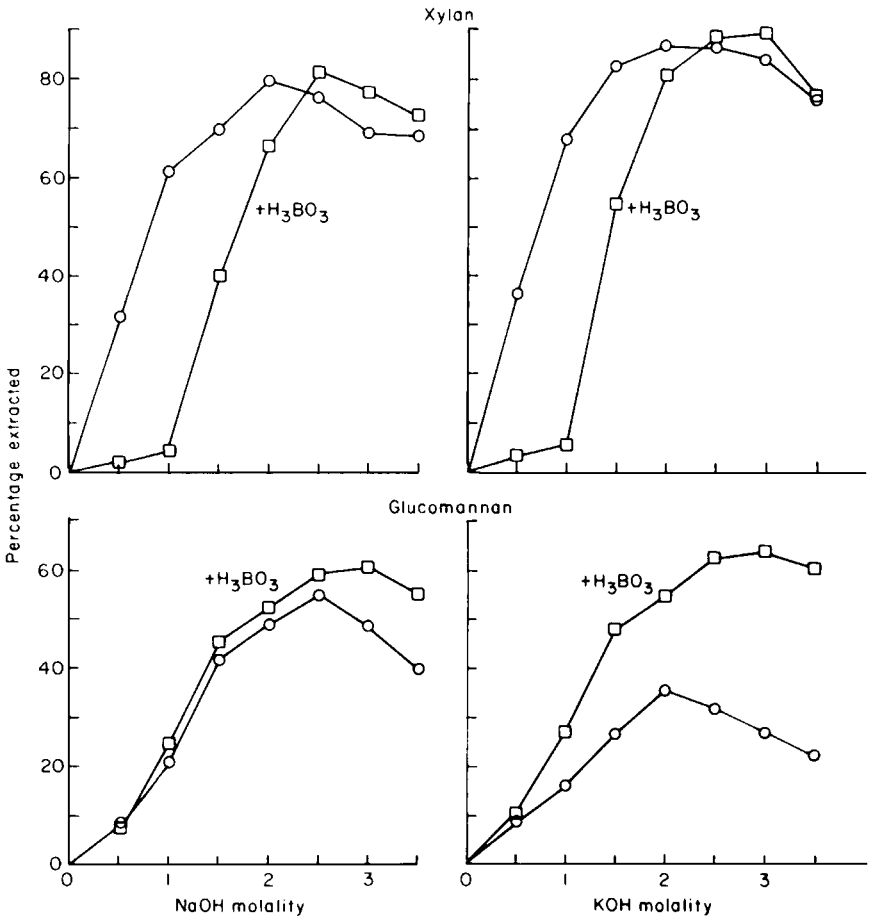


Fig. 3. Percentages of xylan and glucomannan extracted in 1 h by NaOH and KOH from an oxygen pulp [no added $H_3BO_3$ (○), 1.0*m* added $H_3BO_3$ (□)]. Unextracted pulp had 6.7% xylose anhydride and 14.4% mannose anhydride (ML875399).

lower graphs in Figure 3 demonstrate the poor extractability of glucomannan by KOH on the right (compared to NaOH on the left) and the improved extraction with KOH by adding 1.0-*m* $H_3BO_3$, an effect of borate found on extractions by LiOH also. The strong additive effect of $H_3BO_3$ on the alkaline extractions of glucomannan is even more apparent if these curves are translated, as suggested, to show the actual $OH^-$ concentration.

The addition of boric acid, $B(OH)_3$, to $OH^-$ produces the $B(OH)_4^-$ ion.[13] This ion is clearly ineffective for xylan extraction from the oxygen pulp, but it promotes glucomannan extraction, presumably by complexing with the mannose units.

Because of interest in being able to extract glucomannan selectively, a range of $B(OH)_4^-$ concentrations was prepared, using equal molal amounts of NaOH and $H_3BO_3$. Extractions of three pulps by these solutions are shown in Figure 4. Yields differ sharply between xylan and glucomannan in extractions of oxygen pulp. For the holocellulose, the pattern is reversed only because of

