2,3,4,6-tetra-*O*-methyl-D-glucose, m.p. and mixed m.p. 101–102°; lit.[25] m.p. 102°.

2. **2,3,6-Tri-*O*-methyl-D-glucose.**—Component 2 (Table IV, 2.29 g.) crystallized spontaneously and after recrystallization from ethyl ether, gave 2,3,6-tri-*O*-methyl-D-glucose, m.p. and mixed m.p. 112–115°, $[\alpha]^{24}D$ +62° equilibrium value in water (*c* 1); lit.[26] m.p. 121–123°, $[\alpha]D$ +70.5° equilibrium value in water. Treatment of the trimethyl sugar with *p*-nitrobenzoyl chloride in the usual way[27] gave the 1,4-di-*p*-nitrobenzoate of 2,3,6-tri-*O*-methyl-D-glucose, m.p. and mixed m.p. 190–191°, $[\alpha]^{24}D$ −32° in chloroform (*c* 2); lit.[27] m.p. 189–190°, $[\alpha]D$ −33° in chloroform.

3. **2,3-Di-*O*-methyl-D-glucose.**—Component 3 (Table IV, 0.119 g.) crystallized spontaneously from ethyl ether and methanol, giving 2,3-di-*O*-methyl-D-glucose, m.p. and mixed m.p. 85–86°, $[\alpha]^{24}D$ +49° in methanol (*c* 4); lit.[28] m.p. 85–87°, $[\alpha]D$ +48.3° in acetone. Treatment with aniline gave the characteristic N-phenyl-D-glucopyranosylamine 2,3-dimethyl ether, m.p. and mixed m.p. 134°, $[\alpha]^{22}D$ −83° in chloroform (*c* 4) (after recrystallization from ethyl acetate); lit.[29] m.p. 134°.

4. **2,6-Di-*O*-methyl-D-glucose.**—Component 4 (Table IV, 0.240 g.), a sirup, showed $[\alpha]^{24}D$ +63° equilibrium value in water (*c* 5); lit.[30,31] $[\alpha]D$ +63.3° in water. Chromatographic analysis using solvents A and B indicated that it was 2,6-di-*O*-methyl-D-glucose. Treatment with *p*-phenylazobenzoyl chloride in pyridine gave the 1,3,4-triazobenzoate of 2,6-di-*O*-methyl-D-glucose, m.p. and mixed m.p. 202–206° (after recrystallization from ethyl acetate–petroleum ether), $[\alpha]^{23}D$ −260° in chloroform (*c* 0.1); lit.[31] m.p. 205–207°, $[\alpha]_{6252}$ −275° in chloroform.

5. **2-*O*-Methyl-D-glucose.**—Component 5 (Table IV, 0.029 g.) crystallized spontaneously and afforded 2-*O*-methyl-D-glucose, m.p. and mixed m.p. 157–158°, $[\alpha]^{24}D$ +65° equilibrium value in water (*c* 1) (after recrystallization from ethanol); lit.[32–34] m.p. 157–158°, $[\alpha]$ +66° equilibrium value in water.

6. **3-*O*-Methyl-D-glucose.**—Component 6 (Table IV, 0.01 g.) crystallized spontaneously from ethanol and appeared to be essentially pure 3-*O*-methyl-α-D-glucose, m.p. and mixed m.p. 157–158°, $[\alpha]^{24}D$ +56° equilibrium value in water (*c* 1); lit.[28,35] m.p. 161°, $[\alpha]D$ +55.5° equilibrium value in water.

In addition to the six components identified above, column chromatography of the hydrolysate of the methylated dextrin yielded 10 mg. of material whose R_f value, 0.062, corresponded to D-glucose. However, the substance failed to crystallize, and since its rotation, $[\alpha]^{24}D$ +17° in water (*c* 0.2), showed that only one-third of it could be D-glucose, it was not examined further.

