[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY, AND THE WOOD CHEMISTRY DIVISION, PULP AND PAPER RESEARCH INSTITUTE OF CANADA]

The Oxidation of Spruce Periodate Lignosulfonic Acids with Aqueous Chlorine Dioxide[1,2]

BY D. MORISON SMITH AND C. B. PURVES

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It was hoped that this selective oxidant would degrade the phenolic portions of the lignosulfonic acids preferentially, and that the positions of the sulfonic acid groups could be determined by identifying aliphatic sulfonic acids of low molecular weight among the products. To secure lignosulfonic acids condensed internally to the minimum degree, a search was made for the minimum conditions of acidity, alkalinity and temperature necessary to prepare them conveniently. These conditions involved heating periodate lignin under reflux in 16% aqueous sodium bisulfite (*p*H ~5.2) at 100° for 20 hr., and autohydrolysis of the insoluble, stage I lignosulfonic acids so formed (S ~2.7%) in boiling water (*p*H 2.5) for 15 hr. This autohydrolysate, which contained Hägglund's soluble stage II lignosulfonic acid and was light yellow-brown in color, was kept saturated with chlorine dioxide for two weeks. Aliphatic sulfonic acids were not formed; oxylignosulfonic acids and oxylignins amounted to 70% by weight of the starting material, and up to 54% of the sulfonic acid groups were recovered as free sulfuric acid. The current view that these groups were of at least two types thus received support, and the molecular size of the major products suggested that a low rate of diffusion might sometimes be a limiting factor in the bleaching of wood pulps.

Over ten years ago,[3] it was shown that the oxidation of the polysaccharides in a wood meal with aqueous periodic acid near *p*H 4 and 20°, alternated with the extraction of the oxidized carbohydrates with boiling water near *p*H 6, eventually left most of the wood lignin as a light brown, insoluble powder free of carbohydrates. Although somewhat oxidized,[4] this "periodate" lignin retained in high degree the ability to dissolve normally when heated near 135° and *p*H 2 in an aqueous calcium bisulfite–sulfur dioxide solution of the type used in the pulping of woods. The availability of this lignin thus made it possible to study the details of the sulfite process in a system uncomplicated by the salts and carbohydrate debris present in a technical waste sulfite liquor. It was later realized[5] that the temperature and acidity of a technical cook promoted an internal chemical condensation that rapidly destroyed the ability of periodate lignin to dissolve in bisulfite. When milder cooking conditions were used,[6] it was possible to confirm Hägglund's view[7-9] that wood lignin on sulfonation first yielded an insoluble (stage I) lignosulfonic acid, which in sufficiently acidic conditions hydrolyzed to a soluble, stage II, form. The initial object of the present research was to find the minimum conditions of time, temperature and acidity necessary to prepare the lignosulfonic acids I and II in a satisfactory way (Fig. 1). The latter preparation would presumably have undergone a minimum of chemical condensation, and be a particularly suitable sample for a preliminary study of oxidative degradation by aqueous chlorine dioxide. This oxidant was expected[10,11] to degrade phenolic units preferentially, but to leave the saturated aliphatic portion of the lignosulfonic acid molecule intact.

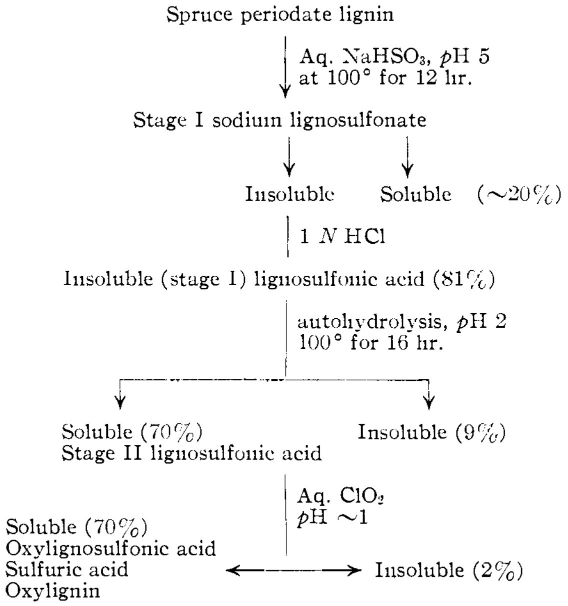

Fig. 1.—Preparation of soluble lignosulfonic acid and its oxidation with chlorine dioxide. Percentage yields based on original lignin and not corrected for any change in molecular weight.