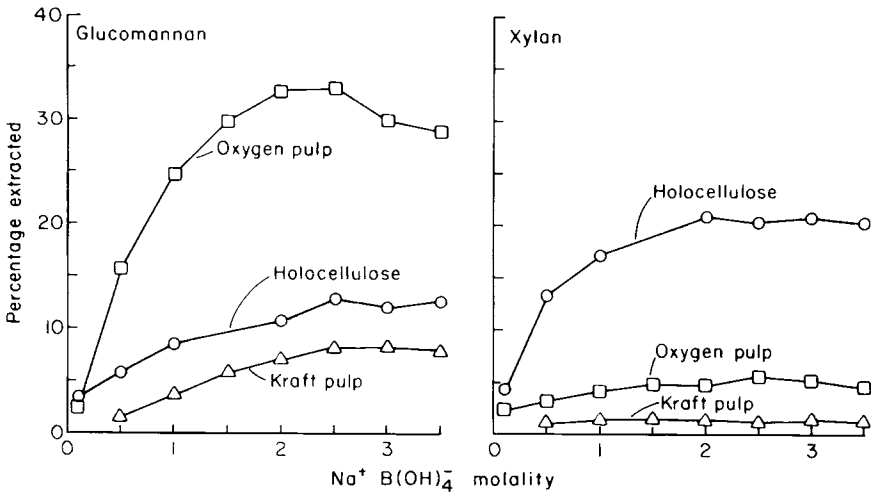


Fig. 4. Extractabilities of xylan and glucomannan into mixtures containing equal molalities of NaOH and $H_3BO_3$ (ML875398).

the highly extractable portion (25–30%) of holocellulose xylan, previously mentioned. Apparently, most of this accessible portion of xylan can be extracted by the $B(OH)_4^-$ ion (see also Fig. 2 at zero molality). When this portion was first removed by 0.1-*m* NaOH, only 9.5% of the remaining holocellulose xylan was extracted by 2.5-*m* $NaB(OH)_4$, but 16% of the glucomannan was extracted.

The ability of $B(OH)_4^-$ to remove glucomannan while leaving much of the xylan raises a question about the ability of $B(OH)_4^-$ to swell the cellulose structure. An alpha cellulose was extracted with alkali, washed, and air-dried to provide samples that would not lose weight during moderately alkaline extractions. Approximate water-retention values were obtained by weighing the samples after suction filtration and moderate pressing, as in the extraction procedure. It was found that the cellulose retained 1.74 mL/g pulp after soaking in 2.0-*m* NaOH + 2.0-*m* $H_3BO_3$, but retained 1.82 mL/g when soaked in 2.0-*m* NaOH. The retention volume of the borate solution was equivalent to the measured retention volume of 0.5- to 0.75-*m* NaOH. Likewise, the extraction of holocellulose glucomannan was about the same for the 2.0-*m* borate-containing solution (Fig. 4) and for 0.5- to 0.75-*m* NaOH (Fig. 2) in agreement with the water retention of alpha cellulose. The same was true for the kraft pulp. These observations can be understood if the extraction of glucomannan by $B(OH)_4^-$ is limited by the amount of cellulose swelling and if the extraction of xylan by $B(OH)_4^-$ is limited by the low ionization of xylan carboxyl groups.

Oxygen pulp differed from holocellulose pulp and kraft pulp in the greater extractability of its glucomannan. In contrast to the nearly equal amounts mentioned above, over twice as much of its glucomannan was extracted by 2.0-*m* $NaB(OH)_4$ as by 0.5- to 0.7-*m* NaOH (Figs. 3 and 4). Furthermore, extraction by 1.5-*m* NaOH released 41% of the oxygen pulp glucomannan Fig. 3) but only 26% of holocellulose glucomannan (Fig. 2). These differences may result from molecular weight decrease of glucomannan and/or its relocation to more accessible positions during oxygen pulping.

## CONCLUSIONS

Extraction of xylan and glucomannan from pine pulp fibers depends on the ability of alkaline solutions to swell the cellulose structure and also on their ability to form polyanions with the two hemicelluloses. These anions are the carboxylate groups of xylan, the borate complexes of glucomannan, and the alcoholates of both polymers at sufficient concentrations of alkali.

The $B(OH)_4^-$ anion swells cellulose to a small extent and can remove xylan that is very accessible (e.g., 20–25% of pine holocellulose xylan). Extraction of chemical pulp xylan and further extraction of holocellulose xylan require $OH^-$ to provide greater swelling of cellulose and more basicity. Glucomannan extraction increases with borate complexing and with the swelling of cellulose provided by $OH^-$ in molar excess over $B(OH)_4^-$.

This study corroborates previous conclusions that extraction techniques can contribute information on hemicellulose distribution in pulp fibers and on differences between pulps.[1] Pulp comparisons lead to the following conclusions: (1) Chemical pulping removes a very accessible portion of pine xylan; (2) a portion of the glucomannan becomes more extractable in oxygen pulping: (3) resorption of xylan during kraft pulping does not increase its extractability; and (4) glucomannan and xylan located in the smallest pores of the cellulose structure resist pulping and alkaline extraction.

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