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(25) Sister P. Litecky and F. Smith, unpublished results.
(26) J. C. Irvine and E. L. Hirst, *J. Chem. Soc.*, **121**, 1213 (1922).
(27) P. A. Rebers and F. Smith, THIS JOURNAL, **76**, 6079 (1954).
(28) J. C. Irvine and J. P. Scott, *J. Chem. Soc.*, **103**, 575 (1913).
(29) Elsa Schlüchterer and M. Stacey, *ibid.*, 776 (1945).
(30) D. J. Bell and R. L. M. Synge, *ibid.*, 833 (1938).
(31) K. Freudenberg and G. Hüll, *Ber.*, **74B**, 237 (1941).
(32) P. Brigl and R. Schinle, *ibid.*, **68B**, 2884 (1930).
(33) W. N. Haworth, E. L. Hirst and E. G. Teece, *J. Chem. Soc.*, 2858 (1931).
(34) J. W. H. Oldham and J. K. Rutherford, THIS JOURNAL, **54**, 1086 (1932).
(35) J. C. Irvine and T. P. Hogg, *J. Chem. Soc.*, **105**, 1386 (1914).

ST. PAUL, MINNESOTA

[CONTRIBUTION FROM PULP MILLS RESEARCH AND THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Lignin. VIII. Molecular Weights of Lignin Sulfonates during Delignification by Bisulfite–Sulfurous Acid Solutions

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The average molecular weight has been estimated of the sodium lignin sulfonates dissolved from hemlock, spruce and maple woods into bisulfite–sulfurous acid solutions after several periods of treatment at elevated temperatures. With the gymnosperm woods, it is found that lower molecular weight lignin sulfonates are obtained first, and then as the time of treatment is extended, the average molecular weight of the dissolved lignin sulfonates increases to a maximum, decreases to a minimum and finally begins to rise again. These changes are attributed to the effects of the following three processes which are thought to be proceeding simultaneously but at different rates: hydrolysis of hydrolyzable bonds in the lignin polymer, polycondensation of some lignin molecules with others and diffusion of soluble lignin sulfonates from the wood tissue into solution. With maple wood, the molecular weights of the dissolved lignin sulfonates obtained are about constant and strikingly smaller than those observed for the gymnosperm lignins].

Introduction

In prior reports from this Laboratory, diffusion[2a] and light scattering[2b] methods have been described for the estimation of the average molecular weights of lignin sulfonate preparations. Fractionation of such preparations followed by estimation of the molecular weights of the lignin sulfonates in the resultant fractions has provided information concerning the distribution in lignin sulfonate molecular weights.[2c] Since these distributions were found to be somewhat different for several preparations examined, the present research was undertaken to obtain more knowledge concerning the average molecular weights and the distribution in molecular weights of lignin sulfonates which exist at various stages of delignification of wood by use of bisulfite–sulfurous acid solutions.

(1) Kokusaku Pulp Industry Co., Ltd., Shinjukuku, Tokyo, Japan.
(2) (a) V. F. Felicetta, A. E. Markham, Q. P. Peniston, J. L. McCarthy, THIS JOURNAL, **71**, 2879 (1949); (b) J. Moacanin, V. F. Felicetta, W. Haller and J. L. McCarthy, *ibid.*, **77**, 3470 (1955); (c) V F. Felicetta, A. Ahola and J. L. McCarthy, THIS JOURNAL, **78**, 1899 (1956).

Experimental

A description previously has been given[2b] of the preparation of the Western Hemlock wood meal (*Tsuga heterophylla;* 10 to 30 mesh; ethanol–benzene and hot water extracted; 6.14% H_2O and 5.15% OCH_3) used for the experiments. Delignifications were carried out by sealing into a Pyrex tube 1.00 or 4.50 g. of wood meal with ten times its weight of an aqueous solution which contained 50 g. of SO_2/liter and 9.67 g. of Na_2O/liter for series I, and 90 g. of SO_2/liter and 9.67 g. of Na_2O/liter for series II. Each bomb was placed in a steel tube which was closed, fastened to a "Ferris" wheel in an oil-bath at 135° (±0.1°) and rotated

TABLE I

DELIGNIFICATION OF HEMLOCK WOOD WITH SODIUM BISULFITE–SULFUROUS ACID SOLUTIONS (4% "FREE" SO_2)