The previous work[6] described a series of small-scale experiments in which 2% suspensions of periodate lignin were heated for various temperatures and times in sealed tubes containing 9% aqueous sodium bisulfite. This concentration simulated industrial conditions and provided a system buffered near *p*H 5.2, or in the range where the autocondensation of the lignin was probably at a minimum. Fourteen more experiments were made by a similar technique on the present occasion. In brief, it appeared that if a stage I sodium lignosulfonate were to give a high yield of a soluble stage II acid, the conditions of the sulfonation also caused the solution of 15–20% of the periodate lignin. Thus, about 10% dissolved almost immediately in cold, aqueous sodium

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(2) Published as a "Condensate" in *Ind. Eng. Chem.*, **49**, 1394 (1957).

(3) P. F. Ritchie and C. B. Purves, *Pulp Pap. Mag. Can.*, **48**, No. 12, 74 (1947).

(4) E. Adler and S. Hernestam, *Acta Chem. Scand.*, **9**, 319 (1955).

(5) I. M. Cabott and C. B. Purves, *Pulp Pap. Mag. Can.*, **57**, No. 4, 151 (1956).

(6) W. J. Brickman and I. M. Cabott, *ibid.*, **60**, No. 2, T 56 (1959).

(7) E. Hägglund, "The Chemistry of Wood," Academic Press, Inc., New York, N. Y., 1951, pp. 215 *et seq.*

(8) E. Adler and B. O. Lindgren, *Svensk. Papperstidn.*, **55**, 563 (1952).

(9) B. Leopold, *Pulp Pap. Mag. Can.*, **55**, No. 3, 184 (1954).

(10) E. Schmidt and K. Braunsdorf, *Ber.*, **55**, 1529 (1922).

(11) P. B. Sarkar, *J. Indian Chem. Soc.*, **12**, 470 (1935).

bisulfite; when heated near 100°, the loss by solution increased rather regularly with time to about 20% after 30 hours. The soluble stage I sodium sulfonate could be freed from salts by dialysis and precipitated in high yield as the free acid. Sulfonation was inadequate at *p*H 5.2 and room temperature for three months[12]; at 77° over a week was taken to achieve the requisite level of sulfonation, but only two days at 91°. The subsequent hydrolysis to the stage II lignosulfonic acid at *p*H 2.5 was within 2% of completion within two hours at 135°, or 24 hours at 100°, but was incomplete after 210 hours at 77°. The rate of hydrolysis at *p*H 2.5 seemed to be more dependent on temperature than was the sulfonation at *p*H 5.2.

Since the results suggested that a temperature near 100° would be suitable both for the sulfonation and the hydrolysis, it seemed probable that both steps could be carried out in reasonable times at atmospheric pressure and without the use of sealed tubes. The temperature of a steam-bath was preferred to that of the boiling point in order to minimize the loss of sulfur dioxide from the sodium bisulfite, and compensation was made for the loss which did occur by increasing the concentration of the bisulfite from 9 to 16%. Trial showed that the latter solution retained *p*H 5.2 for prolonged periods when heated under reflux on a steam-bath. Mechanical stirring kept the lignin uniformly dispersed during the sulfonation and the subsequent hydrolysis, and the progress of both could be reliably followed by the withdrawal and analysis of aliquots. The other change made concerned the periodate lignin, which was prepared by a method not requiring the use of an elevated temperature.

