THE OXIDATION OF SPRUCE PERIODATE LIGNOSULFONIC ACIDS WITH CHLORINE DIOXIDE

A Thesis

by

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GENERAL INTRODUCTION

The present research is one of a series concerned with the oxidative breakdown and the sulfonation of lignin. Sulfonation and oxidation are useful because they might give information regarding the chemical nature of lignin, and the particular reagents selected are those used widely in industry. The sulfonation was carried out in a fashion similar to the sulfite cooking process for removing lignin from cellulose in the pulp and paper industry, and the oxidants used, chlorine dioxide or alkaline hypochlorite are both bleaching agents used widely in the same industry. Bleaching involves the removal by oxidative attack of some lignosulfonic acid which survives the pulping process and imparts an undesirable color to the pulp. The present Thesis describes a study of the oxidation of an isolated lignosulfonic acid with aqueous chlorine dioxide.

The lignin required for the research was prepared by oxidizing wood with aqueous sodium periodate, and by removing the oxidized carbohydrate by extraction with cold aqueous alkali. This method was used in a previous research by Sacks. The sulfonation procedures of Brickman and Cabott were then investigated and an even milder and much more convenient procedure was discovered. Then the oxidation with chlorine dioxide was studied in more detail to find out exactly what took place with respect

to the sulfur in the lignosulfonic acid. This effort was combined with the search for precipitating agents for the end products of the oxidation. Finally, the intermediates and end products were examined analytically, by infra-red absorption spectra and also by a new technique elaborated by Aulin-Erdtman, the ultraviolet difference spectrum.

HISTORICAL INTRODUCTION

In view of the excellent books by Brauns (1) and Hägglund (2) dating from 1952, only the lignin chemistry appearing after that date and pertinent to the present Thesis will be reviewed. Furthermore, similar surveys have been made in the theses of Cabott (3), Brickman (4), and Sacks (5). The emphasis in this Introduction will therefore be on certain general concepts in the field of lignin and on previous work which leads into the present research. Recently it has been more and more generally realized that to regard lignin as a chemical compound of invariable constitution is probably erroneous. Many early attempts to give a formula to lignin (6, 7, 8, 9, 10, 11, 12, 13) have been later modified, frequently by the same authors, towards the idea of a less definite chemical entity.

It is well known that the lignins from various species of trees differ in the fundamental building units that they contain, but analytical work also indicates variation in the lignin from a given species of tree, a natural variation which may not be caused entirely by differences in the method of preparation of the lignins. Thus in a series of data for spruce lignin, the methoxyl analysis of the isolated lignin was between 10.7 and 15.4% (14, 15), the analysis for carbon between 62.1 and 66.7%, (14, 16) between 5.3 and 6.4%

for hydrogen (17, 18) and figures for the molecular weight varied between 320 and 7350 (19, 20). In the case of molecular weights, however, careful consideration must be given to other factors as well as to the method of preparation of the lignin. Some of these other factors are the limits of accuracy of the method, the ideality of the system in the Raoult sense and the range of molecular weights for which the method is applicable. Most lignins, when obtained in a soluble form, are found to be non-homogeneous, and can be fractionated by one method or another into a series which exhibits only a gradual change in gross properties and analysis. For example, this has been done with Brauns' "native lignin" (21), with lignosulfonic acids in the form of their salts (22, 23, 24) and with the oxylignin obtained with hypochlorite (5).

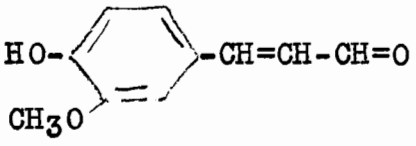
It would seem likely, then, that lignin has neither a definite composition nor a definite molecular weight, being a heterogeneous random copolymer of a variety of molecular sizes. It is probably not a chemical individual. The physical behaviour of lignin also supports this view. Like a complex polymer, it is insoluble in chemically indifferent organic liquids, and does not appear to dissolve without itself being changed (25). It has no definite melting point. Most investigators agree that X-ray patterns obtained from lignin are those of an amorphous material (26). According to Maass and co-workers (27) the consistent departure of the sulfonation reaction from the first order relation indicates that it is not chemically

homogeneous. Indeed, Maass has stated (28) that the physical properties of lignin are those of a lyotropic gel with enormous surface area, and it resembles some other complex biological products in this respect.

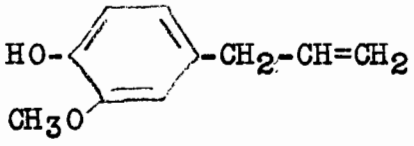
A look into the way in which lignin grows in the plant is called for by the foregoing indications of its heterogeneity. Lignin is formed mostly in the compound middle lamella and to a smaller extent in the primary cell walls (29), and does not appear to be transported as free lignin in the sap, unless as a colloid (30). Thus lignin is probably deposited in its final resting place by a chemical synthesis at that place. Certain constituents of the sap, such as coniferin, have been shown to go into the formation of the lignin molecule by Freudenberg (31), using radioactive tracer techniques in the living tree. Lignin is formed to the greatest extent during the transition period at the end of the active life of the cell, when the cellulose is also building up in the cell walls (1). This deposition may occur by means of a definite enzyme system such as the glucosidases and reductases (phenolases) Freudenberg (32) has suggested. Using radioactive carbon dioxide, Stone (33) has found that the radioactivity is incorporated into the lignin. There is probably a sequence of synthetic steps leading from photosynthesis to the holocellulose portion of the plant on one hand and on the other to the lignin, and other aromatic portions. Many theories have been proposed for such syntheses, with a multiplicity of postulated intermediates. The only

valid conclusions which can be drawn about proposed mechanisms should be based on experiments where the proposed intermediates are shown to have been incorporated into the lignin in the wood by natural processes. This has been done by Freudenberg as mentioned above (31).

Various attempts have been made to achieve an *in vitro* synthesis of lignin by enzymatic agents in an effort to produce simpler and more tractable modifications. Thus Freudenberg, by the action of the enzymes from mushrooms, has been able to condense coniferaldehyde (I) into a presumably uniform polymer which exhibited many of the characteristics of lignin (32). Recent work (34) has shown that it is not the mushroom polyphenoloxidases which cause this oxidation in the presence of air. It may be adventitious bacteria or other enzymes. Siegel has reported (35) that tissue slices from a variety of plants could transform such compounds as eugenol (II) into a lignin which was almost identical to spruce lignin in chemical composition, solubility, location in the cell wall and response to various colour tests. The formation begins with a reaction between eugenol and hydrogen peroxide which is catalyzed by peroxidase. Wacek has found that coniferin increases the lignification of tissue grown *in vitro* (36). The synthetic lignins of Freudenberg, Siegel and Wacek are probably the same, for the work of Adler and his collaborators (37) shows that eugenol on standing gives the coniferaldehyde formed by the glucosidic cleavage of the coniferin used by Freudenberg. Presumably this

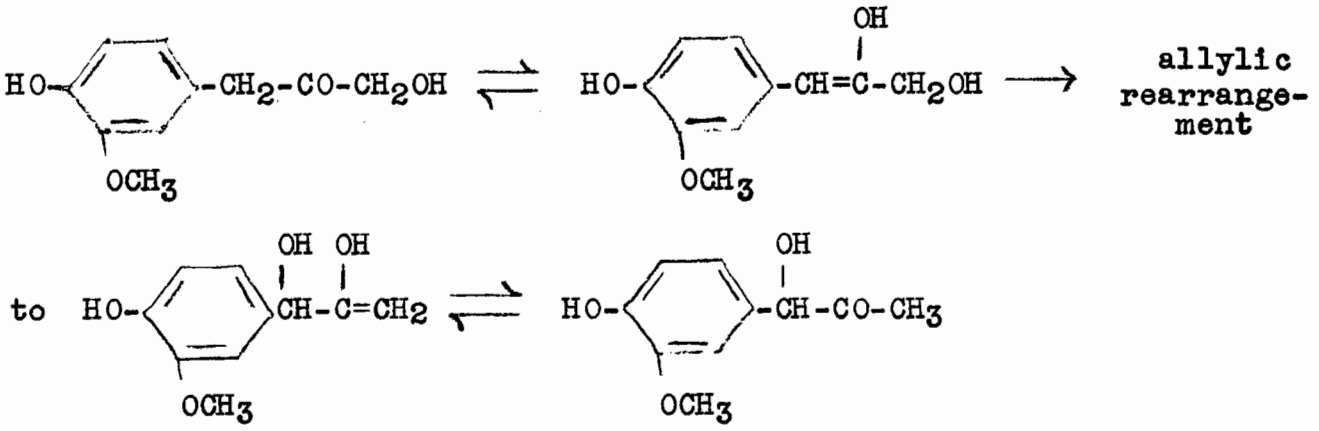


I



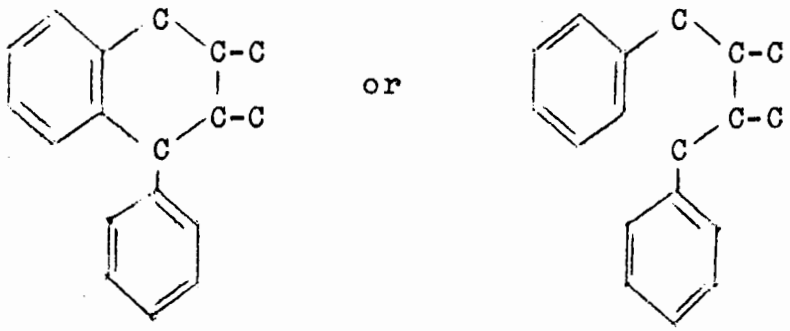
II

was an air oxidation of the allylic eugenol to the conjugated vinylic coniferaldehyde. These findings are not conclusive evidence that coniferaldehyde is the only precursor of lignin in the plant. It would seem that there probably might be a variety of precursors, several of which might be linked to coniferaldehyde in a respiration cycle, such as that proposed by Hibbert (70).



Whatever the actual mechanism may be, these biosynthetic methods do not give a material absolutely identical to the lignin in the wood. The observations seem to suggest that lignin is one of those items in nature which is not uniformly made by a repetitive process from identical building blocks.

As Erdtman states, "Lignans (crystalline phenylpropane dimers of the general types (III) and (IV)) and lignins are presumably



III or IV

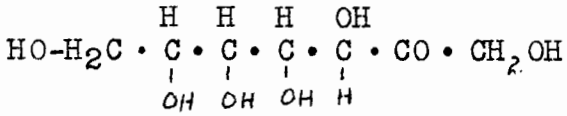
formed in nature by dehydrogenation of simple C_6-C_3-progenitors of the coniferyl type and it is noteworthy that most lignans, in contrast to lignins, are optically active. This tends to show that the biosynthesis of lignans requires rather specific enzymatic conditions." (3) It may be inferred, then, that the biosynthesis of lignin does not require specific, but rather more general enzymatic conditions. The idea seems to be current that no naturally occurring substance is haphazard in its chemical formation because enzymes govern each step along the way by specific "lock and key" mechanisms. This is perhaps an over-simplification imposed upon us by the fact that most substances which have been studied successfully are homogeneous. Up to now complex substances, such as lignin, have not proven tractable to definition by classical methods and have been termed "impure" and "mixtures" because they are by nature inhomogeneous.

Perhaps we have reached the end of such relatively simple investigations, because recent work in other biological fields has revealed structures apparently based on random units. Bone and certain general proteins are examples.

Considered from a functional and therefore somewhat teleological viewpoint, the purpose of the lignin is to give the wood the necessary mechanical strength to support itself, which is analogous to the function of the bone and protein in the animal organism. In the case of the bone, many ions which form insoluble salts will be incorporated; in the case of the protein, amino acids in the locality may be "grist to the mill". Similarly with lignin, any compounds of an activated aromatic nature might be incorporated. There are of course limits to this rough analogy. There is no compelling reason why one enzyme "lock" should not be adaptable enough to react with several compound "keys" to build up a polymer. Indeed, such a looseness between "lock" and "key" is found when several inhibitors are discovered for a given enzyme. For example, there is a wide range of structures in the "sulfa" drugs, which fit the bacterial enzyme using para-aminobenzoic acid.