Reaction time, hr.	Wood residue: Yield, %	Wood residue: OCH_3, %	Wood residue: Delig.,[a] %	Solutions: pH[b]	Solutions: $\lambda_{min.}$,[d] Å.	Solutions: A_{2800}	Solutions: $A_{2800}/A_{min.}$	Solutions: A_{2800}/A_{3100}	Solutions: D_A, $10^7 \times$ cm.^{2} sec.$^{-1}$	Solutions: Estim. mol. wt.
0.5	86.5	4.75	20.3	..	2580	83	1.67	4.72	25.9	3,000
1.0A	76.7	4.64	30.8	5.76	2600	137	1.50	4.39	23.4	4,200
1.0B	76.6	..	..	..	2600	138	1.53	4.16	..	....
3.0A	56.0	2.28	75.2	5.45	2600	342	1.47	3.75	15.8	11,000
3.0B	53.0	..	..	..	2600	386	1.44	3.68	..	....
6.0A	45.5	..	..	..	2600	477	1.49	3.82	16.9	10,000
6.0B	45.8	0.49	95.7	5.86[c]	2605	475	1.48	3.57	16.8	10,000
9.0	44.2	0.22	98.1	4.22[c]	2605	508	1.49	3.64	18.1	9,000
12.0A	41.9	0.11	99.1	1.98	2620	570	1.35	3.05	21.3	5,500
12.0B	42.1	..	..	..	2620	555	1.36	3.26	..	....
15.0A	40.0	0.08	99.4	1.80[c]	2620	626	1.29	2.54	22.2	5,000
15.0B	41.5	..	..	1.80	2620	625	1.29	2.67	21.3	5,500
20.0	40.1	0.075	99.4	1.70	2625	760	1.18	2.22	20.3	6,500

[a] Delignification percentage = 100 − (% OCH_3)(% yield of wood residue)/(5.15). [b] Recorded pH values are those found for a tenfold diluted and steam-stripped solution. [c] Sulfate in samples 6.0B, 9.0 and 15.0A was 0.0, 0.28 and 1.92 g. of SO_3/liter, respectively. [d] $\lambda_{min.}$ = wave length of minimum ultraviolet absorption near 2600 Å.

TABLE II

DELIGNIFICATION OF HEMLOCK WITH SODIUM BISULFITE–SULFUROUS ACID SOLUTIONS (8% "FREE" SO_2)

Reaction time, hr.	Wood residue: Yield, %	Wood residue: OCH_3, %	Wood residue: Delignif.,[a] %	Solutions: pH[a]	Solutions: $\lambda_{min.}$,[a] Å.	Solutions: A_{2800}	Solutions: $A_{2800}/A_{min.}$	Solutions: A_{2800}/A_{3100}	Solutions: D_A, $10^7 \times$ cm.^{2} sec.$^{-1}$	Solutions: Estim. mol. wt.
0.5A	76.7	..	..	5.91	2585	140	1.51	4.00	21.1	5,700
0.5B	74.7	..	..	..	2590	142	1.55	4.27	22.1	5,000
1	63.5	3.44	57.5	5.64	2600	256	1.48	3.68	17.9	9,200
2	49.6	1.08	90.4	5.92	2600	461	1.46	3.64	17.0	10,000
3A	44.7	0.56	95.1	5.82[b]	2600	471	1.48	3.66	16.0	11,000
3B	44.5	..	..	..	2600	489	1.49	3.62	15.4	12,000
4.5	43.5	..	98.7	5.54	2610	510	1.48	3.59	..	....
6	44.3	0.15	99.5	2.84	2610	520	1.50	3.53	19.1	7,700
9	40.5	0.067	99.6	1.84	2615	594	1.32	2.90	22.5	4,700
10	40.4	..	..	..	2620	650	1.26	2.58	22.5	4,700
12	39.2	..	..	1.53[b]	2625	700	1.18	2.33	22.9	4,500
15A	39.5	0.035	99.7	1.62	2650	837	1.10	2.01	18.2	9,000
15B	36.3	..	..	..	2650	840	1.09	2.01	18.2	9,000
17	34.7	..	..	1.35	2650	866	1.07	1.91	17.7	9,500
18	33.8	..	..	1.39	2650	878	1.05	1.92	18.7	8,200

[a] Same as footnotes *a*, *b* and *d* for Table I. [b] Sulfate in samples 3A and 12 was 0.34 and 1.89 g. SO_3/liter, respectively.

at 25 r.p.m. for the desired time. The bombs were cooled, opened and the contents were filtered. The wood residues were washed with distilled water, dried overnight at 60° and 1 mm. pressure, then weighed and analyzed. The filtrates and washings were combined, diluted with distilled water to about 100 times the original wood weight, then stored at 3° after adding a few drops of toluene to prevent or minimize microörganism action (Tables I and II).

