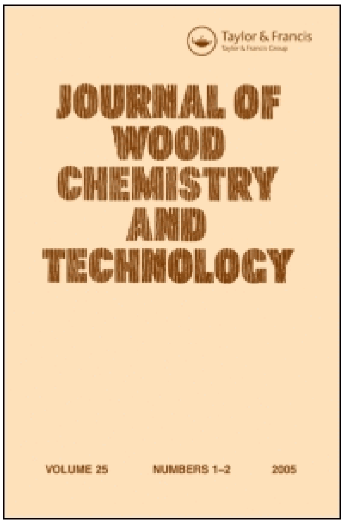

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PHYSICOCHEMICAL ANALYSIS OF A SPENT SULFITE LIQUOR FROM A CMP PULP

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ABSTRACT

The lignosulfonates (LS) of an industrial spent sulfite liquor originated from a chemimechanical pulping process (CMP) of softwood have been examined by different physicochemical and spectroscopic methods. Gel permeation chromatography shows an average MW of 1600 daltons. Analytical data reveal the characteristics of sulfonated guaiacylpropyl units. FABMS analysis gives some additional structural features of a typical LS model. This work also shows that sugars react with $NaHSO_3$ and prevent their detection by GLC as silylated derivatives.

INTRODUCTION

It has recently been reported[1] that the daily production of dry solids spent sulfite liquor (SSL) from the pulp and paper industry in Canada exceeds 4000 metric tons. The interest for lignosulfonates (LS) has grown continuously as concerns for more complete utilization of biomass as well as ecological considerations. Lignosulfonates are used in a wide variety of industrial applications[2-4].

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This paper reports the elemental analysis, MW and sugar determinations together with spectroscopic data (^{1}H and ^{13}C NMR, and FABMS) of an industrial lignosulfonate.

RESULTS AND DISCUSSION

Fractionation of SSL

The precipitation of our lignosulfonates occurred abundantly at about 40% by volume of 1,4-dioxane added, and then it decreased markedly for further addition until the amount of dioxane attained 77% by volume where the precipitated materials became more abundant again. It should be recalled that dioxane can form strong interactions with water molecules through hydrogen bonds[5]. The resulting binary solvent must be less polar than pure water and this lowering of polarity will be more and more accentuated on increasing the proportion of dioxane.

The fact that little precipitation occurred in the range between 40 and 75% of dioxane suggests that the crude LS may be made up principally of two broad classes of lignosulfonate materials: one, of high molecular weight (above 20,000 daltons) issued from repolymerisation of degraded LS during the cooking period in addition to hemicellulose materials and the other, of low molecular weight, about 1600, according to our GPC results.

The quantitative results obtained from the fractionation of SSL are outlined in Table 1.

Gel Permeation Chromatography

It has been pointed out[6] that the elution of lignosulfonates through Sephadex gels using water as eluent may be seriously influenced by Donnan retardation effects, by changes in molecular size of LS due to polyelectrolytic expansion and by ion exclusion effects (repulsion or adsorption) due to negatively charged groups fixed on Sephadex gels.

TABLE 1

Fractionation of SSL by addition of 1,4-dioxane in SSL aqueous solutions

Fraction	1,4-dioxane (% vol.) added	Weight of fraction (g)	Yield (%)
LS-40	40	1.87	31.2
LS-50	50	0.80	13.3
LS-60	60	0.23	3.8
LS-70	70	0.35	5.8
LS-85	85	1.43	23.8
Residue	-	1.32	22.1
Total	-	6.00	100.0

Taking into account these considerations, gel permeation chromatography was performed on the crude LS sample (Fig. 1) using LH-60 gel and 0.4N NaCl aqueous solution as eluent. One observes seven peaks for the whole distribution. The first, corresponding to the exclusion limit (about 20,000 daltons), suggests that only a low concentration of high molecular weight LS or sulfonated lignocarbohydrate complexes are present in the spent sulfite liquor. The fourth peak is the major one having a molecular weight of about 1,800 daltons according to the calibration curve established with the sulfonated polystyrene standard samples.

