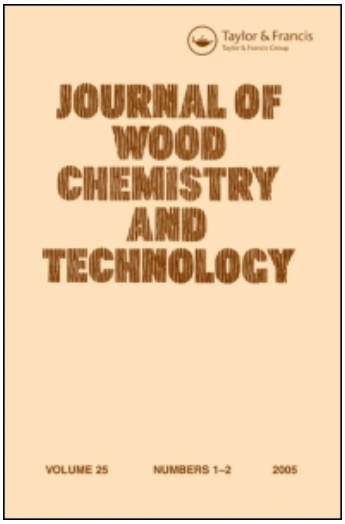

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Sugars and Sugar Acids in Lignosulphonate Products

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SUGARS AND SUGAR ACIDS IN LIGNOSULPHONATE PRODUCTS

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ABSTRACT

The monosaccharide contents of solid lignosulphonate products from spent sulphite liquors were determined by capillary gas chromatography. The predominant monosaccharide was mannose in two softwood calcium bisulphite cases, and xylose in a hardwood calcium bisulphite case. Monosaccharide analysis before and after ultrafiltration of lignosulphonates showed that about 10-25% of the neutral sugars did not pass through the membranes, and presumably remained associated with the lignosulphonates. Chemical "de-sugaring" treatments removed all but traces of the monosaccharides; when hot aqueous sodium hydroxide was used for this purpose, the main products were 3-deoxy carboxylic acids derived from the hexoses.

INTRODUCTION

The major organic components of spent sulphite liquor are lignosulphonates and low-molecular-weight, water-soluble products derived from carbohydrates. During sulphite pulping, the lignin in

the wood is solubilized by sulphonation and acid hydrolysis, and its macromolecular structure is also changed substantially. Further radical changes in the lignosulphonates may occur during subsequent treatments used for the preparation of chemical products therefrom.

Simultaneously, some wood carbohydrates are also solubilized during pulping, primarily through hydrolysis of hemicelluloses, and these compounds are equally subject to a variety of chemical changes during the remainder of pulping and in subsequent treatments of the spent sulphite liquor (SSL). In most SSL-derived chemical products, the spent sulphite liquor is used without fractionation; hence, chemical changes in both of the major components are potentially important. The lack of detailed information on changes in the carbohydrate fraction is certainly hindering rational product development.

Major industrial uses of SSL products are: binder applications, such as animal feed pelletizing, briquetting, road treatment, and components in phenol formaldehyde and urea formaldehyde resins; dispersant applications, such as oil well drilling, organic dyes, concrete, and gypsum; and tanning applications.

The five common "wood sugar" monomers (arabinose, xylose, mannose, galactose, and glucose) are usually found in varying proportions in lignosulphonate samples obtained from spent sulphite liquor. The presence of these monomers poses two important questions: Do they affect the performance of a lignosulphonate product? And does their fate in lignosulphonate processing indicate suitable treatment conditions?

Before such questions could be answered, an accurate means of determining the neutral monosaccharide contents of solid lignosulphonate products was needed. The methods already in use were

generally unsatisfactory — either they didn't identify the individual monosaccharides[1], were only qualitative[2-4], or involved tedious work-up procedures before analysis[5]. To solve this problem, a new analytical method was developed. In it, the monosaccharides in a dry lignosulphonate sample are derivatized directly to trimethylsilyl ethers, which are then analyzed quantitatively by capillary gas chromatography. We have now applied this technique to a wide range of lignosulphonate samples.

RESULTS AND DISCUSSION

Monosaccharides in commercial lignosulphonate products

Three different lignosulphonate samples were analyzed for monosaccharide content. Sample A was the spray-dried product from the spent liquor of a low-yield calcium bisulphite cook of spruce chips. Sample B was produced by ion-exchanging Sample A into the sodium form; this was done in an industrial operation. Sample C was derived from a low-yield calcium bisulphite cook of mid-western U.S. hardwood chips. All three were commercial samples. Table I shows the individual and total monosaccharide contents of samples A, B, and C; the details of the analytical procedure are given in the Experimental section.