In the first series of experiments under the new conditions, the time of sulfonation was varied, and the resulting stage I lignosulfonic acids were autohydrolyzed in water at *p*H 2.5 for a uniform time of 24 hours, a period sufficient to ensure almost complete solution in favorable cases. Figure 2 (solid lines) shows that the sulfonation had to proceed for 16–24 hours if 75% or more of the product was to dissolve in the subsequent autohydrolysis. In the earlier work,[6] sulfur dioxide was produced during the autohydrolysis of lignosulfonic acids prepared by sulfonation at 120° or more, and these acids had to acquire a sulfur content of about 3.5% before autohydrolysis proceeded nearly to completion. The new periodate lignin, sulfonated with the milder conditions just described, became almost completely hydrolyzable when it acquired slightly less than 3% of sulfur, and liberated no detectable amount of sulfur dioxide, even when the hydrolysis was carried out in a sealed tube. The lack of sulfur dioxide and other interfering substances made it possible to follow the production of the stage II lignosulfonic acid by noting the increase in the optical absorbance of the autohydrolysate at wave length 280 mμ, where unoxidized lignin derivatives show a maximum absorption. Figure 2 (broken lines) reproduces the corresponding plots on an arbitrary absorbance scale, and the shape of these plots conformed well with that of the solid lines representing the percentage of lignosulfonic acid dissolved. In both experiments the plots suggested that solution was nearly complete after 20 hours of sulfonation, which was the time adopted in later work.

Insoluble, stage I sodium lignosulfonate recovered after 50 hours of sulfonation at 100° was exchanged to the free acid and used to determine the optimum time for the autohydrolysis. The plots of the yields of stage II lignosulfonic acid and the absorbance of the solutions at wave length 280 mμ once more were similar in shape and could be made to coincide by adjusting the arbitrary absorbance scale (Figure 3). The very close concordance between the yield and absorbance plot in this case was fortuitous, because the absorbance of a clear solution of lignosulfonic acid increased by 10% when heated for 24 hours at 100°. Compounds of greater absorbance were therefore slowly formed from material already in solution.[13] Over 90% of the lignosulfonic acid had dissolved to give a light straw-colored liquor after 12–15 hours of autohydrolysis, and this yield and time were accepted as convenient. As a matter of interest, spruce wood-meal was cooked in 16% sodium bisulfite at *p*H 5.2 and then hydrolyzed at *p*H 2.4 in the 2-stage process just described for periodate lignin. Three-quarters of the lignin and one-third of the hemicellulose were removed from the wood, and the yield of pulp was 56%.

The oxidation of the lignosulfonic acid autohydrolysate with a large excess of unbuffered chlorine dioxide was not a swift process, and appeared to be still proceeding at a very slow rate after 15 days at room temperature, when the experiments were terminated. Even after this drastic oxidation, 15% of the product failed to pass through a cellophane membrane when dialyzed against running tap water for 24 hours, and therefore retained a fairly high molecular weight, just as periodate lignin did in similar circumstances.[11] Between 1.5 and 3% of the lignosulfonic acid separated from solution during the oxidation, and proved to contain only 0.7% of sulfur. This product was qualitatively similar to the β-fraction of chlorine dioxide oxylignin,[11] which was insoluble in water at *p*H 1 but which could be dispersed on the alkaline side of *p*H 4.

The problem of isolating the dialyzable, alkali-labile,[14] oxylignosulfonic acid from the hydrochloric and chloric acids formed as by-products in the oxidation proved to be a difficult one. When calcium or barium hydroxide was added to the oxidation liquor, a precipitate of calcium or barium sulfate immediately separated, but the oxylignosulfonates stayed in solution until the acidity was reduced to *p*H 5; precipitation of the latter became complete only in strongly basic solution. By restricting the precipitation of the barium salt to *p*H 1, it was found that 35% of the original sulfonic acids were present as free sulfuric acid in one oxidized liquor, and 54% in another. When salts of the oxylignosulfonic acid were precipitated by adding alcohol to the solutions at *p*H 5, the completeness of the precipitation decreased in the

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(12) *Cf.* G. A. Richter and L. H. Pancost, *Tappi*, **37**, 263 (1954).

(13) E. Hägglund (and B. Nelson), *Svensk Papperstidn.*, **47**, 226 (1944).

(14) N. Levitin, N. S. Thompson and C. B. Purves, *Pulp Pap. Mag. Can.*, **56**, No. 5, 117 (1955).