For the experiments with spruce (*Picea sitchensis*) and maple (*Acer saccharum*), small air-dry wood blocks obtained from Professor H. D. Erickson of the College of Forestry of this University were reduced to a fine meal by use of a cross cut saw. Delignifications were conducted using solutions containing 41.2 g. of SO_2/liter and 10.2 g. of Na_2O/liter at 135° (±0.1°) for various periods of time (Table III).

One sample of the hemlock lignin sulfonates was fractionated. Preliminary to this fractionation, toluene was evaporated from an aliquot of the solution containing the lignin sulfonates, and metal cations were then removed using a Dowex 50 resin column. The solution was then extracted five times with ether to remove such non-lignin substances as conidendrin and furfural which absorb ultraviolet radiation, and residual ether and sulfurous acid were removed under vacuum. Usually the solution was neutralized to pH 5, vacuum evaporated to 50 ml., then concentrated to 10 ml. or less in a vacuum desiccator over $CaCl_2$.

For fractionation, a 7-ml. aliquot was weighed exactly and added to a culture tube (1.5″ × 7″) containing 300 mg. % of crystalline NaCl. To secure the first fraction, at 25 ± 0.1°, 133 ml. of dry ethanol was added dropwise with vigorous stirring which was continued for an additional five minutes. The contents were then transferred to a centrifuge bottle and centrifuged for about five minutes after which the clear solution was poured off, vacuum evaporated at 50° with periodic additions of distilled water to complete ethanol removal and then made to 50 ml. with distilled water and designated as fraction A. Precipitate in the culture tube was then dissolved in 10 ml. of 0.5 *N* NaCl and combined with that in the centrifuge bottle, and the fractionation of this solution was then continued in general as already described with appropriate ethanol additions, and the results as well as final alcohol concentrations are given in Table IV.

Analyses for methoxyl were conducted by the Zeisel method. Ultraviolet absorbances were determined from 2500 to 3100 Å. at 50-Å. intervals on aliquots of lignin sulfonate solutions from which sulfur dioxide had been removed and after dilution such that absorbance was not more than about 0.80. Lignin sulfonate concentrations were estimated for the experiments with spruce and maple from measurements of absorption at 2800 Å. Two absorptivity ratios, A_{2800} Å./$A_{min.}$ and A_{2800}Å./A_{3100} Å., were calculated. The acidity of some of the samples weas measured after expelling sulfur dioxide and diluting ten times. Sulfate in certain samples was determined by a conductometric method.[3]

(3) Q. P. Peniston, V. F. Felicetta and J. L. McCarthy, *Anal. Chem.*, **19**, 332 (1947).

TABLE III

ESTIMATED MOLECULAR WEIGHTS OF SPRUCE AND MAPLE LIGNIN SULFONATES DURING DELIGNIFICATION

Delignif. time, hr.	Lignin dissolved,[a] % A[c]	B[c]	Est. $D_A \times 10^7$, cm.²/sec. A	B	Est. NaLS mol. wt.[b] A	B
Spruce (*Picea sitchensis*)						
0.5	19	20	..	28.8	....	2300
1.0	31	27	26.8	23.5	2800	4200
2.0	53	43	20.0	22.4	5900	4800
4.0	80	78	14.2	15.8	14,000	11,000
6.0	91	91	13.9	16.5	14,000	11,000
8.0	100	97	18.3	20.6	8,800	6,200
Maple (*Acer saccharum*)						
0.5	18	15	35.7	39.9	1200	800
1.0	27	26	38.0	34.5	1000	1300
2.0	48	53	38.1	32.3	1000	1600
4.0	73	79	33.1	29.5	1500	2100
6.0	87	87	41.4	34.5	700	1300
8.0	97	98	38.2	31.6	1000	1700

[a] Estimated from the absorbance of the lignin sulfonate solutions for 2800 Å radiation. [b] Diffusion coefficients are D_A averages for solutes absorbing 2800 Å. radiation. Molecular weights have been estimated from D_A using a previously reported correlation.[2b] [c] A and B designate results of duplicate experiments.