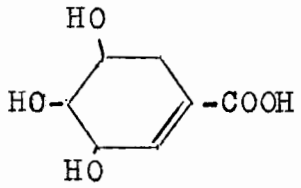
In wood there is a rigid enzymatic sequence which leads from photosynthesis to glucose to cellulose. The evolutionary latecomer, lignin, might be produced by a more flexible path from a certain range of compounds which occur in the sap. An indication of a possible route for biosynthesis exists in

Nord's report (40) that Lentinus lepideus, grown on glucose, forms, via a heptulose, e.g. (V), shikimic acid (VI) and para-hydroxyphenyl pyruvic acid (VII), methyl para-methoxycinnamate (VIII). In other words, there is a possible and in vivo

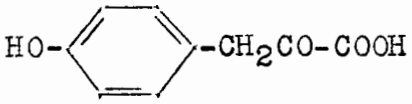


Sedoheptulose

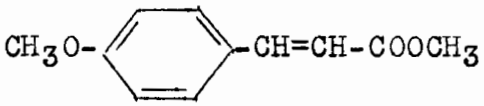
V



VI



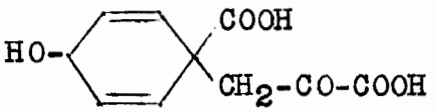
VII



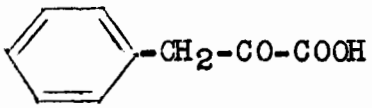
VIII

change from glucose to an aromatic compound which could be a lignin precursor. Thus, possibly, glucose may be transferred by other enzymes in the plant to the other lignin predecessors of Freudenberg or Siegel (31, 35). The prior work of Brown and Neish (41) with C^{14} labelled shikimic acid (VI) also shows this acid to be a forerunner of lignin. They suggest that the process of aromatic biosynthesis in plants is similar to that of the Escherichia coli, involving prephenic (XX) and phenyl-pyruvic (X) acids. The sequence of reactions for lignification would seem to be the attachment of a three carbon chain to a

non-aromatic ring, aromatization and then substitution of the ring.



IX



X

On the other hand, the condensation of these phenolic materials may not require enzymes but may occur as a polymerization induced by weak alkali in the presence of oxygen, as postulated by Eller for humic acids (42). An example of this reaction is the darkening of phenols on standing owing to the self-condensation of the quinone-like substances formed on oxidation. Any substances occurring in the plant which might undergo condensations with phenols, such as activated aldehydes and alcohols, etc., might enter into the lignin as well as any adventitious phenolic compounds. Against this hypothesis is the mounting volume of enzymatic work, particularly that of Wacek (36) who shows that lignification is not merely a physicochemical but also an enzymatic process. Still other conjectures lead to the postulation of a colloidal mechanism, as Wislicenus (30) suggested, the condensation occurring at a suitable surface. A closer glance at these three postulates, the generalized enzyme, the condensation induced by weak alkali, and the surface reaction, might show them all to be different facets of

the same phenomenon. The enzyme might act as a topochemical agent for localizing the ionic charges necessary for the adsorbed reacting molecule to polymerize with the lignin already formed. Indeed, the surface of the lignin already formed might act as its own enzyme-catalyst.

Lignin, then, might be assumed to be made up of a variety of units linked together (43). Since the constituent units are different, then probably there are a variety of linkages corresponding to the variable reactivities, concentrations, etc. of the ingredients in the sap which form the lignin. The following questions, which are usually asked about a copolymer, might therefore be relevant. What kind of a reaction was used to polymerize the monomers? What are the linkages between the units in the lignin copolymer? Is there a repeating unit containing several monomer residues, or, is the polymer purely random? What is the distribution of molecular weights? How much cross linking and chain branching are there? Can the end groups be identified and determined? The methods of organic chemistry should provide answers about the nature of the building units and the linkages between them. It would seem that the technique best adapted to this purpose would be of an analytical kind, whereby the lignin would be broken down and the fragments identified. Oxidation is commonly used for this purpose. Even relatively mild oxidizing agents often break lignin down so extensively that the fragments are too small to give much information about the probable building units of the polymer.

Oxidations with alkaline permanganate, however, can reveal some of the aromatic nuclei involved. Read (44) and Cabott (3) have isolated benzenepolycarboxylic acids in small yields from isolated lignins (up to 5%) and lignin *in situ* (0.14%). Since the conditions of the oxidation have been shown not to cause condensation (45), a few aromatic rings substituted with carbon in up to five positions are indicated in isolated lignins. The yields are so small that the greater part of the lignin is assumed to have some other structure which in this oxidation must have been destroyed. Richtzenhain has isolated 4,5-dimethoxy-o-phthalic acid from neutral permanganate oxidations of lignins (46) and of methylated woods (47). This work indicates that a benzenoid nucleus with carbon chains attached in two places is present. Oxidations of lignin and lignosulfonic acids, the latter often as waste sulfite liquors (48), have also given aromatic compounds such as vanillin and vanillic acid. These compounds are usually obtained by using oxidants such as nitrobenzene with alkali, or sodium hydroxide and oxygen with various catalysts. The yields indicated the presence in spruce of up to 36% of the type of nuclei which can give vanillin (1). This conclusion does not mean that there must necessarily be a free *para*-hydroxyl group as in vanillin, for veratraldehyde with this treatment has been shown to give vanillin (4). These nuclei could not give the above mentioned polycarboxylic acids. Hydrogenation, another method for the cleavage of lignin, has provided evidence for the aromatic nature of

some of the lignin monomeric building units. This evidence supports that given by the oxidations of lignin and lignosulfonic acids mentioned above. By the isolation of variously substituted propyl cyclohexanes, and under other conditions various phenylpropanes (49, 50), hydrogenation has indicated in addition that the phenylpropane skeleton probably is fundamental.

Only about half of the lignin can be accounted for by oxidation and hydrogenation, for these methods overlap in the sense that the units which produce vanillin also produce some of the hydrogenation products. Thus only half of the lignin can be definitely stated to be aromatic in nature. If the remaining 50% or less were aliphatic, a demonstration of the fact would call for a method of degradation which would attack aromatic, or at least suitably activated aromatic rings, without attacking aliphatic systems. The work of Sarkar (51) and of Schmidt and Braunsdorf (52) indicates that chlorine dioxide would be such a reagent, for it oxidizes aromatic nuclei with free phenolic hydroxyl groups almost instantly, phenolic ethers more slowly, and most saturated aliphatic compounds not at all. In order to facilitate such degradative studies, the lignin should be isolated with minimum chemical change from the cellulose and other polysaccharides of the wood. The process for isolating periodate lignin (14, 53) seems to fulfil these requirements with the exception that superficial oxidation occurs, to judge from the lowered

methoxyl content of the product. Adler and Hernestam have recently shown that lignin model substances with guaiacol type units are oxidized by periodate with the loss of methoxyl groups, and they recovered methanol in about 90% of the yield expected from this loss (54). Using this method on lignins, they have obtained values for the ratio of phenolic hydroxyl to methoxyl groups similar to those given by Aulin-Erdtman (55) and Goldschmid (56) from their spectral methods. This oxidation is not important in the present connection, since the chlorine dioxide to be used finally has been shown to remove methoxyl groups from aromatic compounds (57, 58, 59). A recent modification of the periodate process for isolating lignin uses dilute sodium hydroxide at room temperature to hydrolyze the oxycellulose, instead of boiling the partially oxydized wood in water. This treatment ensures that self-condensation of the lignin provoked by heat is at a minimum. The conditions of concentration and time for this hydrolysis are based on the results of Davidson (60) for the solution of periodate oxycellulose in alkali. Furthermore, self-condensation caused by strong acids is avoided in the periodate process, and there has been no introduction of extraneous groups by the use of solvents. The only other method for producing lignin which does not use acids, yet gets more of the lignin out of the wood than the process for Brauns' "native lignin", is that reported by Bjorkman (61). This process involves grinding the wood during a period of weeks to colloidal dimensions and

in presence of a suitable inert organic liquid, after which it is ground with the solvent, usually dioxane. Moist solvents are necessary, so it might be that there is solvolysis of some links either in the lignin or between the lignin and the holocellulose, this solvolysis being catalyzed by acid extracted from the wood and ionized in the aqueous solvent.

Periodate lignin prepared by the original, unmodified process involving boiling water was used in the investigation of the action of chlorine dioxide on lignin by Levitin and Thompson (57). Their work had shown that fairly extensive degradation took place. The fractions were not homogeneous with respect to molecular weight and varied in properties and amounts depending upon the concentration of oxidant and the duration of the oxidation. Extensive chlorination also occurred. The oxylignins no longer showed the spectral maximum in the ultraviolet at 280 mμ, which was probably characteristic of phenols and phenol ethers, but were probably still aromatic in character, for the maximum at about 200 mμ was still present. These oxylignins were the larger, more insoluble fragments left behind in the oxidation. Possibly such aliphatic fragments as might have been formed were too soluble to be precipitated and recovered. The oxylignins were fractionated on the basis of solubilities into oxylignin α, β and γ. As with any fractionation of polyelectrolytes based on solubilities, molecular weight and the number of solubilizing, polar substituents were the governing factors, and the sub-

fractions differed only gradually in properties. Oxylignins β and γ were acidic and had neutral equivalents which were found to vary with the length of time the sample had been kept in basic solution. The explanation suggested was that this behaviour was due to the slow opening of lactonic rings. An alternative interpretation would be that these oxylignins were polyelectrolytes containing many acidic groups. In common with polyelectrolytes such as the soil conditioners, these acidic groups were involved in the steric nature of the polymer. The rapidity of their titration thus depended on accessibility, which in turn might depend upon the "unwinding" of a complicated chain or upon the desolvation of the colloidal micelle. Still another interpretation would be that these oxylignins had quinone groups which condensed under the influence of alkali (62) to more complex hydroxy hydroquinones which then consumed extra base, being themselves strongly acidic (2).

The difficulties in the methylation of the oxylignin-β fraction and the discovery that the oxylignin acid catalyzed its own esterification were also revealed in the studies of Levitin and Thompson (57). Acetylation of the oxylignin was not found to occur readily except when strong acidic acetylation catalysts (acetyl chloride, sulfuric acid) were used. It was suggested that a Thiele acetylation of quinones was actually taking place at this juncture. The estimation of carbonyl groups in oxylignin-β gave ambiguous results.

One of the most important industrial reactions of lignin is that of sulfonation, whereby the lignin is attacked chemically by the sulfite cooking liquor and is in some way solubilized. The lignosulfonate may then be washed away from the cellulosic portion of the wood. The word "solubilization" is used, for, if lignin is to be regarded as a polymer, then the lignosulfonates made from it will be polyelectrolytes. The lignin might be considered to be dispersed in water through a mechanism which first involves the formation of a colloidal dispersion, of somewhat sulfonated material, perhaps micellar in nature, and finally, as sulfonation proceeds, the colloid breaks down into a "true solution" of highly solvated, perhaps associated, molecules of lignosulfonic acid salts. When wood is pulped, the process could thus be stated to be merely the separation of the compound "lignin" from the compound "cellulose". A closer approximation would be to call it the gradual solubilizing of the lignin so that it might break away from the many ties it has to the rest of the plant material. These ties are presumably of all varieties, probably ranging from a few outright chemical bonds (63) with the holocellulose to numerous colloidal and mechanical adhesions. Most of these adhesions might be formed by the more or less random deposition of lignin among the cellulose at the cell boundaries. Although in the middle lamella the solid might be almost entirely the lignin copolymer, shot through with a few cellulose fibres, at the cell boundaries the lignin and holocellulose would be intimately mixed (43).