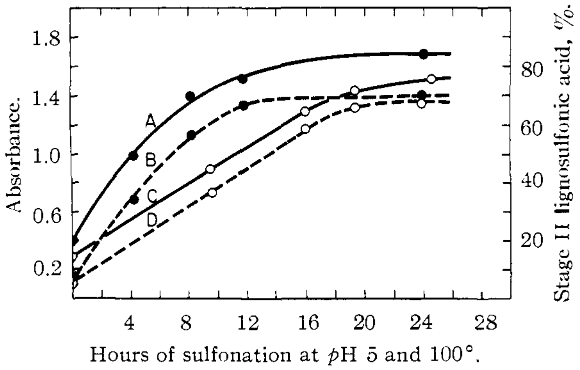

Fig. 2.—Plots of time of sulfonation to stage I lignosulfonic acid against the fraction of this acid subsequently converted to soluble stage II acid by hydrolysis at *p*H 2 and 100° for 24 hr. Plots A and C (right-hand ordinates), percentage by weight of stage I acid rendered soluble in independent experiments; plots B and D (left-hand ordinates), corresponding optical absorbance of hydrolysate in arbitrary units at wave length 280 mμ.

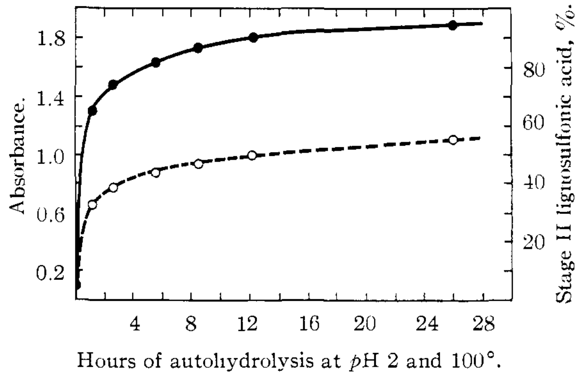

Fig. 3.—Plot of time of autohydrolysis of a stage I lignosulfonic acid against yield of stage II acid. Solid line (right-hand ordinates), percentage dissolved by weight; broken line (left-hand ordinates), corresponding optical absorbance of autohydrolysate in arbitrary units at wave length 280 mμ.

order Ba, Ca, Zn and Cu, the zinc and copper salts being moderately soluble in the alcohol. The use of this procedure yielded precipitates of barium and sodium oxylignosulfonates which were contaminated with large amounts of the corresponding chlorides. Precipitation with calcium ion obviated this difficulty, since calcium chloride was freely soluble in alcohol, but the product was contaminated with 4% of calcium sulfate. This salt could not be removed by solution and reprecipitation of the crude products because drying caused a change in the calcium oxylignosulfonate which greatly decreased its solubility in water. Attempts were made to fractionate an aqueous solution of the crude calcium lignosulfonate by dialysis or by the addition of increments of alcohol, but the sub-fractions contained 4.9 ± 2.4% of sulfur and 15.5 ± 2.9% of calcium, and no clear evidence of fractionation according to sulfur or calcium content was obtained. The sulfur–calcium ratio suggested that one to three carboxyl groups were present per sulfonic acid group, depending on the extent to which the salts were basic rather than neutral in character, and the infrared spectra contained the absorption maxima at 6.3 and 8.3μ, respectively, characteristic of these two groups. Exposure to limewater or to a sodium hydroxide–sodium carbonate buffer at *p*H 11.8 reduced the chlorine content of the calcium oxylignosulfonate from 7% to 1 ± 0.4%, but left the combined sulfur unchanged at 1.8–1.9%. Most of the chlorine in the oxylignosulfonate was therefore of the labile type previously noted in chlorine dioxide oxylignin.[14]

In order to eliminate interference from the insoluble sulfate of calcium, another oxidized lignosulfonic acid solution was neutralized with zinc hydroxide, and the clear, concentrated liquor was diluted with ethanol. More than half of the product was precipitated as a crude zinc salt which probably was derived from a polycarboxylic acid, since it contained practically no sulfonic acid groups. Another portion, containing 0.5% of sulfur, separated when the mother liquor was diluted with acetone. The remainder must have had more than 3% of combined sulfur, but was lost when an attempt to dry the residue caused it to explode. This experiment showed that the oxidation of 54% of the original sulfonic acid groups to sulfuric acid was associated with the complete or partial loss of these groups by most of the substrate, which could be fractionated according to sulfur content. The accumulation of by-product chlorate from the chlorine dioxide oxidation was probably the reason why the residue exploded.