The chromatograms of the fractionated LS samples are essentially bimodal. As shown in Fig. 1, the chromatogram of the LS-85 fraction appears to be the most homogeneous one with the major peak corresponding to 1600 daltons. This homogeneous fraction LS-85 was thus utilized throughout this study.

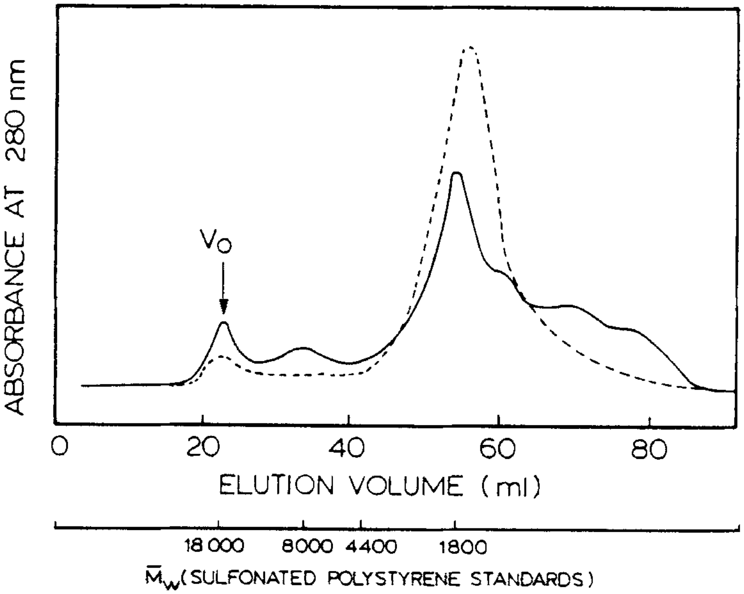


FIGURE 1. Elution profile of crude LS and LS-85 on Sephadex LH-60. Solid line = crude LS, dotted line = LS-85.

Free Monosaccharide Analyses

The five common «wood sugar» monomers (arabinose, xylose, mannose, galactose, and glucose) are usually found in varying proportions in LS samples obtained from spent sulfite liquors. For reference, several calibration mixtures containing various amounts of these five monosaccharides were silylated and analyzed by capillary gas chromatography. We observed all the peaks of the isomers related to the five common sugars. The response factor of each was linear from 1 µg to 10 µg. These results are in good agreement with a previous study[7].

With regard to LS sample analyses, silylations were performed on the crude LS, LS-40 and LS-85 samples. Only very small quantities of free monosaccharides were detected in the samples.

Indeed, we found about 0.5% by weight of monosaccharides in LS, LS-40 and LS-85. Similar results were obtained when some of the experimental conditions of silylation such as the length of the heating period, the temperature and the quantities of DMSO and LS samples used were modified.

The absence of larger quantities of free sugars in our LS samples can be explained in the following manner. First, the severe conditions of the industrial process such as elevated temperatures, the high degree of acidity of the digestion mixture and the long period of digestion, might degrade partially or almost completely the free sugars from the spent sulfite liquors. Similar observations have been previously reported[7]. Secondly, it has already been shown[8,9] that aldoses may react with $NaHSO_3$ to give a bisulfite adduct. As it is usual to find a certain amount of free sugars in SSL, they could react with free $NaHSO_3$ which might be present in excess in SSL. If this reaction occurs to a large extent, it might be expected that derivatized sugar products issued from silylation would become undetectable, i.e. non volatile, in capillary gas chromatography, due to the fact that the silylation was effected on sugar bisulfite addition products. In order to ascertain the effective role of $NaHSO_3$ in the presence of free sugars, the following tests were performed: aqueous solutions (at pH 4.5) of the five pure monosaccharides plus $NaHSO_3$ in the proportion of one mole of sugar for each mole of $NaHSO_3$ were heated at 60°C for two hours followed by silylation. As expected, no peak of derivatized sugars was detected on the chromatogram. Concerning the presence of $NaHSO_3$ in excess in our SSL, we have observed[10] by potentiometric titrations, that the content of $NaHSO_3$ may reach 20% by weight of the dry lignosulfonate. These findings are also confirmed by elemental analyses. The reversibility[11] of the bisulfite addition reaction should be recalled here. Many carbonyl groups in lignin and lignosulfonates are indeed susceptible to undergo the reversible reaction.