The preliminary work of Cabott (3) and Brickman (4) had unearthed a milder method of cooking which apparently did not cause too much auto-condensation of the lignin and gave a completely soluble lignosulfonic acid. In this two-stage cooking process, periodate was heated in 9% sodium bisulfite at 100°C. for 72 hours, the insoluble sodium salt (in about 80% yield) isolated and the sodium replaced with hydrogen by means of an acid wash. The insoluble lignosulfonic acid so obtained was digested in distilled water at a concentration of about 2%, which was sufficient to give a pH just above 2. Cabott and Brickman carried out this autohydrolytic digestion at 135°C. for 2 hours. This two-stage process probably corresponded to Hägglund's concept of the solubilization of lignin in the wood as occurring in two steps; first, sulfonation and then hydrolysis, with hydrolysis being the rate controlling step above pH 2 (2). Under more acid conditions, the sulfonation would be the rate controlling step, as shown by the work of Calhoun, Yorston and Maass (27) on wood. Another factor in the preponderance of hydrolysis over sulfonation, or vice versa, is the concentration of "free sulfur dioxide" (64).

Brickman (4) found a correlation between the amount of sulfur necessary for complete solubilization, the cooking time necessary to attain this amount of sulfonation, and the solubility in the autohydrolysis step. Preliminary experiments by Cabott (3), amplified by Brickman, indicated that a kinetic study should be possible on the first step, the sulfonation, but

that both the sulfonation and the autohydrolysis should be studied under varying conditions in order to correlate such data with those obtained from the standard cooks on wood done by Yorston and co-workers (27, 65). In some experiments the sulfonation was carried out partially, so that there was only 2% of sulfur in the insoluble lignosulfonic acid. The products from the autohydrolysis of this insoluble acid consisted of a soluble fraction containing over 3% of sulfur, and an insoluble residue with less than 1% sulfur. This result again confirmed the correlation between percentage sulfur content of the Stage I acid and percentage solubility upon autohydrolysis. Brickman also showed that the portion soluble in the original sulfonation was low in methoxyl groups. This solubility of a less highly methylated fraction was a corroboration of Cabott's finding that in the treatment of lignin with superheated water the soluble portion was low in methoxyl. Brickman incidentally confirmed the fact that some of the sulfonic acid groups introduced in the sulfonation could be removed by alkali.

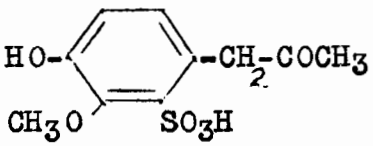
Other studies by Brickman indicated that previous methylation of the lignin limited sulfonation and decreased the per cent solubility after autohydrolysis, the amount of sulfur introduced and the amount of methoxyl present being inversely related. When the Stage I insoluble lignosulfonic acid was methylated, the methyl ester so formed was less soluble on autohydrolysis in buffered solutions than the unmethyl-

ated material. In both cases, intensive methylation with diazomethane in dioxane lowered the methoxyl content of the major product by solubilizing the most highly methylated fraction in the dioxane used to suspend the solids. Thus any conclusions about the sulphur and methoxyl content of the products after the maximum degree of methylation were dubious.

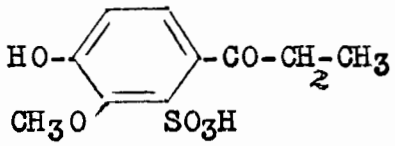
Cabott's work on the effects of pretreatments of periodate lignin confirmed the results obtained by Corey, Calhoun and Maass (66) on wood meal. Pretreatments which inhibited solubilization during cooking were elevated temperatures and a hydrogen ion concentration above or below pH 4 to 5; the conditions in both cases being such as would cause condensation of activated aromatic nuclei. The occurrence of this nuclear condensation was borne out by the production of greater amounts of benzene polycarboxylic acids in permanganate oxidations of pretreated lignin than in oxidations of ordinary lignin.

An aspect of sulfonation not discussed in this Thesis is the detailed theory drawn up by Hägglund (2) and Adler (67), and reviewed recently by Leopold (68). Tentative formulae for lignin have been suggested by these workers on the basis of sulfonation data and the behaviour of model compounds. These formulae, as well as those based on degradation experiments and mentioned at the beginning of this section, (6 - 13) do not and cannot reveal the complete chemistry of lignin. A chemical formula is a symbolic convenience to summarize observed chemical behaviour and to assist in the prediction of chemical

behaviour. If the material being dealt with is a polymer or colloid, there is no satisfactory symbolic representation except that vaguely implied by the number n in $(monomer)_n$, for the difference between its behaviour and that of a monomer. Among the postulates of the theories based on the sulfonation of model compounds is that the sulfonation occurs at the carbon atom alpha to an aromatic ring. Model compounds, such as XI and XII used by Wacek and Kratzl (69, 70, 71), have been found to give respectable yields of vanillin upon oxidation with alkaline-nitrobenzene, just as lignosulfonic



XI



XII

acid itself does (72). There have been no compounds reported from any treatment of lignosulfonic acids which have sulfonic acid groups on the aromatic ring, in spite of the known stability of aromatic sulfonic acids. The assumption that the sulfonation of lignin does not occur in the aromatic portion is supported, but not proved, by this negative piece of evidence. On the other hand, neither have aliphatic fragments containing sulfonic acids been found. Aliphatic sulfonic acids are also stable compounds (73), but probably they have not been isolated because the free acids to be expected are soluble in practically

all liquids and most of the salts are soluble in water. This is probably why the failure to isolate aliphatic sulfonic acids has not been used as an argument in favour of an aromatic sulfonation. In a word, there is no definite evidence concerning the location of the sulfonic groups in lignosulfonic acids.

Finally, it seems necessary for the purposes of this Thesis to review recent work on the infra-red and ultra-violet spectra of lignins. As already mentioned, in the ultra-violet there is at 280 mμ wavelength a maximum characteristic of lignins. This maximum has been interpreted by Hillmer (74) as being indicative of a di- or tri-hydroxybenzene, partially or completely etherified. Hägglund and Klingstedt (75, 76) came to similar conclusions about the band at ca. 280 mμ, and inferred from the relatively strong absorption at longer wave lengths that there is a ring with conjugated double bonds, i.e. with the furan or quinone structure. A series of papers by Aulin-Erdtman (77, 78, 79, 80, 81, 55) has shown that when the methoxyl content is used as a basis for the calculation of the extinction coefficient (77), most lignins exhibit spectra similar in intensity at the maximum of 280 mμ as well as having that wave length peak in common. Further, a method has been developed for estimating the number of hydroxyl groups per methoxyl group. This method is based on a comparison of the spectrum of the lignin with the spectra of model compounds, taking the spectra both in neutral and in basic solutions. The difference found between the spectra of a phenolic group

in the two solutions is attributed to a change of the unionized phenol to the phenolate ion. The more rapid method of Goldschmid (56) is based on the same theoretical foundation as that of Aulin-Erdtman.

The infra-red spectra of several lignins have been determined by Jones (82, 83), by Schubert and Nord (84), by Freudenberg (85, 86) and by Kratzl (87). Jones (83) states that the spectrum of Brauns' "native lignin" is very similar to that of Freudenberg (cuoxam), Klason, periodate and Willstätter spruce lignins taken in Nujol. The spectra of hydrochloric acid and periodate lignins were practically identical, but Klason lignin showed an almost complete absence of hydroxyl bands and had no carbonyl bands. The infra-red spectrum of alkali spruce lignin was very similar to that of other lignin preparations with the exception that the carbonyl band at 1663 $cm.^{-1}$ was absent. Since this band was also absent in the spectrum of methanol lignin isolated directly from wood, it seems probable that an aldehyde or ketone group was involved in the reaction of lignin with methanol and hydrochloric acid. The spectra of three barium lignosulfonates of varying sulfur content were similar to that of lignin, with the exception that the absorption bands in the carbonyl region disappeared with increasing degree of sulfonation. Fractional precipitation of Brauns' "native lignin" used gave sub-fractions which differed only in the absorption in the carbonyl region,

this absorption being strongest in the least soluble sub-fraction.

Schubert and Nord's work (84) showed the spectral identity in the infra-red of "native lignin" extracted from "fresh" wood and the larger amount of lignin obtained by extraction of the decayed wood.

Freudenberg states (85) that unmethylated lignin derivatives show a stronger bant at 2.7 and 2.8 μ than at 3.4 μ. Only for Brauns' "native lignin" are these bands the same in intensity, although Nord did not find them so in his spectra (84). The situation is the reverse for methylated lignins, for if there is no hydroxyl group, there is no band at 2.7 to 2.8 μ. Freudenberg's lignin-like "dehydrogenation polymer" (DHP) from coniferyl alcohol, and Brauns' "native lignin" from spruce were quite similar, in their infra-red spectra, whether in the form of the original material, or after sulfonation or after methylation. These similarities support Freudenberg's view, already mentioned, that lignin arises from the dehydrogenation of coniferyl alcohol and from the concurrent polymerization of the manifold di-radicals and quinone methides formed. In a later paper (86) Freudenberg attributes the 5.8 μ carbonyl band of lignin to oxidation during the preparation, and gives spectra of model compounds and their mixtures with "DHP".

Kratzl (87) attributes the aldehyde bands above 6.0 μ to sugar aldehydes, and points out the similarity in spectrum between 6-trityl cellulose and lignins in this range.

RESULTS AND DISCUSSION

Sulfonation and Autohydrolysis of Periodate Lignin

As was mentioned in the Historical Introduction, periodate lignin, produced by the process of Ritchie and Purves (53) as modified by Sacks (5) could be assumed to have undergone only a small amount of self-condensation, particularly condensation caused by heat. Sacks' process, using cold dilute sodium hydroxide for the decomposition of the oxycellulose, also had the advantage that the time required for the production of the lignin was reduced by one-half. In addition, preliminary experiments showed that the large volumes of dilute sodium hydroxide used removed the extractives; the extraction of the woodmeal with ethanol-benzene was therefore omitted. The 50% yield of lignin, however, was lower than expected. Losses of fines in the decantations and filtrations were high because the residual material was gelatinous and flocculent. Perhaps another method of separation of the lignin from the liquors, such as the use of a cream type separator, would be more satisfactory. Yields were calculated on the wood basis, and also as the percentage of Klason lignin in the wood recovered as Klason lignin in the final product. The results are compared in Table I with those for preparations made by other workers.

TABLE I

ANALYSES AND YIELDS OF SPRUCE PERIODATE LIGNINS

Lignin Prepared by	Moisture %	Ash % (a)	Methoxyl % (a, b)	Klason Lignin % (a, b)	Yield on Wood %	Yield on Klason Lignin in Wood % (a, b)
(1) Ritchie (53)	...	2.0	12.2	93.7	29.8	97.2
(2) Brounstein and Cabott (3)	7.1	3.2	11.6	90.2	22.5	78
(3) Brickman and Thompson (4, 57)	9.2	3.4	11.6	91.1	15.8	53
(4) Sacks (5) (with boiling water)	18.9	1.8	12.0	88.4	26.8	79
(5) Sacks (with dilute NaOH)	...	1.8	12.4	88.7	..	..
(6) Present author (with dilute NaOH)	7.0	4.0	12.5	89.6	14.3	50

(a) Moisture free basis
(b) Ash free basis

Samples of all the preparations available were submitted to a sulfite cook under identical conditions. The calcium base cooking liquor used, when analyzed by the Palmrose method (90), contained 6.6% of "total sulfur dioxide" and 1.1% of "combined sulfur dioxide", and was thus slightly stronger than the "standard" liquor with 6% and 1% respectively. In the previous work by Sacks, the residue was from the cook on a coarse grained sintered glass filter funnel, while the author used a centrifuge in order to prevent the washing away of the fines. Table II, columns 1 and 2, shows that this change in procedure greatly increased the amount of residual lignin. The ash content was not responsible for this increase, for the percent ash in the residue accounted roughly for the amount of ash in the original lignin. The liquors from periodate lignin prepared according to the modified procedure (preparations 4 and 6) were straw coloured, as compared to the dark red colour of the liquors from the lignins prepared by hydrolysis with boiling water.