Discussion

The degrees to which lignins were removed from hemlock wood by treatment with sodium bisulfite–sulfurous acid solutions have been estimated from determinations of methoxyl in the original wood and in the wood residues (Tables I and II) assuming that the methoxyl content of lignin or lignin sulfonates is approximately constant. As shown in Fig. 1, delignification of hemlock is nearly completed after about 8 hr. treatment at 135° where the solution contains about 4.0% "free" SO_2 or after about 3 hr. with 8.0% "free" SO_2.

The several hemlock lignin sulfonate solutions obtained were diluted appropriately, absorbances for 2800 Å. radiation were measured and the absorbances were calculated back to the uniform basis of the undiluted reaction mixture. These absorbances are plotted in Fig. 2 against the degree of delignification estimated from methoxyl. An apparently linear relationship is obtained up to about 90 or 95% delignification indicating that, within this range, the absorptivities of lignin sulfonates on a methoxyl basis are approximately constant and thus that the degree of delignification can be estimated from measurements of ultraviolet absorbance.

TABLE IV

ESTIMATED DISTRIBUTIONS IN MOLECULAR WEIGHTS OF CERTAIN HEMLOCK LIGNIN SULFONATES (8% "FREE" SO_2)

Sample fraction[a]	0.5B Σw_i,[b] %	0.5B D_A[c]	0.5B Estim. mol. wt.	3.0B Σw_i,[b] %	3.0B D_A[b]	3.0B Estim. mol. wt.	10.0 Σw_i,[b] %	10.0 D_A[c]	10.0 Estim. mol. st.	15.0B Σw_i,[b] %	15.0B D_A[c]	15.0B Estim. mol. wt.
A	31.4	31.9	1,600	15.6	41.3	800	17.1	41.9	730	14.3	39.1	900
B	45.8	27.4	2,600	31.2	25.3	3,300	33.2	29.4	2,100	27.1	31.7	1,700
C	54.3	23.8	4,000	41.4	19.8	7,000	44.7	25.2	3,300	35.8	27.8	2,500
D	69.4	21.4	5,500	61.1	17.3	10,000	68.3	16.8	10,000	51.7	18.7	8,200
E	81.6	15.7	12,000	82.7	10.9	22,000	83.6	13.5	15,000	64.5	16.9	10,000
F	88.0	11.8	19,000	92.3	7.8	40,000	89.0	11.4	20,000	70.9	12.5	17,000
G	91.8	10.6	23,000	98.8	4.4	100.000	93.3	9.5	28,000	82.4	11.4	20,000
H	96.9	10.5	23,000	99.3	..	....	95.8	12.4	17,000	100.6	10.9	22,000
$(\Sigma w_i D_i^{-0.5})^{-2}$	..	21.3[d]	5,600[e]	..	14.9[d]	13,000[e]	..	19.9[d]	7,000[e]	...	17.9[d]	9,300[e]
Unfractd.	..	22.1	5,000	..	15.4	12,000	..	22.5	4,700	...	17.7	9,500

[a] For fractions A, B, C, D, E, F and G final ethanol concentrations were 95, 90, 85, 80, 76, 73 and 70% by volume, respectively. H designates the material insoluble in 70% ethanol. [b] Weight percentages of lignin sulfonates in fractions were estimated from absorbances observed at 2800 Å. [c] Units of D_A are $10^7 \times$ cm.²/sec. [d] Average D_A for unfractionated samples estimated from values found for fractions. [e] Average molecular weight for unfractionated sample estimated from average D_A calculated from values found for fractions.