All three samples contained appreciable amounts of monosaccharides. Samples A and B, which originated from the cooks of softwoods, were characterized by high mannose contents, while Sample C from the hardwood cook was highest in xylose content. These results are indicative of the hydrolysis of glucomannan in the softwood cases and xylan in the hardwood case. Note that the results in Table I reflect the fate of the most easily hydrolyzed carbohydrate components of the wood at the end of sulphite cooking, and cannot be related to the carbohydrate composition of the undissolved polysaccharide fraction (i.e., the pulp) unless the total carbohydrate composition of the wood is known.

TABLE I

MONOSACCHARIDES (AS WEIGHT PERCENT) IN COMMERCIAL LIGNOSULPHONATE PRODUCTS

Sample	Arabinose	Xylose	Mannose	Galactose	Glucose	TOTAL
A	1.1	4.3	10.1	2.8	2.6	20.9
B	0.6	2.0	6.9	1.7	2.1	13.3
C	0.5	10.7	3.3	0.8	1.2	16.5
S(a), by GC analysis	13.0	29.4	15.5	22.7	19.4	100
S(a), by weight	13.7	30.2	15.3	21.8	19.0	100

(a) Sample S was a "blind" calibration sample containing the five monosaccharides of interest.

A capillary gas chromatogram of sample B is illustrated in Figure 1. Because the monosaccharides were derivatized as trimethylsilyl ethers, one peak appears for each stable isomer of each neutral sugar. Thus, arabinose and xylose are represented by four peaks each, corresponding to the α- and β-furanose and α- and β-pyranose isomers. Mannose and glucose, on the other hand, are found only in the α- and β-pyranose forms in these samples. Unlike our earlier experience with packed GC columns, the excellent resolution on the 30 m glass capillary column used in this work permitted us to identify all the isomers and to properly recombine them to determine the monosaccharide contents. For reference, Figure 1 also shows a calibration chromatogram containing all five monosaccharides of interest, and Table I shows the analysis of a "blind" calibration sample (S).

Monosaccharides in lignosulphonate samples after chemical and physical treatments

Sample B was also the parent material of a family of lignosulphonate products derived by physical and chemical means. As Figure 2 shows, five different lignosulphonate retentate fractions