The original lignin, when air dried from water, was a hard resinous substance, similar in appearance to the substances obtained when other hydrophilic gels, such as glue, were dried. No evidence of the botanical structure of the wood remained, although up to the final drying, the moist material did maintain the shape of the wood meal particles much swollen by the reagents. When similar preparations were dried through acetone and benzene, the material retained some of the structure

TABLE II

RESULTS OF STANDARD SULFITE COOKS(a)

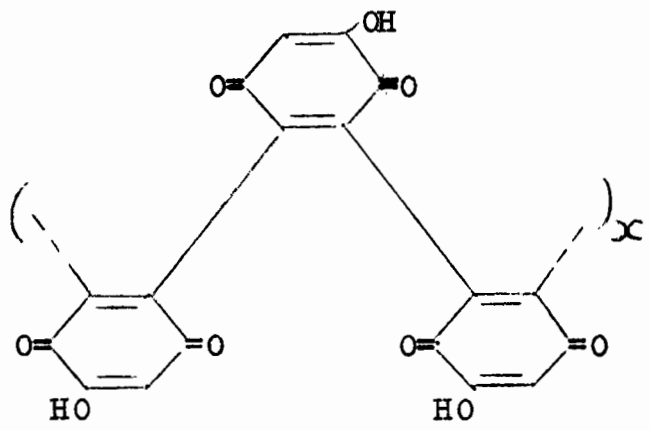
Lignin Prepared by	Insoluble in Cooking Liquor %		Ash in Residue %
	Determinations by Author	Sacks (5)	
(2) Brounstein and Cabott (3)	20	5.4	19
(3) Brickman and Thompson (4, 57)	17	2.1	15
(4) Sacks (5) (with boiling water)	10	1.7	10
(6) Author (with dilute NaOH)	10	...	16

(a) Calcium bisulfite; 6.6% total and 1.1% combined sulfur dioxide at 135° for 6 hours.

of the wood and was rather soft and chalky, instead of being hard and resinous in texture. When put in water, the resinous material swelled to about its former dimensions after several hours and regained some of the wood structure. It therefore seemed probable that when the dry material was cooked in sodium bisulfite solution, part of the time apparently taken for the cook was used to swell the dry lignin granules. If the periodate lignin were kept as a slurry in water, the cooking time might be still further reduced.

When the lignin was sulfonated and changed into the sodium salt, the same behaviour after drying was observed. The dried sodium lignosulfonate had to be kept overnight in 1N hydrochloric acid to change it to the free, insoluble lignosulfonic acid, whereas if the lignosulfonate were used as a moist cake, a very brief period in the acid sufficed for the change. This change was accompanied by a visible change of colour from dark red brown in basic media to a pale yellow brown in acid media. A similar colour change could be observed in a suspension of the extracted wood meal itself in acid or alkaline solutions, and became more pronounced with each repetition of the oxidation with periodate. Such behaviour was not inconsistent with the formation or exposure of chromophoric groups in the lignin which served as acid-base indicators like phenolphthalein or other phenols capable of forming coloured, usually quinone-like, compounds. The humic acid-like substances obtained by Eller (62) from the oxidation of polydric phenols and hydroxyquinones appeared to be very similar. Eller's amorphous products were red brown and displayed acidic and quinonoidal properties, dissolving in alkaline solutions with a deep red colour. They were probably polyhydroxypolyquinones of the type described by Erdtman (91) and illustrated in formula XIII.

The conditions specified by Cabott and used by Brickman (3, 4) for the sulfonation of the lignin with sodium bisulfite were chosen on the basis of only a few pilot experiments.



XIII

The concentration of sodium bisulfite used was 9%, which gave a pH of 5.2, near the optimum pH range 4-5 for sulfonation without side reactions promoted by acidity or alkalinity (3). These conditions gave a total sulfur dioxide concentration which was approximately the same as that used in the standard sulfite cook of previous studies. The aim in the present investigation was to find a method which would give a suitable starting material for the oxidation with chlorine dioxide, namely, an autohydrolyzed lignosulfonic acid, corresponding to a carbohydrate-free, ash-free waste sulfite liquor, in as uncondensed a state as possible. Table III records the results of many additional pilot experiments in which the four variables, time and temperature of both the sulfonation and the autohydrolysis, were systematically changed. Not considered, and, it was hoped, kept constant, were such factors as hydrogen ion concentration, state of subdivision, effect of pretreatment, as well as other unanticipated variables. The work of Cabott

TABLE III

DATA USED TO REVEAL OPTIMUM CONDITIONS FOR THE PRODUCTION OF A SOLUBLE LIGNOSULFONIC ACID FROM SPRUCE PERIODATE LIGNIN

	Sulfonation			Autohydrolysis		
Item Number	Temp. °C.	Time hrs.	Insoluble Sodium Lignosulfonate %	Temp. °C.	Time hrs.	Insoluble Residue After Autohydrolysis %
1[a]	100	4	91	135	6	44
2[a]	100	24	89	135	6	22
3[a]	100	48	89	135	6	15
4[b]	100	48	84	135	2	1
5	100	50	83	100	50	2
6	100	50	83	100	72	2
7	100	57	80	100	72	1
8[b]	100	67	86	135	2	0
9[a]	100	72	88	135	6	1
10[a]	100	72	88	135	2	5
11[a]	100	72	88	135	4	2
12[a]	100	72	88	100	2	46
13[a]	100	72	88	120	2	23
14	100	72	84	120	72	1
15	120	72	58	77	210	12
16	120	72	58	91	72	2
17	120	72	58	100	24	2
18	77	50	95	100	24	33
19	77	100	91	100	25	13
20	77	210	86	100	55	2
21	91	25	93	100	72	17
22	91	50	89	100	72	9
23	91	72	83	90	140	12
24	91	72	79	90	140	4
25	91	100	81	90	170	6
26	991	100	81	100	24	1

(a) Data from Cabott (3) (b) Data from Brickman (4)

indicated that pH 2 was optimum for the autohydrolysis of the insoluble lignosulfonic acid, and in the present experiments an unbuffered pH somewhat above 2 was maintained by restricting the amount of the solid, free lignosulfonic acid to 2% of the distilled water used in the autohydrolysis.

Since the periodate lignins prepared by different workers varied somewhat in analytical properties, it could not be assumed that they reacted in exactly the same manner. Table III therefore includes for comparison some of the data of Cabott and Brickman. Items 1, 2, 3, 9, 10, 11, 12 and 13 are from Cabott's work, while items 4 and 8 are from Brickman. Although item 14 is new, the lignin used was prepared by Brickman and Thompson with extractions with boiling water. The remaining items represent experiments carried out with lignin prepared by extracting the oxidized carbohydrates with cold alkali. The results must be looked upon as indicative rather than quantitative for they were only approximately reproducible. For instance, the yield of 58% of sodium lignosulfonate given in items 15, 16, 17 was the average of seven identically treated samples which gave the following individual values: 56.0; 61.2; 55.0; 60.8; 53.0; 52.2; 70.3%.

The work of Richter and Pancost (92) with the action of sulfite solutions on wood confirmed results obtained by the present author, but not reported in the Table, in that there was very little sulfonation at room temperature, even after

three months. More strongly acidic conditions and the use of free sulfur dioxide did bring about sulfonation at room temperature, according to these workers. Possibly there are two modes of the sulfonation of lignin, that caused by sulfite or bisulfite, as illustrated by the present work and that caused by free sulfur dioxide. If so, the free sulfur dioxide present in a technical cook not only hydrolysed the lignin into fragments, but also sulfonated it in a different way.

The optimum conditions for the sulfonation and autohydrolysis of the lignin were selected from the crude data above, bearing the following considerations in mind: temperatures should be kept to a minimum, but should not be so low that the reaction took too long. A convenient period would be about two days or 50 hours. The yield of insoluble sodium lignosulfonate should be above 80%, to avoid excessive losses as soluble sodium lignosulfonate. At present, there is no procedure or justification for recovering this soluble material as autohydrolyzed lignosulfonic acid. The amount of material remaining unautohydrolyzed should be about 5%, to avoid excessive loss at this point, and also to avoid the waste of effort and time involved in a complete solubilization. The last 5% of the lignosulfonic acid to dissolve would also be the fraction least likely to break down in later work to fragments of small molecular weight. It was this effort by previous workers to attain complete solution which doubled the time spent in cooking at a given temperature, and also raised the percent of sulfur

necessary for solubilization to 3.5% in the solid lignosulfonic acid. From the work of Brickman, it can be deduced that sulfonation to the extent necessary to give less than 5% residue upon autohydrolysis at 135° for 2 hours could be achieved by cooking at 100° for 50 hours, or at 90° for 100 hours (Items 5 and 26). These conditions corresponded to the introduction of about 3% sulfur into the lignin. After confirming these results for the lignin preparation used here, it was shown that more prolonged sulfonation at a lower temperature would achieve the same result (Items 20 and 26). Since at pH 5.2 there would be a minimum of acid catalyzed condensation, the higher temperature of 100° and the shorter time of 50 hours could probably be used without any sacrifice in quality.

The situation in the case of the autohydrolysis was somewhat different. A thorough study with respect to the effect of time had not been made, but the temperature of the autohydrolysis seemed to be the dominating factor. For example, in Item 15, no reasonable amount of cooking at 77° would make the last 12% of the insoluble lignosulfonic acid dissolve, despite the fact that the same insoluble lignosulfonic acid dissolved almost completely (only 2% residue) at 100° in 24 hours (Item 17). The minimum temperature necessary to give no more than 5% unautohydrolyzed material appeared to be between 90° and 100°.

Items 23 and 24 differed only in the method of drying. The sodium lignosulfonate in Item 23 was dried in the usual way by solvent-exchange through dioxane and benzene, whereas in Item 24 the salt was dried through acetone and benzene. Although the difference in solubility of the sodium salt (column 4) was not outside the variance which could be expected for identical cooks, the variance in the amount of insoluble residue left after autohydrolysis was outside these limits. The conclusion was that the solvents used in the drying, and perhaps even just drying itself, were enough to influence yields and cooking times. As a result, later work was conducted on undried suspensions or slurries of the insoluble stages, with aliquots being taken to assay the solids contents.

In general, there was 90 - 95% recovery of free insoluble lignosulfonic acid, corresponding to Hägglund's stage I acid, from the sodium salt upon treatment with 1N hydrochloric acid. For example, Item 5, with 83% net yield of the sodium lignosulfonate, gave 76% net yield of the insoluble lignosulfonic acid; item 17, with 58% net yield of sodium salt, gave 54% net yield of the acid. In Item 6, the sulfonation was carried out in the usual sealed bomb, but the autohydrolysis was done in the open, under reflux, as described previously. Similarly in Item 7, the sulfonation was done in the open, but the autohydrolysis took place in sealed tubes.

When the liquor from the sodium bisulfite cook was dialyzed against tap water, yields of soluble sodium lignosulfonate were obtained which indicated that the greater part was undialyzable. In a sample starting with 0.40 gram of lignin, of which 7.0% was moisture and 4.0% ash, (net weight 0.36 gram), an average of 0.23 gram of insoluble Stage I sodium lignosulfonate was obtained; the liquor yielded 0.13 gram of undialyzable soluble sodium lignosulfonate, adding up to the entire amount of pure lignin. This balance does not, however, account for the additional weight contributed by the sodium and sulfonic acid groups.

The soluble sodium lignosulfonate, freed of sodium bisulfite by dialysis, could also be precipitated fairly completely by the addition of strong acid. This behaviour was characteristic of some colloidal polyelectrolytes, and of sulfonic acids. In the former case, precipitation might be consequent upon a replacement of the adsorbed ions which had been stabilizing the colloid. In the latter case, when the polyelectrolyte behaves as a weak acid, the repression of its ionization by the excess hydrogen ion might be the cause of the observed insolubility. Either explanation might be correct. Probably both were so, there being coagulation of the larger, colloidally suspended particles and straight precipitation of the smaller, truly dissolved lignosulfonic acid molecules. Lignin, a high molecular weight copolymer, would be expected to become a polyelectrolyte when sulfonated. Then the fraction of higher

molecular weight would disperse in water as colloidal micelles, and the part of lower molecular weight would form a true ionic solution. McCarthy and co-workers (24) regarded lignin sulfonates as the products of the hydrolysis of a more or less infinite network in the wood. In solution the molecules were to be regarded as non-rigid chains, penetrated and hydrated by the solvent.