The traditional way[12] of determining the sugar content in LS, the Fehling test or «reducing sugar test», yielded 5.4% by weight of «reducing sugar» content in the crude LS and 7.4% in the LS-85 sample. We have also observed that the presence of $NaHSO_3$ does not alter significantly the determination of sugars by the Fehling test. Our experiment was carried out with equimolar quantities of glucose and $NaHSO_3$ using standard conditions[12]. The Fehling test has recently been compared[7] to the silylation technique in the determination of sugar content. These authors concluded that the reducing sugar test in neither a suitable method for determining true monosaccharide content in the lignosulfonate samples, nor a reliable indicator of what could properly be termed reducing sugars. Our results are in good agreement with their findings.

The sugar content of LS-85 was estimated to be 7.4% based on the Fehling test for reducing sugars. The gas chromatographic method with silylated sugars was found to be inaccurate for our samples because of the interference from bisulfite. The important discrepancy in the results of the two methods observed here is of the same order as the one reported earlier[7]. Finally, it is worthwhile to note that some analyses of wood sugars in SSI by high performance liquid chromatography (HPLC) have recently been published[13,14]. Despite the lower resolution presently achieved by HPLC as compared to capillary GLC in sugar analysis, we should consider HPLC as a promising technique in the determination of the bisulfite addition products of sugars as well as an interesting alternative to GLC.

NMR Spectra

Due to the complexity of the lignosulfonates, assignments have been given essentially to the most intense signals in both

^{13}C (CMR) and ^{1}H NMR (PMR). Also, due to the low concentration of sugars found in our fractionated lignosulfonates, we have not taken their NMR assignments into consideration. However, it is known[15] that sugars contained in lignin show absorption between 57 and 109 ppm in CMR. Our assignments in NMR reflect the most important contributing monomer: the sulfonated β-0-4 guaiacylpropyl unit.

CMR Spectrum

The CMR spectrum of the fractionated lignosulfonates LS-85 exhibits 174 signals which can be regrouped into eight series of carbons. Taking into account the main structural unit of softwood LS, i.e. the α-sulfonated phenylpropane unit and the CMR signals of lignins and lignosulfonates both as extracted or as model compounds, one can give assignments to these series of carbons. The assignments proposed in Table 2 are based on the most recent data available[16-20]. The assignments fit well with the major contribution of the sulfonated guaiacylpropyl units and illustrate the great complexity of the LS. In this regard, an interesting fact is the observation of many signals for the methoxyl groups indicating the wide variety of substitutions and conformations affecting these chemical shifts. In a similar way, it is evident that most of the other analog carbons in the lignosulfonates give rise to many signals. In that context, the attribution of a single signal to a single carbon in a specific lignosulfonate molecule seems singularly excessive. However, the utilization of lignosulfonate models[17] appears to be a promising contribution towards the elucidation of the LS structure.

PMR Spectrum

The complexity of LS-85 is also reflected in the PMR spectrum which exhibits a total of 413 signals. Assignments are given for the most prominent groups of signals (see Table 3). If

TABLE 2

^{13}C NMR Data of Lignosulfonate LS-85: General Features.

EN	SIGNALS			ASSIGNMENTS
	No	SHIFTS (range) ppm	INTENSITY	
01	1	190.12	5.11	Carbonyl carbons (conjugated or saturated)
02	2	175.82	1.46	Carboxyl carbons
03	3-16	153.72-148.05	1.45-3.57	Oxygenated aromatic carbons C-3 and C-4 in guaiacyl
04	17-26	131.92-129.38	1.51-2.69	Aromatic carbons C-1 in guaiacyl
05	27-65	128.58-112.29	1.41-7.68	Aromatic carbons C-2, C-5, C-6 in guaiacyl
06	66-145	103.96-60.55	1.41-15.50	Alkoxyl and sulfonated carbons: C_α, C_β and C_γ in side-chains (major) and C in sugars (minor)
		86.92	11.27	C_β, >CH-O- in β-O-4 guaiacyl