Diffusion coefficients,[2a] "D_A," of the sodium lignin sulfonates of Tables I and II were measured by a solution-to-gel method at 25° in 0.02 *M* NaCl after the samples had been de-ashed, extracted with ether, neutralized and then evacuated; the samples of Table III were prepared for diffusion by pulling air through the solutions for at least 24 hr.: for Table IV, diffusions were carried out on the final fractionated samples after ethanol removal. Molecular weights were estimated from diffusion coefficients using a previously developed correlation.[2b]

The relationship between the average diffusion coefficient, D_A, and the diffusion coefficient for an individual molecular species, D_i, is

$$\frac{1}{D_A^{0.5}} = \Sigma_{(wi}\left(\frac{1}{D_i^{0.5}}\right)$$

where w_i = weight fraction of i-th species. The approximate relation between D_i and the molecular weight, M_i, is

$$D_i \cong \frac{b}{M_i^{1/a}}$$

where b and a are constants. Thus the particular average molecular weight, M_A, obtained in the present work is, approximately

$$M_A = [\Sigma(w_i)(M_i)^{0.5a}]\ 2/a \cong [\Sigma(w_i)(M_i)^{1.5}]^{0.67}$$

since $a \cong 3$.

On this basis lignin removals from spruce and maple woods were also estimated (Table III) and the rates of delignification found (Fig. 1) are roughly as expected for the concentration of about 3.1% "free" SO_2 which was used in the delignification solution.

The yield of hemlock wood residue decreases and approaches a limiting asymptotic value as delignification proceeds. However, when delignification is almost completed and this limiting value is nearly reached, the percentage of wood residue begins to decline again and continues to decline at a somewhat increased rate (Fig. 1). This increased degradation and solution of the carbohydrate residue is caused by a large increase in the acidity of the delignification solution as reflected in the *p*H values given in Tables I and II. The increase in acidity is in turn caused at least largely by formation of sulfate which is shown by analyses to be present at a much higher concentration after the acidity increase than before. Corresponding with this in-

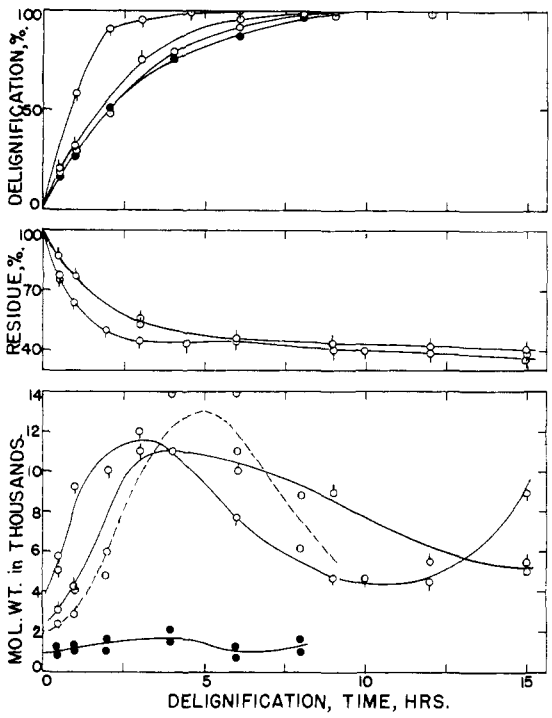

Fig. 1.—Percentage delignification and wood residue and average molecular weights of dissolved lignin sulfonates after various times of delignification with sodium bisulfite–sulfurous acid solutions: O, spruce, 3.1% "free" SO_2; ♁, hemlock, 4.0% "free" SO_2; ♀, hemlock, 8.0% "free" SO_2; ●, maple, 3.1% "free" SO_2.

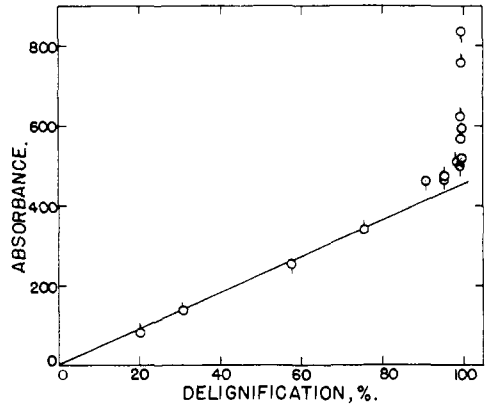

Fig. 2.—Relation between percentage delignification of hemlock and solution absorbance at 2800 Å.: ♁, 4.0% "free" SO_2; ♀, 8.0% "free" SO_2.