On opening the bombs in which the autohydrolyses had been carried out, the odour of sulfur dioxide detected by Brickman and Cabott was not observed. This divergence might be explained by the fact that in the present experiments the material had been sulfonated to not more than 3% sulfur content, and not to the figure of 3.5% which Cabott and Brickman had achieved by more severe cooking. This circumstance implied that the extra sulfur was difficult to put in and was easily removed as sulfur dioxide. The extra sulfur might also have corresponded to the final increment of sulfonation which was necessary to solubilize the last 2 to 5% of the lignosulfonic acid. In the present work, the aim was to find small fragments still containing sulfur after an oxidation with chlorine dioxide. It was therefore not thought necessary to introduce labile sulfur in an endeavour to solubilize the lignosulfonic acids, presumably of higher molecular weight, which were less likely to yield the small sulfur bearing pieces which were sought in the oxidative breakdown. Any process, then, which would give at least 95% of the insoluble lignosulfonic acid (Stage I) as soluble, autohydrolyzed lignosul-

fonic acid (Stage II) would be satisfactory. Within this limitation, the insoluble lignosulfonic acid should be satisfactorily changed to the soluble autohydrolyzed material by a simple heating in water at atmospheric pressure. This proved to be the case, and autoclaving at 100° was successfully replaced by stirring the 2% suspension of lignosulfonic acid in water kept at almost 100° on a steam bath.

The next possible simplification was to carry out the original sulfonation under reflux at atmospheric pressure. The necessary requirements were that the concentration of bisulfite ion would not fall too low owing to consumption as sulfonate or by atmospheric oxidation, or by loss as gaseous sulfur dioxide, and that the hydrogen ion concentration would not deviate too greatly from the optimum value of pH 4-5. Preliminary experiments with boiling 9% sodium bisulfite solution showed that after 12 hours the bisulfite ion concentration had dropped to 7.5%, and the solution had consequently become more alkaline and was at pH 7. Since the bisulfite ion concentration was not critical except insofar as it governed the hydrogen ion concentration, a trial cook was made at a concentration of 16% sodium bisulfite and the pH was followed throughout the reaction. It was assumed that if the acidity remained relatively constant during the cook, the bisulfite ion concentration could not have dropped below 8.5%. Below this concentration, the bisulfite was no longer capable of keeping the solution buffered close to pH 5. These conditions were not satisfactorily

fulfilled by the cook, and the proof was in the subsequent autohydrolysis, where only 1.2% remained undissolved. The yields in this process are also embodied in Table III, Items 6 and 7.

Later work, in which both the sulfonation and the autohydrolysis were carried out at atmospheric pressure, showed that the time for the autohydrolysis could be reduced to 20 hours. The analytical results of this run are summarized in Table IV. These results are within the range of variation obtained by Brickman in his sulfonation at 100° for 72 hours and autohydrolysis at 135° for 2 hours, with the exception that the sulfur contents were consistently lower in the present work. The residue left after this autohydrolysis was 1.5% of the weight of the insoluble Stage I lignosulfonic acid. Of this residue, 33% was ash; therefore only 1% of the Stage I lignosulfonic acid was left behind on autohydrolysis as organic material of large molecular weight.

Another advantage of the open cook was that samples could be taken very easily during the progress of the reaction. To do this in the work of Cabott and Brickman, individual bombs had to be extracted from a hot bath, and there had to be one or two bombs for each sample. In the open cook method, aliquots were simply pipetted out of the flask during the course of the reaction. This method was then used to determine optimum conditions of time for both the sulfonation and the autohydrolysis

TABLE IV

ANALYSIS OF INTERMEDIATES IN THE DISSOLUTION OF LIGNIN IN BISULFITE

Open sulfonation in 16% $NaHSO_3$ for 50 hours at 98°; pH 5.

Open autohydrolysis at 2% solids conc. for 20 hours at 98°; pH 2.5

Intermediate	Net Yield(1) %	Yield From Previous Step %	Sulfur %	Ash %	Methoxyl %
Insoluble sodium lignosulfonate (Stage I) (after sulfonation)	76	76	3.0	5.8	11.5
Insoluble lignosulfonic acid (Stage I) (after de-ashing)	66	87	2.3	< 0.5	12.7
Soluble lignosulfonic acid (Stage II) (after autohydrolysis)	62	98(2)	2.3	< 0.5	...

(1) based on ash-free, moisture-free lignin.

(2) based on the amount of insoluble lignosulfonic acid which actually dissolved; i.e., excluded unautohydrolyzed residue from calculations.

steps. The criterion for both reactions was accepted as the point at which prolonging the reaction did not greatly increase the solubility upon autohydrolysis, that is, where the rate plots tended to become independent of time. In the sulfonation

reaction the amount of material dissolved in the cooking liquors was also taken into consideration.

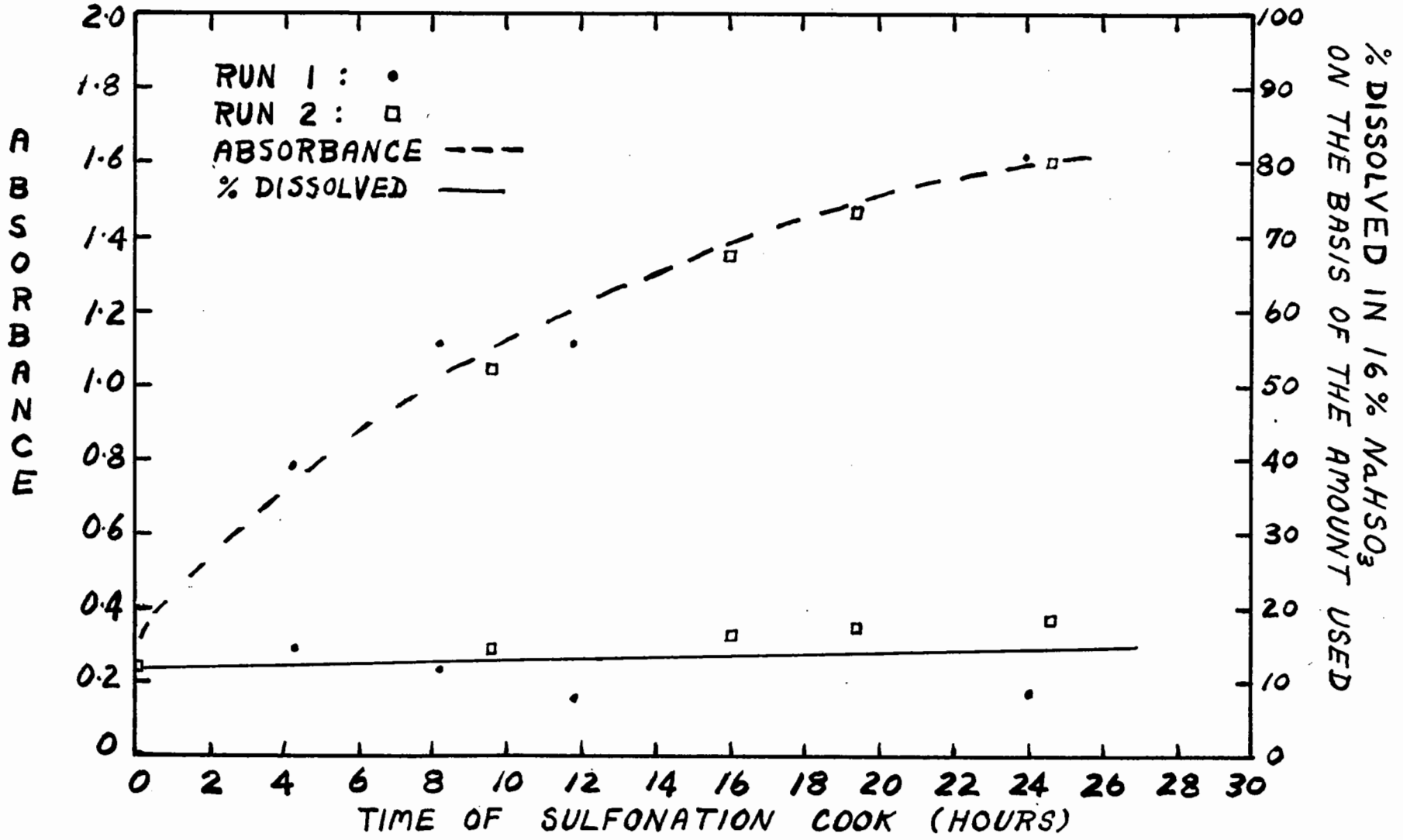
A larger scale cook was made with 10 g. of lignin in 500 ml. of 16% aqueous sodium bisulfite. Samples were taken at intervals, and the concentration of insoluble sodium lignosulfonate in a given sample was determined by drying and weighing the residue after it had been centrifuged and washed. From the aliquot the yield of soluble sodium lignosulfonate at that time could be determined. The liquors from this sample were saved and diluted for spectral measurements in the ultraviolet (at 280 mμ), which were plotted on the same graph (Figure 1) as the yields of insoluble sodium lignosulfonate.

The difference in slope of the absorbance curve and the plot for the yield of material soluble in the sodium bisulfite cook was significant. At the beginning 10 to 14% had been dissolved, and at the end no more than 20%, so that the initial and final solubility differed by a factor of two at the most. But the initial and final absorbances of the same solutions differed by at least a factor of four. This discrepancy could be explained either by the assumption that the material which dissolved was changed on heating in the liquor to a more highly coloured modification, or by the gradual solution of a more coloured component.

In either case, the observations invalidated the use of ultraviolet spectra for the determination of the amount of

FIGURE 1.