		76.96	12.57	C_β, $-CH_2-O-$ in β-O-4 guaiacyl
		74.93,	11.55,	Sulfonated carbons $-CHSO_3Na$
		71.34,	13.25,	
		65.18	15.50	
		60.96,	12.91,	Methoxyl carbons
		60.76,	12.33,	
		60.64,	12.63,	
		60.64,	12.63,	
		60.55	12.80	
07	146-167	41.12-34.32	1.45-5.65	Carbons in α to carbonyl
08	168-174	30.90-2.06	1.51-28.71	Non-oxygenated carbons in aliphatic side-chains
		30.90-28.58	1.51-5.51	CH, CH_2, CH_3
		21.79-16.67	1.61-3.32	CH, CH_2, CH_3
		2.06	28.71	CH_2

TABLE 3

^{1}H NMR Spectrum of Lignosulfonate LS-85: General Features.

EN	SIGNALS		ASSIGNMENTS
	SHIFTS (range) ppm	INT.	
01	1.35-1.53	4.2-9.1	CH_3, CH_2, CH in aliphatic side-chains
02	1.56-1.93	I ≥ 8	CH_3, CH_2, CH in α to carbonyl or alkene
03	3.00-4.08	I ≥ 5	Protons on alkoxy carbons: CH_3O-, -CH_2O-, CH-O- in side-chains (major contribution) or/and in carbohydrates (minor)

	3.6644	11.320	Methoxyl protons
	3.6716	10.286	
	3.6973	9.902	
	3.7039	10.579	
	3.7110	10.877	
	3.7152	11.320	
04	4.14-4.18	4.9-5.7	Protons on γ-alkoxy carbons in β-0-4 guaiacylpropyl
05	4.24-4.49	4.3-29.9	Protons on sulfonated carbons
06	4.87	7.2	Protons on β-alkoxy carbons in β-0-4 guaiacylpropyl
07	6.94-7.08	5.1-9.4	Aromatic protons
08	8.46	5.7	Formyl protons

we consider only the methoxyl group, it can be observed that the proton peaks for this group give a total of six different signals for CH_3O between 3.6644 and 3.7152 ppm with signal intensities between 9.9 and 11.3. Many previous studies[18-20] reported only one chemical shift for the CH_3O group in different lignins; these observations are attributed to the lower resolution spectrometers then used. The assignments in this PMR spectrum are based on either general[16,21] or specific[17,18,22] references.

IR and UV Spectra

Our results in infrared and ultraviolet are not reported in this paper because they don't bring significant new informative results in comparison to the most recent data in IR and UV[23] of lignosulfonates.

Elemental Analysis

One of the most striking figures of this analysis of LS-85 is the low content in carbon (21.74%) and the high proportion of sulfur (15.66%) and sodium (18.48%).

A previous review[24] reported 53% and 6.5% as contents of carbon and sulfur respectively for a lignosulfonate. Our fractionated LS contains a noticeable amount (ca. 20%) of $NaHSO_3$. The contents of oxygen and methoxyl groups were respectively 39.73% and 4.90%. The amount of ash was found to be 9.87% relative to the dry sample. These values fall within the limits of those published earlier[25]. It should be added that our high sulfur content is in agreement with the known[26] fact that it is necessary to maximize the sulfonation and minimize yield losses in order to produce strong CTMP and CMP in high yield.

FABMS

Fast-atom bombardment mass spectrometry (FABMS) has been used to characterize a large number of complex and labile molecules. An optimization[27] of FABMS and a recent review[28] on the subject are noteworthy.

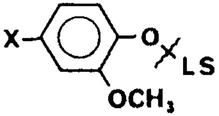
FABMS applied to our lignosulfonate LS-85 leads to the observation of a large number of signals which could be attributed to some substituted guaiacyl units. These assignments are listed in Table 4. Only those signals depicted in both glycerol and thioglycerol supports are reported in Table 4. Some FABMS results (e.g. entries 01, 02, 03, 04 and 08) illustrate the bisulfite addition compounds on a carbonyl -ketone or aldehyde- carbon.