An obvious way to eliminate chloric acid from the oxidation liquors was reduction to hydrochloric acid by means of cold sulfurous acid. Although this method was effective, the oxylignosulfonic acids isolated were unduly rich in sulfur and it became plain that they were sulfonated with great ease in acid solution at room temperature. The reduction of chloric to hydrochloric acid with cold, dilute hydriodic acid was successful. After removing the halogen acid as the silver salts, 35% of the original sulfur was recovered as barium sulfate, 42% as a barium oxylignosulfonate, and 7% as other salts with only 0.2% of sulfur. The presence of about five barium atoms to each sulfur atom in the barium oxylignosulfonate, as well as the infrared absorption, suggested that this salt possessed carboxylic as well as sulfonic acid groups. When allowance was made for the barium content, the oxylignosulfonate accounted for 50% by weight of the original lignosulfonic acid, the corresponding recovery in terms of carbon being less.[14] All of the sulfur appeared to be attached to molecular groupings of considerable size.

A priori, there seemed no reason to assume that oxidation with chlorine dioxide near *p*H 1 and at room temperature would cleave the carbon–sulfur bond in either an aromatic or an aliphatic sulfonic acid, and thereby produce sulfuric acid. Yet such was the fate of up to 54% of the original sulfonic acid groups. These groups could not be identified with carbonyl–bisulfite addition compounds because any units of this type would have been eliminated when the insoluble, stage I sodium lignosulfonate was converted to the free acid.

The present research supported the current view[15] that at least two different types of sulfonic acid unit were present in lignosulfonic acids, but revealed nothing of their nature. Information of this kind must await the discovery of a method of degradation yielding identifiable small molecules to which the sulfonic acid groups are still attached.

Experimental

Materials and Analytical Methods.—Air-dried black spruce woodmeal, of 60–100 mesh fineness, 1250 g., was stirred in a 10-gallon stoneware (not aluminum) crock for 24 hr. with 10 l. of a 4% aqueous solution of sodium paraperiodate buffered to *p*H 4 with glacial acetic acid.[3] After recovery on coarse-grained, sintered glass filters and washing with water, the oxidized wood was stirred for 24 hr. in 25 l. of 0.1 *N* sodium hydroxide at room temperature. Our colleague, W. Sacks, substituted this method of dissolving oxidized carbohydrates for the boiling water previously used, thereby reducing the tedium of the washing operations and avoiding the use of heat. After removing the alkali by decantation and filtration, the residual woodmeal was washed with water until the alkalinity was reduced to *p*H 9. and then with very dilute acetic acid. The slightly acid, moist filter cake was re-oxidized four times by the cycle just described, the final washing to neutrality being with distilled water, and the product was dried in the air. The loss of fines in the decantations reduced the yield to 207 g. (50%).

Anal. Found: Klason lignin, 93.6; ash, 4.3% (cor. for 7% moisture).

When dried in this way, the swollen lignin collapsed to a very hard, brittle resin that was powdered to pass an 80 mesh screen.

A 0.4 *M* aqueous solution of chlorine dioxide was prepared from potassium chlorate, oxalic acid and sulfuric acid,[14] and the exact molarity was determined iodometrically.[16] Solid samples, 10–30 mg., were analyzed for sulfur or chlorine by fusion with sodium peroxide in a Parr micro bomb,[17] followed by precipitation of barium sulfate or silver chloride from the melt.[18] Samples of 10–20 mg. and a micro-muffle furnace were used to determine ash, and methoxyl estimations were also on the semi-micro scale.[19] The precipitation of barium sulfate from a solution made 0.1 *N* with respect to hydrochloric acid was used to determine sulfate or free sulfuric acid. The yields of insoluble material were established with samples isolated by centrifuging, and never by filtration.

Insoluble (Stage I) Sodium Lignosulfonate.—A 3-necked flask of suitable volume was fitted with a mechanical stirrer, a reflux condenser and a thermometer. After 10 g. of the lignin (which passed a 200-mesh screen), and 500 cc. of an aqueous solution containing 80 g. of sodium bisulfite had been added, the assembly was heated on a steam-bath. The bulb of the thermometer was immersed in the suspension and registered 96–98°, while the acidity remained within the limits *p*H 4.8–5.3 during the experiment. When desired, 20-cc. samples of the efficiently stirred, uniformly dispersed slurry were withdrawn, the suspended material was separated on a centrifuge, and was washed five times with distilled water to free it from bisulfite ion. These red-brown samples were dried in tared dishes *in vacuo* over phosphorus pentoxide and weighed to give the yield of stage I sodium lignosulfonate. The portion of the suspension remaining after 50 hr. of heating was saved (see below). Previous workers[6] gave analytical data for similar sodium salts, which were stable substances.