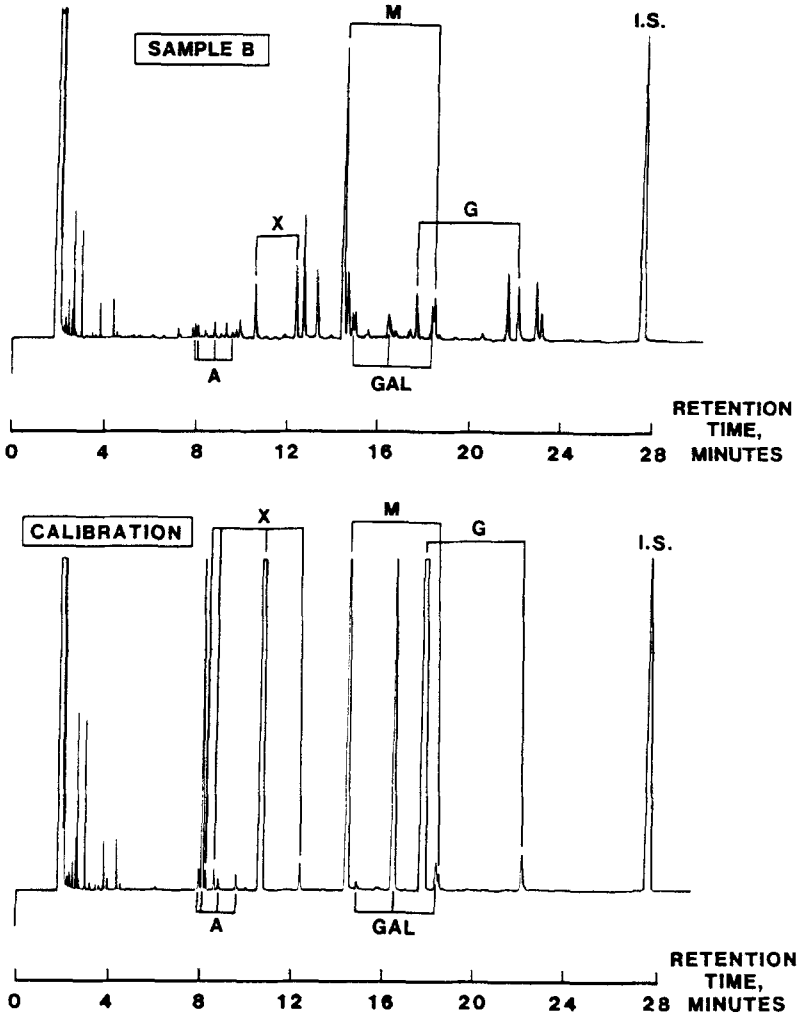

Figure 1. Capillary gas chromatograms of trimethylsilylated monosaccharides in lignosulphonate sample B, and a calibration sample. Some of the unidentified peaks in B are probably sugar acids and lactones. GC Condition A. A = arabinose, X = xylose, M = mannose, GAL = galactose, G = glucose.

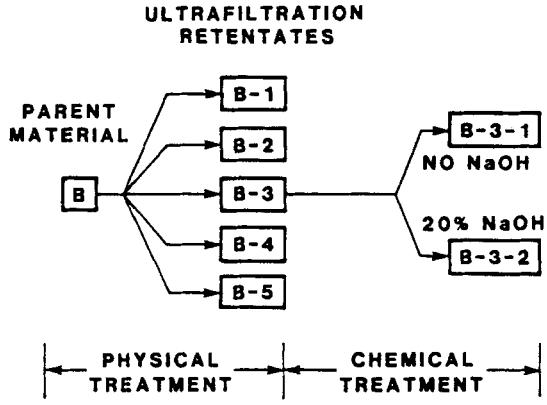

Figure 2. Parent lignosulphonate product B was fractionated by ultrafiltration into five different retentate samples. Aqueous sample B-3 was subsequently exposed to high-temperature treatment with or without NaOH.

(i.e., the material which did not pass through the membrane) were produced from B by ultrafiltration. The processing conditions were such that sample B-1 had the highest retention of lignosulphonates, B-5 the lowest. Because ultrafiltration was being used to fractionate the lignosulphonates in the parent material, the average molecular weight of the retained lignosulphonates increased in the order B-1 to B-5.

It was of interest to determine the monosaccharide contents of the various retentates after ultrafiltration. Table II presents the results. The total monosaccharide contents decreased in the order B-1 ≅ B-2 > B-3 ≅ B-4 > B-5. As might be expected, most of the monosaccharides passed readily through the membrane with the filtrates (also termed permeates), and about three-quarters of the simple reducing sugars were removed in going from B to B-1. As the ultrafiltration process was manipulated to retain ever higher molecular weight fractions of lignosulphonates (i.e., going from B-1 to B-5), the residual monosaccharide contents of the retentates

declined. The results also showed that the monosaccharides were not completely removed, indicating that small amounts of them may be physically or chemically associated with the lignosulphonate material, thus being more difficult to remove than the freely-dissolved neutral sugars.

As in parent material B, products B-1 to B-5 contained more mannose than any of the other four monosaccharides.