Concluding Remarks

The elemental analysis allows us to propose, as shown in Fig. 2a, a sulfonated guaiacylpropyl unit for LS-85. Our results in potentiometric titration[10] indicating the presence of ca. 20% of free $NaHSO_3$ would support this model for the monomeric sulfonated guaiacylpropyl unit. The model and 2 x H_2O will give a composition $C_{10}H_{16}O_{14}S_3Na_4$ which is close to the elemental analysis: $C_{10}H_{15.6}O_{13.7}S_{2.7}Na_{4.4}$. However, the spectroscopic and GPC data show us that LS-85 is far more complex. From our experimental results, we may conclude that LS-85 is composed of oligomers containing at least four and probably less than ten monomers as it can be visualized from the FAB results in Table 4 and the molecular weight determinations. We propose only one typical structure for LS-85 which features the most important contributing unit: the sulfonated β-O-4 guaiacylpropyl unit. A model of this type (Fig. 2b) might conciliate our results in GPC, spectroscopy and elemental analysis in as much as one does consider the contribution of other more sulfonated units as well as the presence of an excess of $NaHSO_3$. Many other structures could have been considered based on recent models suggested for lignins[29-32] and lignosulfonates[33,34] and including C-C bonds as well as models with two and three interunit bonds.

TABLE 4

FABMS Data of Lignosulfonate LS-85. Fragmentation in Guaiacyl Structure.

EN	m/z	Intensity (%)	X (Possible Fragments) 
01	827	1	See Fig. 2b
02	685	2	See Fig. 2b
03	443	9	See Fig. 2b
04	401	7	$-CH(SO_3Na)-CH(OH)-CH(OH)SO_3Na$ $-CH(SO_3Na)-C(OH)(SO_3Na)-CH_2OH$
05	385	9	$-CH(SO_3Na)-CH(OH)-CH_2SO_3Na$ $-CH(SO_3Na)-C(OH)(SO_3Na)-CH_3$
06	383	5	$-CH(SO_3Na)-CO-CH_2SO_3Na$

			$-C(SO_3Na)=CH-CH(OH)SO_3Na$
07	371	13	$-CH(SO_3Na)-CH(OH)-SO_3Na$
08	317	12	See Fig. 2b
09	299	16	$-CH(SO_3Na)-CH(OH)-CH_2OH$
10	297	34	$-CH(SO_3Na)-CH(OH)-CHO$
			$-CH(SO_3Na)-CO-CH_2OH$
11	295	23	$-C(SO_3Na)=CH-CO_2H$
12	281	26	$-CH(SO_3Na)-CO-CH_3$
			$-CH=CH-CH(OH)SO_3Na$
13	279	100	$-C(SO_3Na)=CH-CHO$
14	267	9	$-CH(SO_3Na)-CH_2-CH_3$
			$-CH(SO_3Na)-CHO$
15	167	9	$-CO_2H$
16	165	50	See Fig. 2b
17	151	15	$-CHO$