Hydrolyses to Soluble (Stage II) Lignosulfonic Acid.—(a) Each of the dried products from the 20-cc. samples of the sodium lignosulfonate suspension was swollen overnight in 15 cc. of a potassium chloride–hydrochloric acid buffer at *p*H 2. Each sample with its buffer then was sealed in a glass tube which was heated for 24 hr. in a steam-bath. The contents of the individual tubes were centrifuged, and the insoluble deposits of lignosulfonic acid were thoroughly washed with water, dried and weighed to determine, by difference, the percentage that had dissolved (Fig. 2). Each centrifugate with its washing was made up to a volume of 50 cc. of which 1 cc. was diluted to 10 volumes with water. A further dilution of 2 cc. to 10 cc. was with the buffer at *p*H 2. The absorbance of this solution then was measured in arbitrary units at a wave length of 290 mμ on a DU model Beckman spectrophotometer (Fig. 2).

(*b*) The suspension of sodium lignosulfonate remaining after heating for 50 hr. was centrifuged, the precipitate was well washed with water and was immersed in cold *N* hydrochloric acid in order to convert the insoluble sodium salt to the insoluble lignosulfonic acid. An immersion of one hour was sufficient when the sample was not dried. After being thoroughly washed with water, the moist chloride-free product was diluted with distilled water to form a 2.2% suspension. This suspension was stirred and kept at 96–98° in the apparatus used for the sulfonation, and at intervals 5-cc. aliquots were withdrawn, centrifuged, and the undissolved lignosulfonic acid dried and weighed. The percentage that had dissolved (Fig. 3) was determined by difference, and also by observing the absorbance of the centrifugate and washings. For this purpose the liquors from a 5-cc. aliquot of the suspension were diluted to 25 cc. with water, and 1 cc. of the diluate was made up to 10 cc. with the potassium chloride–hydrochloric acid buffer previously mentioned.

Oxidation with Chlorine Dioxide (Fig. 1).—The periodate lignin, 16.8 g. (OCH_3, 12.5%; ash, 7.0, and moisture, 4.0%) was sulfonated for 12 hr. at 97° in 16% aqueous sodium bisulfite, was washed, de-ashed, and washed with water again. Only an aliquot of the suspension of the resulting free lignosulfonic acid was dried to determine the yield and composition, since the free solid acid rapidly underwent autocondensation; yield 12.4 g. or 81%.

Anal. Found: S, 2.9, 3.2; OCH_3, 11.7, 12.5; cor. for a siliceous ash, 2.0, 1.8%.

The remainder of the product was autohydrolyzed near *p*H 2.5 and 97° for 16 hr., after which time 1.4 g. of insoluble material was removed. Only an aliquot of the liquor was evaporated to dryness to determine the yield, since the free (stage II) acid lost its solubility when dried; yield 10.7 g., cor. for the aliquots removed, or 86%; over-all yield from original lignin, 70%.

Anal. Found: S, 3.2, 3.4; OCH_3, 11.2, 10.8.

The bulk of the clear, pale yellow-brown liquor then was concentrated *in vacuo* to approximately 4% solids and was mixed at room temperature with an equal volume of 0.4 *M* aqueous chlorine dioxide. The consumption of the chlorine dioxide was followed iodometrically,[16] and was corrected for the decomposition of the chlorine dioxide in a blank containing no lignosulfonic acid. For reasons discussed elsewhere,[11] this correction was not accurate. After three or four days, when most of the oxidant had been reduced, the solution was saturated with gaseous chlorine dioxide near 0° and was again kept at room temperature. Excessive frothing had made it necessary to carry out the original oxidation with a solution of the gas, but this difficulty had now diminished. Although the saturation was twice repeated, the apparent rate of consumption of chlorine dioxide was somewhat greater than the decomposition in the blank even after 15 days, when the experiment was terminated. The liquor then was centrifuged to remove a small, white precipitate, 0.3 g. (2%), which had separated during the oxidation but which could be peptized in water.

Anal. Found: S, 0.7, 0.8.