EFFECT OF TIME ON THE AMOUNT DISSOLVED DURING THE SULFONATION IN 16% $NaHSO_3$, pH 5·2, 100°



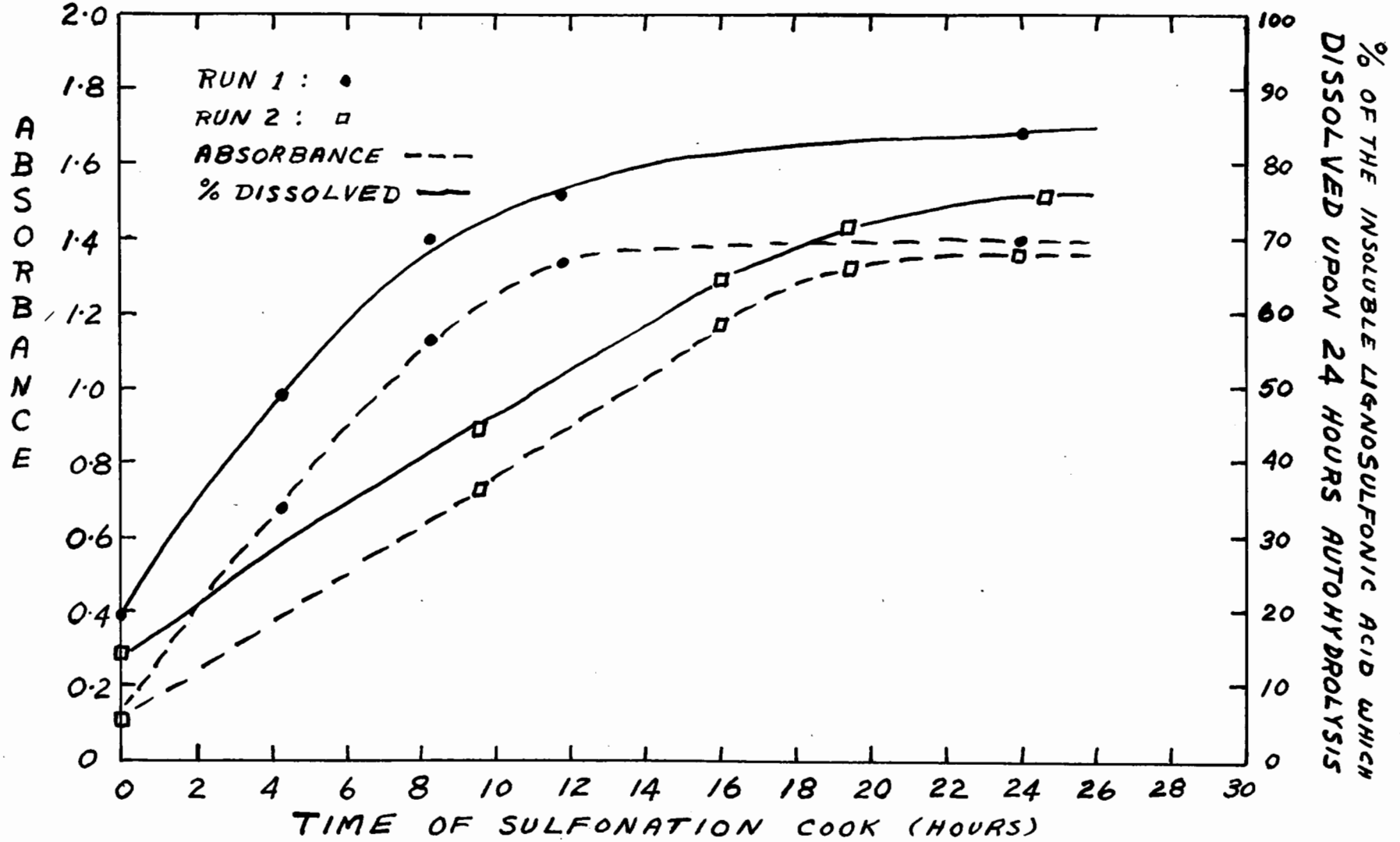
lignin dissolved in this cooking liquor, and probably the same consideration held for other cooking liquors. The broader conclusion might then be drawn that the height of the ultraviolet maximum at 280 mμ was related to the time of cooking as well as to the quantity of lignin, and could not be used to determine the lignin content of cooking liquors in a simple fashion.

The individual samples of dried Stage I sodium lignosulfonate were soaked in water, were acid exchanged, and washed free of chloride ion. It was noticed during the washing that the volume which the lignosulfonic acid gel occupied in the graduated centrifuge increased with the time of sulfonation. When the solids-liquor ratio was about 0.03 g./ml., and the volume occupied by the gel was expressed as a fraction of the total volume, then the fraction increased from 0.2 for no sulfonation to 0.5 for 24 hours' sulfonation. The more or less infinite network of lignin postulated by McCarthy (24) had presumably been expanded and hydrated into the lyotropic gel of enormous surface area postulated by Maass (28).

The individual samples of the insoluble Stage I lignosulfonic acid were autohydrolyzed for 24 hours in separate sealed tubes on the steam bath. The unautohydrolyzed residue was centrifuged, washed with water and dried. The yields of this residue were determined for the various times of sulfonation and the results are presented graphically in Figure 2. The two runs differed somewhat, perhaps because of differences in steam temperature during the sulfonation. As before, the

FIGURE 2.

EFFECT OF TIME OF SULFONATION ON THE SOLUBILITY OF THE LIGNOSULFONIC ACID IN pH2 BUFFER AFTER 24 HRS. AT 100°

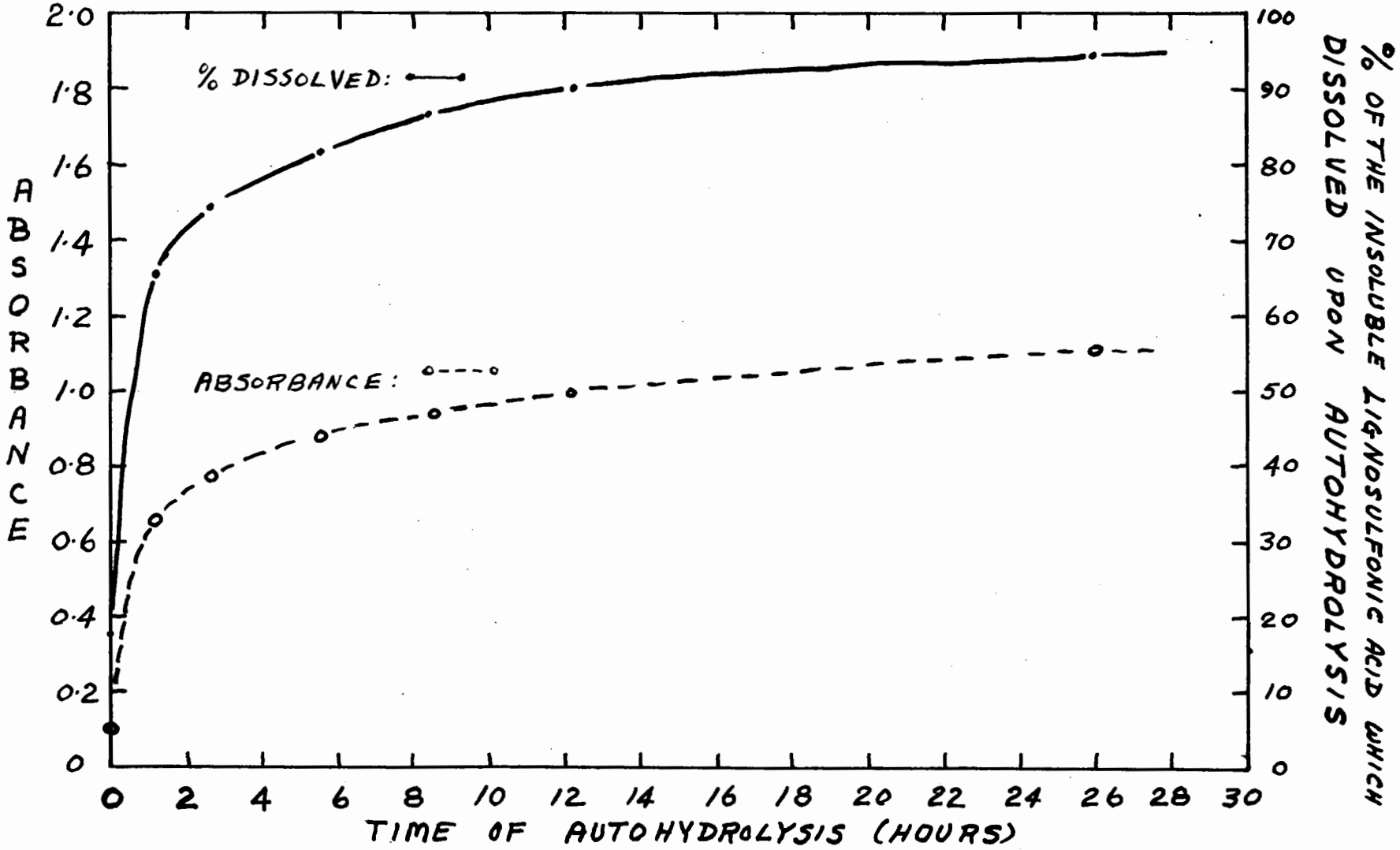


liquors from the autohydrolyses were examined spectrally at 280 mμ and the results were also plotted in Figure 2. Here the absorbance was in greater concordance with the amount dissolved in the two separate runs. As shown below, the small disagreement in slopes was caused by the formation of more highly coloured compounds from compounds which had already been dissolved.

The next series of observations concerned the insoluble sodium lignosulfonate remaining after all the previous samples had been removed. This residue was converted as usual into the lignosulfonic acid corresponding to Hägglund's Stage I insoluble lignosulfonic acid, and, at the proper dilution, was autohydrolyzed, samples being taken and separated into residue and autohydrolysate, the residue being weighed and the absorbance of the autohydrolysate being determined at 280 mμ. The results for this work were expressed in the plots of Figure 3. Here again there was substantial correspondence between the plots for absorbance and for the percentage dissolved (obtained by difference). Samples of the centrifuged liquor both before and after 1.15 hours' autohydrolysis were each heated at 100° for 24 hours. Since the absorbances increased by 10% and 6% respectively, compounds of greater absorbance had been formed from the material already dissolved. Furthermore, when samples of the final autohydrolysate (25 hours) were boiled for ten minutes to remove any sulfur dioxide, the absorbance increased by about 3%. The presence of sulfur dioxide, if indeed there

FIGURE 3.

EFFECT OF TIME OF AUTOHYDROLYSIS (SELF-BUFFERED TO pH 2) ON THE SOLUBILITY OF THE LIGNOSULFONIC ACID AT 100°



had been any at all, was therefore not a factor, for its removal would have brought about a decrease rather than an increase in absorbance. These observations confirmed the known effect of heat on lignosulfonic acids in promoting condensation to more highly coloured materials. The difference in colour between the liquor produced in the milder cooking at 100° and the darker liquor obtained from a cook at 135° illustrated the same trend.

A second autohydrolysis was carried out using a different sodium lignosulfonate made by heating in 16% sodium bisulfite for only 20 hours. The insoluble lignosulfonic acid turned out to be less soluble on autohydrolysis than usual. However, part of this insolubility might have been because both the insoluble sodium lignosulfonate and the insoluble lignosulfonic acid were more thoroughly washed than in the first run. As well, the solids content in this autohydrolysis was only 1.4% compared to the 2.2% solids content in the previous autohydrolysis. Although the "0 time" autohydrolysate might still have contained up to 6% of the soluble material, the absorbance for this solution was negligible because the washing had been more thorough. The main purpose of this experiment was to discover if there were any considerable difference in analyses between the substances which dissolved and the residue left on autohydrolysis. For this purpose samples were taken at various times and worked up as usual. The data were summarized in Table V.

TABLE V

YIELDS AND ANALYSES OF MATERIALS FROM THE AUTOHYDROLYSIS OF AN INSOLUBLE LIGNOSULFONIC ACID

	Insoluble Lignosulfonic Acid(a)	After Autohydrolysis for One Hour		After Autohydrolysis for Fifteen Hours	
		Autohydrolysate	Residue	Autohydrolysate	Residue
Yield of Residue, %	94		39		21
Yield of Soluble Material, %		58		79	
Sulfur, %	3.1	3.1	2.9	3.7	2.2
Methoxyl, %	11.5	10.8	11.1	11.4	11.2
Ash, %	1.8	1.6	1.9	1.4	3.0
Number of Methoxyl Groups/Phenolic Hydroxyl Group(c)		6 - 12		5 - 11	

(a) After standing overnight in water.
(b) At the end of the run.
(c) Calculated from difference spectra according to the method of Aulin-Erdtman (55) as modified and described later in this paper.

The yields from samples taken at 2, 4 and 12 hours were so similar to the final yield at 15 hours that these products were not analyzed. The percentages shown in Table V for the amounts dissolved on autohydrolysis were determined by difference. To check this method, samples of the autohydrolysates obtained after one hour and at the end of the run were cautiously

evaporated and the dry residues were weighed. The solubilities so obtained were less than 5% lower than the figures reported in the Table.

From these data it would appear that the time of sulfonation, i.e. the amount of sulfur, was a deciding factor for solubility on autohydrolysis. The percentage of ash also varied but only as would be expected if insoluble material, probably siliceous matter, formed an increasingly larger portion of the insoluble residue. The amount of methoxyl group was not a governing factor in the rate of solution, nor was the ratio of methoxyl groups per phenolic hydroxyl group as determined by calculations (to be described later) from the difference spectra given in Figure 16.