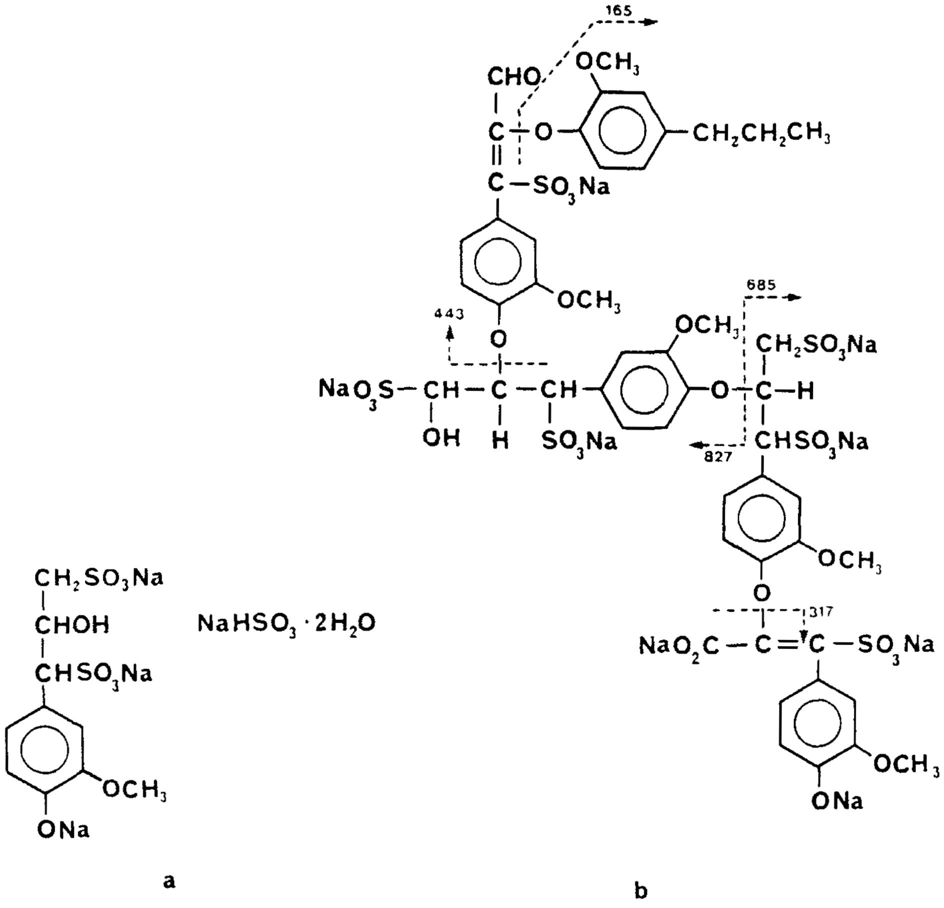


FIGURE 2. Models proposed for lignosulfonate LS-85.

As a conclusion, we consider that the major significant finding of this research is the application of FABMS in the determination of the general features of a lignosulfonate. Another finding is the inhibiting effect of $NaHSO_3$ in the determination of silylated sugars. This study also illustrates the fact that using high resolution instrumentation could reduce oversimplification in data interpretation.

EXPERIMENTAL

Lignosulfonate Samples

The lignosulfonates used in this study were obtained through reduced pressure evaporation of the waste waters of an industrial vapor-phase chemimechanical pulping (CMP) of softwoods composed of equal amounts of black spruce and balsam fir at pH 6; 165°C cooking temperature during 90 minutes. The initial cooking liquor contained 6% total SO_2.

Fractionation of Spent Sulfite Liquors (SSL)

Industrial spent sulfite liquors were filtered and then evaporated under vacuum at 50°C, yielding about 6% by weight of solid materials.

Various methods are available[35] for fractionating lignin and lignin derivatives. This work deals with the fractional precipitation method using the non-solvent 1,4-dioxane. A concentrated aqueous solution of SSL (about 15% by weight) was prepared and set at 20°C. Then dioxane previously purified was progressively added to a well-stirred aqueous solution of SSL. The precipitate begins to appear at about 35% by volume of dioxane. The first fraction (LS-40) was recovered at 40% by volume of the non-solvent. Centrifuging at 2000 rpm was attempted for 20 minutes; unfortunately, the sedimentation of the precipitated solid was not satisfactory, probably because of the small particle size of the precipitate in addition to electrical charges associated with the lignosulfonate material. Therefore, the fraction of interest was placed in a long tube of small diameter and free sedimentation over many hours was prefered to centrifugation. After decantation, the precipitate was washed two times with a dioxane-water mixture of the same composition as the mother solution and the washings were combined with the latter.

The fractionation experiment was continued, allowing the recuperation of four other fractions corresponding respectively to 50, 60, 70 and 85% in volume of dioxane. All the fractions were oven-dried at 75°C.

Gel Permeation Chromatography

Following the fractionation procedure of LS, GPC analysis was one of the most useful means for characterizing the obtained fractions of LS.