An aliquot of the clear centrifugate was evaporated to determine the yield and total sulfur content of the oxylignosulfonic acid as 10.5 g. and 2.6%, respectively, or 273 mg. of sulfur. The small precipitate just described contained 2 mg. and the sulfur in the original autohydrolyzed lignosulfonic acid was 10.7 g. × 3%, or 321 mg. Thus the recovery of sulfur in the oxidation was 86%.

In some experiments, aliquots of the liquor were dialyzed for 16 hr. through cellophane against running tap water, the

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(15) A. Rezanowich, G. A. Allen and S. G. Mason, *Pulp Pap. Mag. Can.*, **58**, No. 11, 153 (1957), quoted the relevant literature. They used radioactive S^{35} to show that some, but not all, of the sulfonic acid units readily exchanged with bisulfite ions in the cooking liquor.

(16) R. M. Husband, C. D. Logan and C. B. Purves, *Can. J. Chem.*, **33**, 68 (1955).

(17) Parr Manual No. 121, "Peroxide Bomb. Apparatus and Methods," Parr Instrument Co., Moline, Ill., 1950.

(18) J. B. Niederl, H. Baum, J. S. McCoy and J. A. Kuck, *Ind. Eng. Chem., Anal. Ed.*, **12**, 428 (1940).

(19) Q. P. Peniston and H. Hibbert, *Paper Trade J.*, **109**, 46 (Oct. 26, 1939).

amount of undialyzed material being determined by evaporating and drying the contents of the dialysis sac. Originally 80% of the stage II lignosulfonic acid failed to dialyze under these conditions; after the first oxidation this value was 40%, and only 15% after the fourth.

A Crude Calcium Oxylignosulfonate.—Nitrogen gas was bubbled through 30 cc. of a clear, centrifuged aqueous solution of the oxidized lignosulfonic acid until any chlorine dioxide had been expelled. The solution was shaken with small increments of calcium hydroxide until *p*H 4.5 was attained, and at this acidity the precipitated calcium sulfate was removed. After the clear mother liquor had been concentrated, the addition of 10 volumes of ethanol caused the precipitation of the crude product.

Anal. Found: S, 3.1, 3.2; OCH_3, 3.9, 3.8; Cl, 6.6, 7.0; Ca, 13.3. (When corrected for 4% of calcium sulfate, the analysis became: S, 2.1; OCH_3, 3.7; Cl, 6.7; Ca, 12.1 %.)

One gram of the crude calcium oxylignosulfonate was kept dispersed for one week in 150 cc. of water containing 7.5 g. of sodium hydroxide and 1.5 g. of sodium carbonate, and the suspension was then adjusted from *p*H 11.8 to *p*H 7 with glacial acetic acid. The residue obtained by evaporating the suspension was extracted with ethanol, was dissolved in 15 cc. of water and was reprecipitated with ethanol. After a second reprecipitation, the powder was dried by treatment with alcohol, then benzene, and finally *in vacuo* over phosphorus pentoxide; yield 0.82 g. or 82%.

Anal. Found: S, 2.7; Cl, 0.6; Ca, 22.5, 22.4. Of the sulfur, 0.8% was present as free sulfate ion and 1.9% was combined; the apparent calcium content included a little sodium.

The replacement of the sodium hydroxide–sodium carbonate buffer with saturated calcium hydroxide solution yielded a product with 1.8% of combined sulfur and only 1.4% of chlorine.

Fractionation of a Zinc Oxylignosulfonate.—Zinc oxide, 5 g., was stirred with 200 cc. of a solution containing 3.36 g. of oxylignosulfonic acid, and free of chlorine dioxide, until the *p*H was 4.9. The oxylignosulfonic acid had 1.2% of combined sulfur and 1.4% was present as sulfate ion; that is, 40.3 and 47.0 mg., respectively. Next day the excess of zinc oxide, 0.32 g., was removed on the centrifuge; the clear liquor was concentrated to about 50 cc. and was poured into 200 cc. of ethanol. The precipitate of zinc "oxylignosulfonate" was washed twice with 200 cc. of acetone before being dried *in vacuo*; yield 2.4 g. or 70% by weight.

Anal. Found: S, 0.9, 0.9; Cl, 4.7, 4.5; Zn, 21.8, 20.2.