The traditional way of measuring the sugar content of commercial lignosulphonate samples is a "reducing sugar test"[1]. Its name implies that it responds only to the reducing sugars in the sample. As Table II demonstrates, however, there was no agreement, either in absolute values or in ranking of samples, between the percent

TABLE II

MONOSACCHARIDES (AS WEIGHT PERCENT) IN LIGNOSULPHONATE SAMPLES

Sample	Arabinose	Xylose	Mannose	Galactose	Glucose	Total	% "reducing sugars"[a]
B	0.6	2.0	6.9	1.7	2.1	13.3	20.3
B-1	0.5	0.3	1.9	0.3	0.8	3.8	15.5
B-2	0.6	0.3	1.9	0.2	0.9	3.9	13.7
B-3	0.2	0.2	1.4	0.3	0.5	2.6	12.0
B-3	0.2	0.2	1.4	0.3	0.5	2.6	-
B-4	0.4	t	1.1	0.3	1.0	2.8	20.5
B-5	0.1	0.1	0.6	0.1	0.2	1.1	7.2
B-3-1	t	0	0	t	0	0	6.8
B-3-2	t	0	0	t	t	0	10.0

[a] The method is described in Reference 1. For comparison, the following compounds also gave positive responses to the test: lactic acid, 6.0%; 3-deoxy-2-C-hydroxymethyl-D-pentonic acid (common name, glucoisosaccharinic acid), 9.2%; cellopentaose, 53.6%; the percentages refer to the response per unit weight where glucose = 100%.

[b] Duplicate samples.

[t] Denotes trace amount.

"reducing sugars" and the actual monosaccharide contents of family B samples. Product B-4, for example, had a low monosaccharide content, but a very high "reducing sugar" content. When non-reducing compounds such as carbohydrate-derived carboxylic acids were subjected to the reducing sugars test, they also gave positive results (see footnote, Table II). Cellopentaose, a pure reducing sugar but not a monosaccharide, had about half the theoretical 100% response. Thus, the reducing sugars test is neither a suitable method for determining true monosaccharide content in these samples, nor a reliable indicator of what could properly be termed reducing sugars.

Sample B-3 was the starting material for two different chemical treatments (see Figure 2). In one, an aqueous solution of B-3 was heated at about 150°C for 1 hour; the initial pH of the solution was 5.5. In the other, aqueous B-3 was reacted with 20% NaOH (based on dry lignosulphonate content) for 1 hour at high temperature. Both processes removed virtually all the monosaccharides from B-3 (see Table II), demonstrating that "de-sugaring" did not require treatment in strong caustic solution.

The alkaline degradation of simple reducing sugars (e.g., glucose) has been the subject of many studies[6,7]. To get a qualitative picture of the fate of the hexoses in going from B-3 to B-3-2, sugar degradation products from B-3-2 were analyzed by gas chromatography-mass spectrometry. Figure 3 shows gas chromatograms of the B-3 and B-3-2 products. Note that any monosaccharide degradation product bearing hydroxyl groups will be converted to its trimethylsilyl derivative, and thereby appear in the chromatogram.

Gas chromatographic-mass spectrometric analysis of the compounds in sample B-3-2 (Figure 3) showed that none contained the ions characteristic of trimethylsilyl derivatives of hexoses (i.e., m/e 191, 204, 217, 231, and 361)[8,9]. The four most prominent