GPC was performed using the Michel-Miller (Ace Glass) glass columns (50 x 1.7 cm) and three different Sephadex (Pharmacia) gels: LH-60, G-25 and G-10. An aqueous 0.4N NaCl solution previously degassed was used as eluent, the presence of NaCl was to prevent unwanted effects due to the strong electrolytic behaviour of our lignosulfonates. The GPC columns were monitored by a variable wavelength detector (Varian UV-50) set at 280 nm. The concentration of injected LS aqueous solutions was fixed at 1% by weight, with an injected volume of 100 μl. The flow rate of eluent was kept at 0.50 ml/min. Blue Dextran (Pharmacia) and acetone were used to determine the superior and inferior limits of molecular exclusion for the GPC columns.

Standard sulfonated polystyrene samples (Dupont Instr.) of molecular weights 18,000, 8,000, 4,000 and 1,800 daltons were used for the determination of the calibration curve for the GPC column using the gel LH-60. This curve allowed us to estimate the average molecular weights of the LS samples.

Free Sugar Analysis

The capillary gas chromatography analysis method[7] described earlier was adapted to the crude LS, LS-40 and LS-85 samples as follows:

Silylation of Samples

Small portions of LS (about 50 mg) were placed in 5 ml glass vials, then oven-dried to constant weight. Silylation-grade dimethyl sulfoxide (DMSO) (B.D.H.) (2.0 ml) was added to dissolve the sample; since the LS samples are strongly electrolytic, their solubilization was only partial. However, this fact would not disturb the silylation reaction of the free sugars which are completely soluble in DMSO. Tri-sil concentrate (Pierce Chemical) (0.5 ml) was added to the vials. After heating at 50°C and shaking for 2 hours or more, the vials were kept in the refrigerator for a few hours in order to allow the mixtures to settle into two layers; this manipulation was necessary because the insoluble part of LS sample that has a tendency to floating into the tri-sil layer. As soon as the vial was taken out of the refrigerator, the GC sample was already drawn from the upper layer (the tri-sil one) and was injected into the chromatograph.

Gas Chromatography

A Hewlett-Packard 5750 chromatograph with a flame ionization detector was used; the column was a J & W 15 m x 0.25 mm i.d. fused silica coated with SE-30; helium as carrier gas; split-mode injection; injected volume 0.2 µl; ration 1:60. Temperatures: injector, 230°C; detector, 250°C. Heating schedule of column: 152°C to 160°C at 2°C per min, then 160°C to 220°C at 4°C per min.

The calibration was conducted with various mixtures of the five monosaccharides at various concentrations. The response factor of each pure sugar was obtained using a Hewlett-Packard 3390A integrator.

For each silylation mixture, several injections were carried out in order to insure that the retention times and the response factors were reproducible.

NMR Spectra

NMR spectra were recorded at 25°C on a Bruker WH-400 spectrometer operating at 100.62 MHz for ^{13}C and 400.13 MHz for ^{1}H. The solvent was D_2O and the concentration 15% (m/v). TMS was used as internal reference for ^1H and 1,4-dioxane as external reference for ^{13}C determinations. In the CMR spectrum, 0 ppm is given to the highest field signal of LS-85. In order to adjust to the reference signal, a value of 2.25 ppm was added to all carbon chemical shifts. Signal multiplicity was determined by using the DEPT method[36,37]. NMR spectra were taken at the High-Field NMR Regional Laboratory, Department of Chemistry, University of Montreal.

Elemental Analysis

Lignosulfonates samples were analysed for C, H, O, S, Na, CH_3O and ash content by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Availability of Spectra

The IR and UV spectra of LS-85 with assignments together with the ^1H and ^{13}C spectra are available upon request.

FABMS

The FABMS spectra were recorded on a ZAB-2f instrument (VG Analytical, England) at Carleton University, Ottawa and at the University of Montreal on a Kratos MS-50 TA-TC (Kratos, England). Two spectra were determined using respectively glycerol and thioglycerol as matrices. The best spectra were obtained in the positive mode as reported.

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