The free chloride and sulfate content corresponded to the presence of 0.13 g. and 0.07 g. of the respective zinc salts. Correction for these impurities gave the composition of the zinc oxylignosulfonate as S, 0.0; Cl, 3.6; and Zn, 19.3.

The ethanolic mother liquors and the acetone washings, when mixed, deposited a second fraction which was recovered and dried; yield 0.71 g. or 22%.

Anal. Found: S, 0.5; Cl, 6.2; Zn, 23 (cor. for 1% of zinc sulfate and 10% of zinc chloride).

The analyses of aliquots showed that the mother liquors contained 45 mg. of sulfur as sulfate ion, or 96% of the original sulfate. The residue from these liquors was not analyzed because it was extremely deliquescent, and also exploded when attempts were made to dry it by heat. Since only 3.6 mg. of combined sulfur had been recovered in the second fraction of zinc oxylignosulfonate, the residue contained (40.3 − 3.6) mg., or about 37 mg. The organic material in the residue weighed about 1 g., and therefore contained about 3.7% of combined sulfur.

Isolation of a Barium Oxylignosulfonate.—A solution, 30 cc., containing 0.62 g. of oxylignosulfonic acid (S, 2.9% or 18 mg.) but no chlorine dioxide, was mixed with 10 cc. of cold, redistilled 47% hydriodic acid to reduce the chloric acid present. After extracting the liberated iodine with ether, the aqueous solution was shaken with moist silver carbonate, freshly prepared from 11 g. of the nitrate and 5.5 g. of potassium carbonate. The insoluble silver salts were removed on the centrifuge, and were extracted with dilute hydrochloric acid. Since the extract gave no precipitate with aqueous barium chloride, the salts included no sulfate. The supernatant solution, now containing silver oxylignosulfonate and silver sulfate, was mixed with an exact equivalent of dilute hydrochloric acid, and the precipitated silver chloride removed.

Concentrated aqueous barium hydroxide was added to the resulting solution of free oxylignosulfonic and sulfuric acids until the acidity was reduced to *p*H 4.8. The precipitated barium sulfate was removed and after ignition weighed 46.5 mg., corresponding to 6.4 mg. of sulfur or to 35% of the original amount. After concentrating the mother liquor to 5 cc., the barium lignosulfonate was precipitated by the addition of 50 ml. of ethanol, and was dried *in vacuo*; yield 0.45 g.

Anal. Found: S, 1.7; Ba, 36.6.

The sulfur content, 7.6 mg., was 42% of the original amount. Evaporation of the alcoholic filtrate to dryness left 0.67 g. of salts.

Anal. Found: Ba, 43.4; S, 0.2. The sulfur content corresponded to 1.3 mg. (7%).

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MONTREAL, CANADA

[CONTRIBUTION FROM THE DIVISION OF APPLIED BIOLOGY, NATIONAL RESEARCH COUNCIL OF CANADA]

Uronic Acid Components of Jute Fiber Hemicellulose[1,2]

BY H. C. SRIVASTAVA[3] AND G. A. ADAMS

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Jute fiber hemicellulose produces upon partial hydrolysis a number of neutral and acidic sugars and oligosaccharides. The acidic components isolated by ion exchange and cellulose-column chromatography have been identified and shown to be 4-*O*-methyl-D-glucuronic acid, 2-*O*-(4-*O*-methyl-α-D-glucuronopyranosyl)-D-xylose and, tentatively, *O*-α-4-*O*-methyl-D-glucuronopyranosyl-(1 → 2)-*O*-β-D-xylopyranosyl-(1 → 4)-D-xylose.

The jute plant (*Corchorus olitorius* and *C. capsularis*) gives, after a proper treatment of retting, long glossy fibers which are used for making burlap and sacking materials. Associated with cellulose, the jute fiber has a considerable quantity of hemicellulose (about 30%).[4] The structure of this hemicellulose has been studied by Sarkar, *et al.*[5–7] On the basis of periodate oxidation data

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(3) Postdoctorate Fellow of the National Research Council.

(4) P. B. Sarkar, A. K. Mazumdar and K. B. Pal, *J. Textile Inst.*, **39**, T44 (1948).

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(7) P. C. Das Gupta and P. B. Sarkar, *ibid.*, **24**, 1071 (1954).