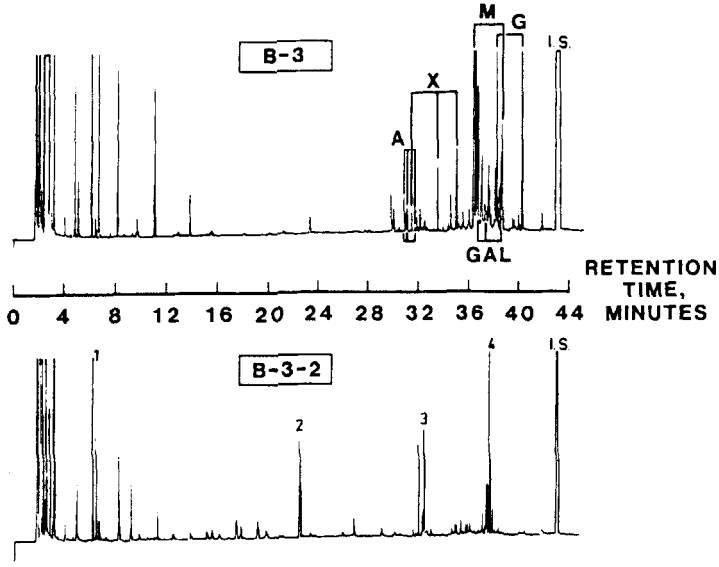

Figure 3. Exposure of sample B-3 to high-temperature treatment in 20% aqueous NaOH gave sample B-3-2; the capillary gas chromatograms show the trimethylsilylated compounds in each sample. GC Condition B. The treatment almost completely destroyed the neutral monosaccharides in B-3. The mass spectra of the products labelled 1, 2, 3, and 4 are illustrated in Fig. 4.

degradation products in B-3-2 were identified as the trimethylsilyl ethers of lactic acid (Peak 1), 2,4-dihydroxybutyric acid (Peak 2), 3-deoxypentonic acid (Peak 3), and 3-deoxyhexonic acid (Peak 4). The mass spectra of these products are illustrated in Figure 4; they showed good correlation with previously published mass spectra of this family of 3-deoxy aldonic acids[6,10]. The deoxy acids were not determined quantitatively, but this could be done easily if the pure compounds were available. All four compounds are major products of the reaction of glucose (or mannose) with aqueous sodium hydroxide[6].

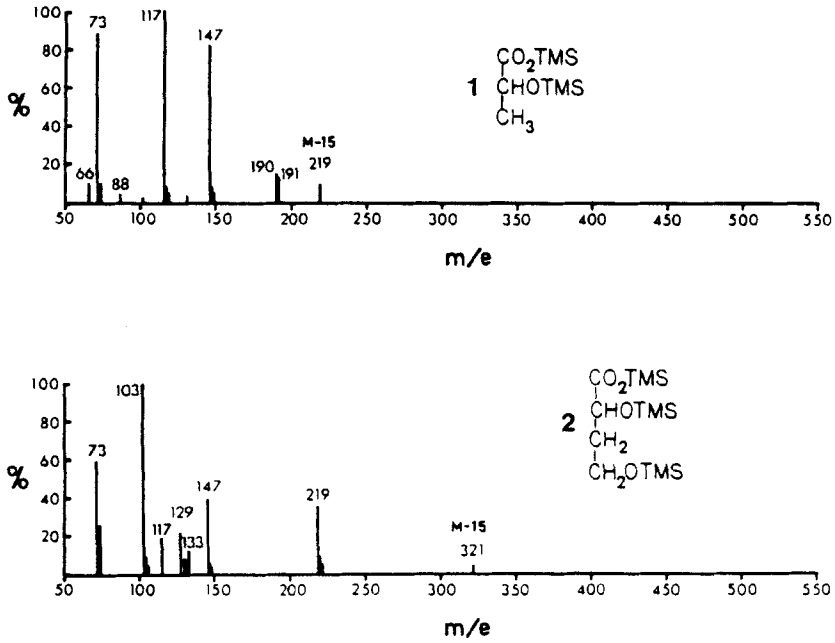

Figure 4. Major components of sample B-3-2 were identified by their mass spectra: 1 — lactic acid; 2 — 2,4 dihydroxybutyric acid; 3 —3-deoxypentonic acid; 4 — 3-deoxyhexonic acid.

SUMMARY

Capillary gas chromatographic analysis of monosaccharides in lignosulphonate products is a quantitative and relatively simple technique. It can show the amounts and identities of the individual neutral sugars, and how their concentrations change as a result of physical and/or chemical treatments. The derivatization procedure (trimethylsilylation) also has a bonus —low molecular weight acidic products bearing hydroxyl groups will also be derivatized, and can be determined along with the monosaccharides.