creased acidity is a substantial increase in absorbance (Fig. 2) which may arise from lignin hydrolysis or condensation reactions or formation of such sugar derivatives as furfural and hydroxymethylfurfural which absorb ultraviolet radiation.[4]

Examination of the ultraviolet absorption spectra of the several solutions showed that the usual spectra[2] was obtained for the samples up to about 90% delignification. The wave length of the minimum absorption was about 2580 Å. in the first samples obtained and this shifted to longer wave lengths as delignification proceeded. The absorptivity ratios, $A_{2800\ \text{Å.}}/A_{2600\ \text{Å.}}$ and $A_{2800\ \text{Å.}}/A_{3100\ \text{Å.}}$, were largest in the first samples obtained and decreased and became nearly constant as treating time was extended toward completion of delignification, thus indicating an increase in molecular weight in view of prior work.[2c] However, after the solutions underwent the substantial increase in acidity, the values for the ratios again decreased.

The average molecular weights of the dissolved lignin sulfonates in the several solutions were estimated from diffusion coefficients, and the results are given in Tables I–III and are graphed in Fig. 1. With hemlock and spruce woods, it is found that the molecular weights of the lignin sulfonates first obtained are about 2000–4000. As delignification proceeds, the molecular weight increases and reaches a maximum value in the range of about 11,000 when the delignification has been nearly completed. Continuation of treatment brings about a decrease in molecular weight to a minimum value of about 5000 and thereafter an increase is again observed. Similar trends were observed at concentrations of 40, 50 and 90 g. total SO_2/liter, although the changes occurred more rapidly in the solutions of higher acidity.

With maple wood, the molecular weight of the lignin sulfonates is found to be strikingly smaller, *i.e.*, of the order of 1000–1500. These values remain nearly constant as the time of treating is increased. In prior work in this Laboratory by Dr. J. C. Aggarwala similar low average molecular weights have been indicated for the lignin sulfonates from a bamboo (*Dendrocalamus strictus*), since it was found[5] that only some 15% of the original methoxyl remains associated with the non-dialyzable bamboo lignin sulfonates, whereas around 50% of the methoxyl in gymnosperm lignin sulfonates is usually non-dialyzable.

The lignin sulfonate samples obtained in one set of experiments with hemlock wood were fractionated by a "reprecipitation" method and the results are summarized in Table IV and Fig. 3. The lignin sulfonates obtained after 0.5 hr. reaction time, which comprise about one-quarter of the total lignins, are found to be distributed predom-

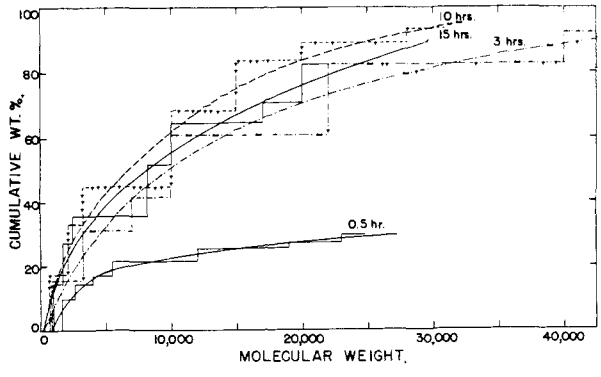

Fig. 3.—Estimated distribution in molecular weights of dissolved hemlock lignin sulfonates after various times of treatment.

(4) A. P. Dunlop and F. N. Peters, "The Furanes," Reinhold Publ. Corp., New York, N. Y., 1953.

(5) J. C. Aggarwala, Ph.D. Dissertation, University of Washington, Seattle, Washington, 1948.

inantly in the molecular weight range of about 500 to 10,000. However after 3 hr. when the delignification has been nearly completed, the molecular weights are found to range on up to around 100,000. Longer reaction time to a total of 10 hr. brings about a general shift in the cumulative distribution curve into a substantially lower range of molecular weights while still further treatment again shifts the curve but this time into a higher range of molecular weights.