The preparation of the soluble lignosulfonic acid could now be standardized, on the basis of the above experiments, at 20 hours of sulfonation at 98° in 16% sodium bisulfite, acid exchanging and washing, and then 12 to 15 hours of autohydrolysis at 98° and about pH 2.5 in a solution of 2% concentration. As a matter of curiosity, dry, extracted wood meal was cooked in the open substantially according to the above directions. A citrate-phosphate buffer of McIlvaine (93) was used to maintain pH 2.5 in the hydrolysis because there was probably an insufficient amount of the insoluble lignosulfonic acid formed in the wood to act as a buffer by itself. The yield of pulp was 56%, but 14.4% of Klason lignin was still present, or 8.1% of the

original wood. Of the 28% of lignin in the wood originally, about three quarters had been removed in the cook. Since one-third of the holocellulose had also dissolved, the yield seemed too small to make this process technically useful for producing pulp.

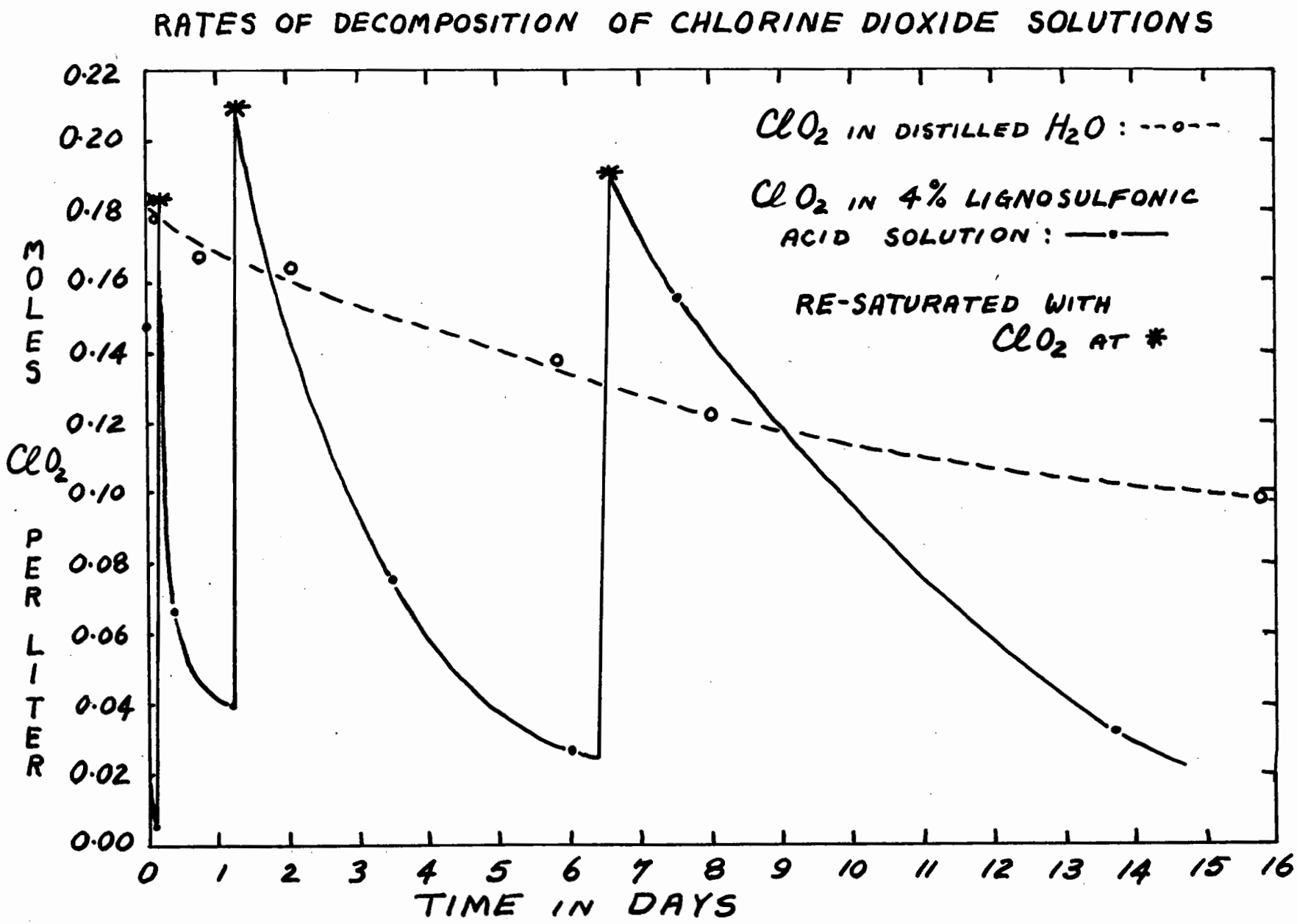
Action of Chlorine Dioxide on Soluble (Stage II) Lignosulfonic Acid

It had been suggested by Schmidt and Braunsdorf (52) as well as by Sarkar (51), that chlorine dioxide attacked aromatic rings preferentially, but could be expected to leave saturated aliphatic chains intact. In an attempt to isolate the aliphatic portion of lignosulfonic acid, the clear centrifuged liquors of an autohydrolysed sample were concentrated to 4% solids and then mixed with aqueous chlorine dioxide. Trial showed that the oxidation was not particularly rapid. Although an initial lightening of the colour of the lignosulfonic acid seemed to be complete within an hour, the consumption and concomitant decomposition of chlorine dioxide continued for over a week, as indicated by the disappearance of green gas from above the liquid after each fresh addition. In the initial stage of the oxidation, the chlorine dioxide was added as an aqueous solution to the concentrated autohydrolysate, because direct bubbling of the gas into the liquor caused an inordinate amount of frothing. After the first oxidation, the lignosulfonic acid had presumably been broken down enough so that it was no longer such an effective frothing agent.

More quantitative work on the consumption of chlorine dioxide, using the titration method of Husband (58), was carried out. The results for one example (Fig. 4) showed that even after four oxidations over the space of 15 days the rate of consumption of chlorine dioxide by the lignosulfonic acid still had not decreased to the rate of decomposition of chlorine dioxide in the absence of any organic material. Even after 15 days further oxidation of the lignin was taking place. The oxylignosulfonic acids obtained from this repeated oxidation had properties which indicated that they had been more degraded than even the most degraded oxylignin, the oxylignin γ, of Thompson (57). Thus there does not appear to be any definite stopping place in the breakdown of lignin, or lignosulfonic acid, with chlorine dioxide, in contrast to the "limit oxylignin" obtained on oxidation with hypochlorite above pH 11 (5).

The excess chlorine dioxide was readily removed by bubbling air through the solution, which was now near pH 2. Before the product was isolated, in the first experiments, the oxidizing acids present, mainly by-product chloric acid, were removed by reduction to hydrochloric acid with sulfur dioxide. Heat was generated during the process, and the solution was pre-cooled to prevent any side reactions. Excess sulfur dioxide was removed by bubbling air through the liquor. Unfortunately further sulfonation of the lignosulfonic acid occurred in this process, for even after thorough washing the sulfur content of the products remained excessively high. Possibly, sulfonation

FIGURE 4.


RATES OF DECOMPOSITION OF CHLORINE DIOXIDE SOLUTIONS
ClO2 IN DISTILLED H2O : --o--
ClO2 IN 4% LIGNOSULFONIC ACID SOLUTION : —•—
RE-SATURATED WITH ClO2 AT *
MOLES ClO2 PER LITER
0·22
0·20
0·18
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
0·00
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
TIME IN DAYS

of quinone rings formed in the oxidation was brought about by the sulfurous acid added. This method of removing any chlorate and chlorite was abandoned, and in later experiments any by-product oxidizing anions were assumed to be eliminated with the chloride ion, or were reduced by a procedure involving hydriodic acid (see later).

The percent of dialyzable material was used as a measure of the efficiency of the oxidation. After the first oxidation about 40% of the original solids in the autohydrolysate remained in the dialysis sack, whereas after repeating the oxidation on the same material three times only about 15% was non-dialyzable. Even though all of the lignosulfonic acid was in a soluble form to begin with, after the oxidation from 1.5 to 3% recovered as an acid-insoluble, white precipitate, which could be peptized in water, and which was probably a polyelectrolyte. This precipitate had a lower sulfur content (less than 1%) than either the parent material or the oxylignosulfonic acids later precipitated as salts from the solution, and probably separated at this point because it did not have enough sulfonic acid groups left to keep it in solution. On the other hand, the fraction was probably of too high molecular weight, and had too few polar groups, (for example, carboxylic acid groups,) to remain dissolved. This insoluble product was probably analogous to the chlorine dioxide oxylignin β of Levitin, Thompson and Purves (57), which was precipitated at pH 1, but remained dispersed on the alkaline side of pH 4. In the present work, the oxylignosulfonic acid

solution was near pH 1 at the natural acidity of the lignosulfonic acid.

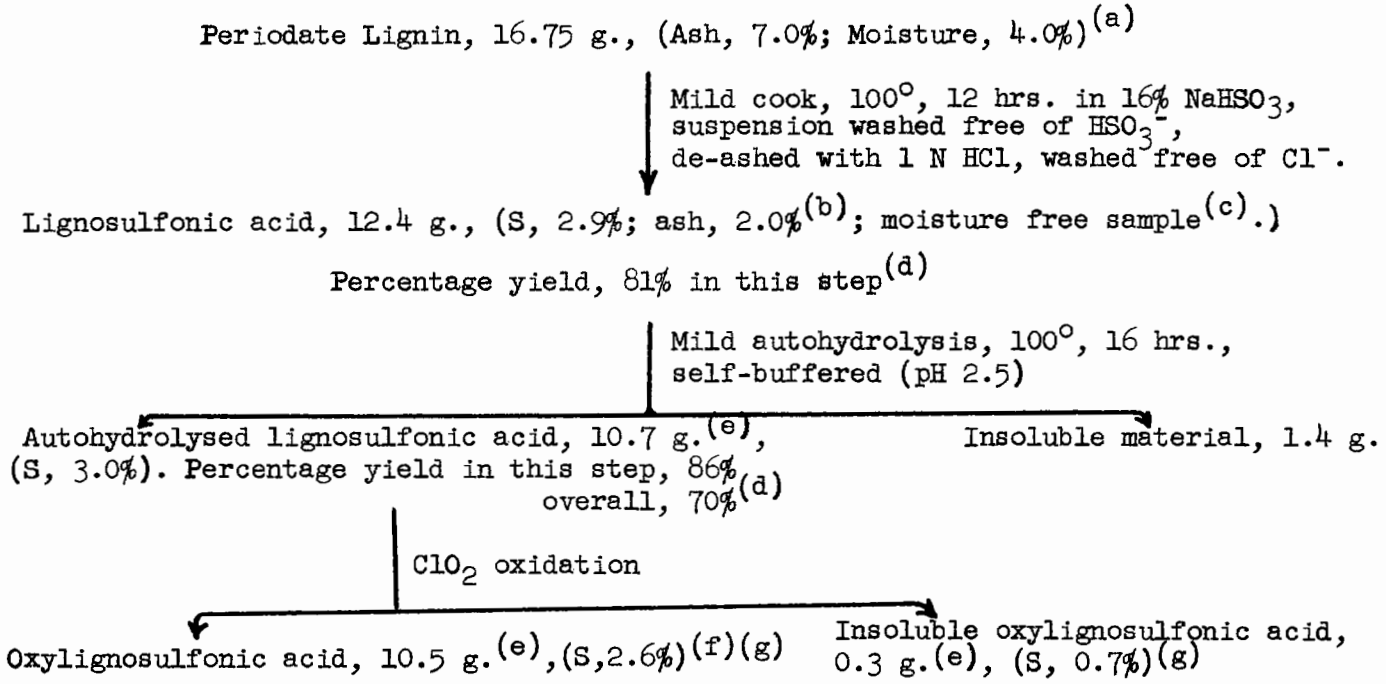
The analytical results for a sample sulfonation, autohydrolysis and oxidation are given in Figure 5. The yields quoted did not take into account any changes in the molecular weight during the process. For example, in the sulfonation there was the addition of sodium sulfonate groups; after the acid exchange there were hydrogen atoms in place of the sodium atoms; chlorination and the formation of carboxylic acid groups during the oxidation led to an apparent yield of over 100% in this step. This yield was obtained by the evaporation of an aliquot of the oxidation liquors and did not include any volatile products. This fact, together with the high percentage of non-dialyzable material, would suggest that very little of the oxidation, if any, had proceeded to small molecules like carbon dioxide. Since the oxylignosulfonic acid obtained by evaporation was not very stable, a salt was made and used in subsequent work.