EXPERIMENTAL

Derivatization of samples: Small portions of lignosulphonate samples (10-50 mg, depending on estimated total monosaccharide con-

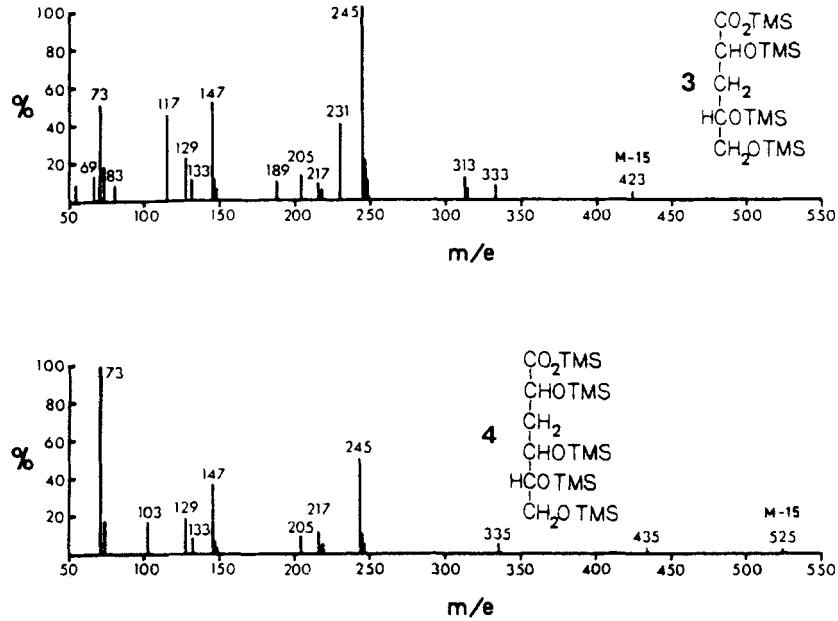

Figure 4

tent) were placed in 4 mL glass vials, then oven-dried (105°C) to constant weight. Silylation-grade dimethyl sulphoxide (1.0 mL) was added to dissolve the sample; the DMSO contained a known amount of myo-inositol, the internal standard. Tri-Sil Concentrate (Pierce Chemical Co., Rockford, IL) (0.5 mL) was added. After warming and shaking for 2 h or more, the solution was allowed to settle into two layers; the GC sample was taken from the upper layer and was injected into the chromatograph. When stored in a refrigerator, the trimethylsilylated monosaccharides were stable for several months.

Gas chromatography: Hewlett-Packard 5880 chromatograph with flame ionization detector; J & W 30 m x 0.25 mm i.d. fused silica column coated with SE-30; helium as carrier gas; split-mode injection, ratio 1:40. Temperatures: injector, 230°C; detector, 250°C; column, Condition A, 160°C to 220°C at 1.5°C/min, or Condition B,

85°C to 130°C at 2.0°C/min, then 130°C to 220°C at 5.0°C/min. The internal standard method was used for quantitation of the five key monosaccharides, the response factor of each being determined from the pure compound.

With either pure xylose or glucose, the lower detection limit was ~1 μg, and the detector gave a linear response from 1 μg to at least 20 μg. Several different lignosulphonate samples were subjected to multiple determinations of total monosaccharide content; the results agreed to ±2% by weight. Four different lignosulphonate samples were analyzed by GC and by liquid chromatography[11]; both methods ranked the individual monosaccharides in the same order, and the weight percent values agreed to ±4%.

Gas chromatography–mass spectrometry: Hewlett-Packard 5985A instrument with computer-based operations and data system; electron impact ionization mode, 70 eV; scan range, 50–550 amu; ionizing chamber temperature, 200°C; GC Condition B.

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