These results, together with others previously obtained here and in other laboratories, are believed to provide additional evidence in support of the following concepts: (a) that lignins are branched chain polymers existing in woody tissue at least mostly as relatively large molecules, probably combined with each other and/or with carbohydrates to make three dimensional networks; (b) that the bonds between the lignin structural units are of at least two types, one relatively easily hydrolyzable in acidic aqueous solution and the other not; (c) that for removal of lignin from wood into acidic aqueous solution, hydrolysis of some linkages between structural units must occur to set free segments or "ζ-lignins" from the presumed proto lignin polymer and also these segments must have already been sulfonated or must become sulfonated to the degree necessary to permit them to dissolve in water; (d) that lower molecular weight lignins are first removed during delignification because the distribution of hydrolyzable and of hydrolyzed linkages may be approximately random, and the smaller ζ-lignins diffuse out from the wood residue into solution more rapidly than the larger fragments which are removed later with the result that the average molecular weight increases as delignification proceeds; (e) that acidic hydrolysis of the ζ-lignin sulfonates continues even after they have become dissolved in the aqueous medium so that although the average molecular weight observed for dissolved lignin sulfonates reaches a maximum at about the time that the delignification is completed, thereafter the molecular weight decreases as hydrolysis proceeds, (f) that the average molecular weight of the lignin sulfonates finally reaches a minimum value at which presumably all of the hydrolyzable linkages have been hydrolyzed to provide an "ω-lignin"; and (g) that an increase may then become evident in the average molecular weights of the lignins as a result of progress of irreversible condensation reactions, perhaps of the phenol-carbonyl type, which have presumably continued throughout the delignification process and can finally bring about condensation of the lignin sulfonates to a water-insoluble state.

Additional research is in progress toward the development of a quantitative formulation of these relationships.

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Lignin. IX. Molecular Weights of Lignin Sulfonates as Influenced by Certain Acidic Conditions

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Lignin has been removed incrementally by treating hemlock wood in five steps with sodium bisulfite–sulfurous acid solutions of progressively increasing acidity. Low molecular weight lignins were removed first, and the later removed lignins were found generally to be of progressively increasing molecular weight. The lignin sulfonates in each increment were hydrolyzed in bisulfite–sulfurous acid solutions and a substantial decrease in molecular weights occurred. Generally similar results were obtained when purified non-dialyzable lignin sulfonates were hydrolyzed in acidic bisulfite–sulfurous acid solutions and also in hydrochloric acid solutions. Hydrolysis proceeds only to a limiting degree and condensation seems to occur simultaneously but more slowly. The new end groups may be carbonyl and phenolic hydroxyl.

Introduction

Many studies have been made of the removal of lignin from woody tissue,[1] and evidence has recently been submitted[2] indicating that as lignin is removed from gymnosperm woods using bisulfite–sulfurous acid solutions, relatively low molecular weight lignin sulfonates are first obtained in solution. Then, as the time of treatment is extended, the average molecular weight of the dissolved lignin sulfonates increases to a maximum, decreases to a minimum and finally begins to rise again. These changes are attributed to the effects of the following three processes which are thought to proceed simultaneously but at different rates: hydrolysis of hydrolyzable bonds in the lignin polymer, polycondensation of some lignin molecules with others and diffusion of soluble lignin sulfonates from the woody tissue into solution.

However, the usual delignification procedure which was used in our prior study comprised the heating of wood with aqueous bisulfite–sulfurous acid solutions in a closed autoclave or bomb. Under these batch conditions, the lignin sulfonates dissolved early in the period of reaction remain exposed to an acidic environment at elevated temperature for the remaining reaction time. In this situation hydrolysis and polycondensation reactions may be important. Thus the now-reported investigation was carried out using an "incremental" delignification method designed to minimize progress of these reactions during delignification. Experiments also have been conducted to establish

(1) F. E. Brauns, "The Chemistry of Lignin," Academic Press, Inc., New York, N. Y., 1952.

(2) E. Nokihara, M. J. Tuttle, V. F. Felicetta and J. L. McCarthy, THIS JOURNAL, **79**, 4495 (1957).