Separation of the Oxidation Products

In accord with the decision to isolate the oxidized fragments of the lignosulfonic acid as metallic salts, soluble salts of various bivalent metals were tried as precipitating agents. In strongly basic solution, barium hydroxide and calcium hydroxide gave precipitates of lignosulfonates, but below pH 5 there was no such precipitation. Basic solutions, however,

FIGURE 5

PREPARATION AND OXIDATION OF A LIGNOSULFONIC ACID



(a) Corresponding to 15.0 g. lignin.
(b) Siliceous material.
(c) The yield, and percentage of sulfur and of ash were determined on an aliquot of a slurry which had been dried.
(d) On an ash free, moisture free basis from the original lignin.
(e) Amount adjusted to compensate for samples taken.
(f) Corresponding to S, 1.9% combined, plus S, 0.7% as sulfate ion.
(g) Corresponding to over 90% recovery of sulfur from the previous step.

had been shown to have an adverse effect upon the oxylignins (57). For this reason it was decided to precipitate the salts with alcohol from a solution of pH 5. In the case of barium, large amounts of barium chloride separated upon addition of the alcohol and it was difficult to remove this contamination from the precipitate. For the same reason other bases, such as sodium hydroxide, having chlorides insoluble in ethanol or other polar organic solvents, could not be used. From this point of view, calcium hydroxide was suitable since the chloride was readily soluble in ethanol. Zinc oxide and basic copper carbonate were also tried as precipitants. The metallic ions ranged themselves in the following series with regards to completeness of precipitation upon addition of alcohol to a solution of pH 5: Ba>Ca>Zn>>Cu. The copper salt precipitated only slightly upon addition of alcohol, and even more non-polar solvents, such as acetone and dioxane, did not give complete precipitation. The zinc salt was moderately soluble in the alcohol. The drawback to the use of calcium ion was the relative insolubility of calcium sulfate in water and its complete insolubility in alcohol. Thus precipitates of calcium lignosulfonate were difficult to purify. The solubility of zinc sulfate in water and to some extent in alcohol led to the use of zinc oxide as the precipitating agent in later work.

When fractional dialysis and fractional precipitation were tried on the calcium oxylignosulfonate, as illustrated in the flow sheet, Figure 6, all fractions had approximately the

same sulfur content of about 5%, none having the higher sulfur content of over 15% necessary for a sulfonated aliphatic fragment of 4 or less carbon atoms (see Table VI).

TABLE VI

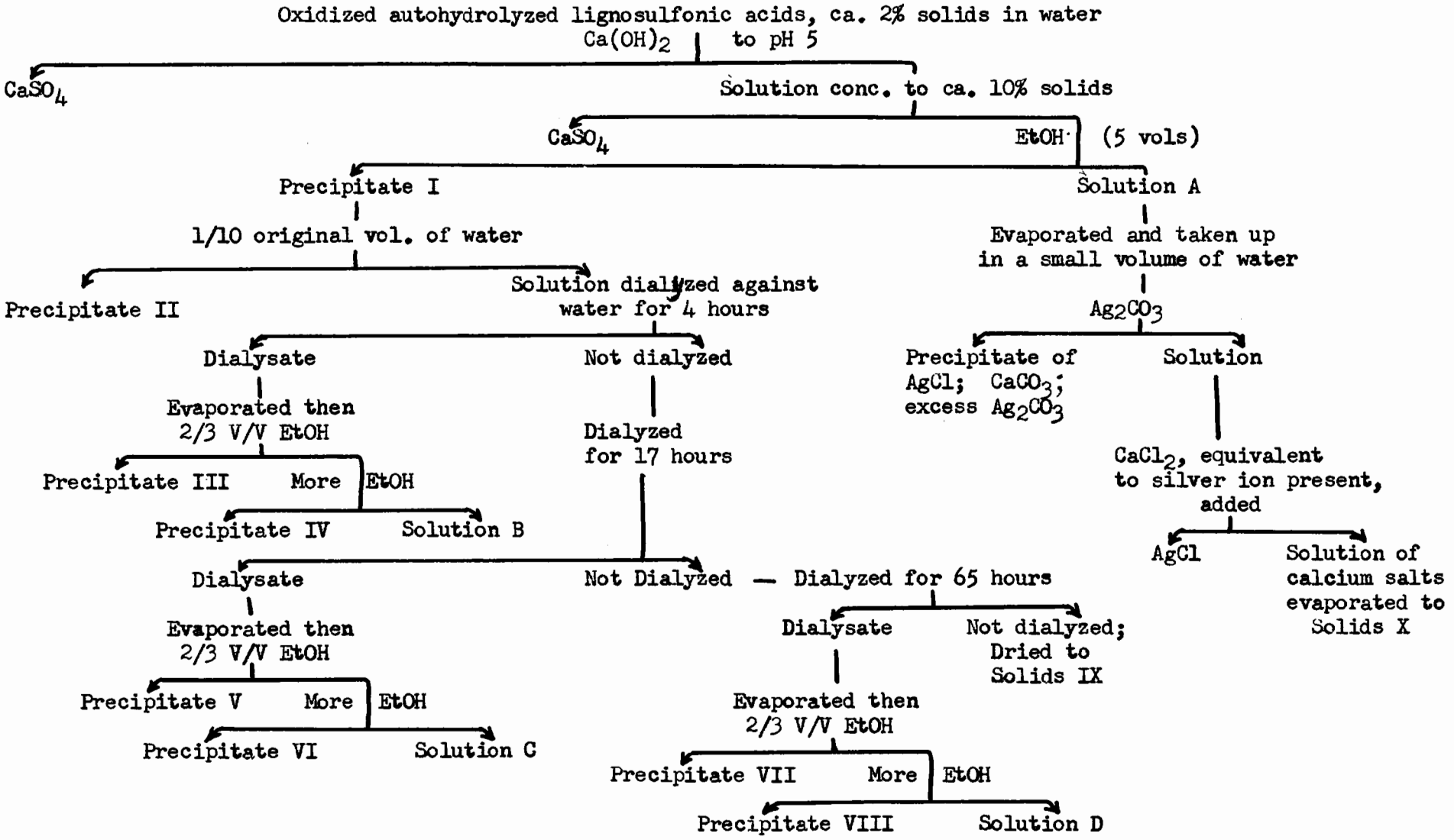
ANALYTICAL DATA FOR THE CALCIUM LIGNOSULFONATES SEPARATED AS IN FIGURE 6

Nomenclature of Material (from Fig. 6)	Precipitates							Solids		
	II	III	IV	V	VI	VII	VIII	IX	X	XI
Sulfur, %	7.1	4.7	6.3	2.8	5.4	5.4	5.6	5.0	2.5	4.5
Calcium, % (a)	17.6	13.7	15.5	14.2	14.0	13.6	14.2	19.0	15.7	17.8
Molar Ratio of Calcium to Sulfur of	3.1	3.7	3.1	6.3	3.2	3.1	3.2	4.8	7.8	5.0

(a) From sulfated ash

The molar ratio of sulfur and calcium in these materials (Table VI) appeared to indicate, if the calcium were bound bivalently to the lignin, a ratio of 5 carboxylic acid or other acidic groups to 1 sulfonic acid group in the case of precipitates II, III, IV, VI, VII and VIII (from Figure 6). It was likely, however, in view of the conditions of precipitation (pH 5) that the precipitate existed partly as a basic salt of calcium with groups of the type $-SO_2O-Ca-OH$ and $-COO-Ca-OH$

FIGURE 6 — THE PRELIMINARY SEPARATION OF THE CALCIUM LIGNOSULFONATES



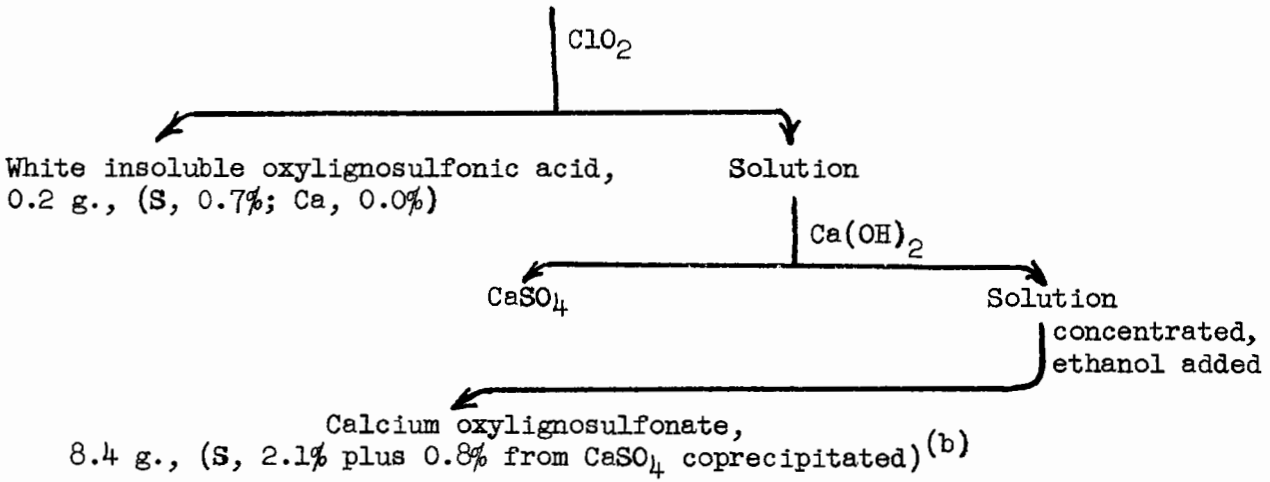
Solutions B, C, and D were combined and treated as Solution A was treated to give Solids XI.

attached to the lignin residue. This circumstance would have decreased the ratio of sulfonic acid groups to carboxylic acid groups to 1:2. If, as was most probable, there was a mixture of both these forms, then the ratio would have been somewhere between these limits for the above mentioned precipitates. Only one precipitate (V) and one of the solids (X) seemed widely outside this range and outside the rather narrow range of sulfur content of between 4.7 and 7.1%. It would appear, then, that no major variation in sulfur content was obtained in this fractionation, although the precipitated fractions appeared to be richer in sulfur than the original ethanol-soluble materials (solids X). This increased sulfur content was caused by coprecipitated calcium sulfate, because the separation was carried out before the necessity was seen for a change in procedure to eliminate the use of sulfur dioxide as a reducing agent for the by-product oxy-acids of chlorine produced in the oxidation. Nevertheless, the work was not entirely invalidated, for the coprecipitated calcium sulfate would change the calcium-sulfur ratio in the direction of more carboxylic acid groups per sulfonic acid group.

Various attempts were then made to separate the lignosulfonate from the chlorides, sulfates and other inorganic salts with which they were associated. The precipitation of another sample of calcium oxylignosulfonate is outlined in Figure 7.

FIGURE 7

FRACTIONATION OF A CALCIUM OXYLIGNOSULFONATE



(a) In solution.

(b) Corresponding to 8.1 g. of calcium oxylignosulfonate, (S, 2.1%; Ca, 11.2%; Cl, 7.0%; OCH_3, 3.0%) mixed with 0.3 g. of $CaSO_4$.

On treatment of some of the final material in Figure 7 with sodium carbonate-sodium hydroxide buffer (pH 11.5) for one week, a fraction which represented two-thirds of the material was reduced from 7% chlorine to 0.6% chlorine. The sulfur content of the same fraction apparently decreased from 2.1% to 1.9%, but correction for extra ash in the sample showed that the value had remained unchanged. Similarly when the same sample was treated with a saturated solution of calcium hydroxide at pH 11.6 for one week four-fifths of the material was isolated with a chlorine content of 1.4%, in contrast to the 7% in the original material. Once more the sulfur content, determined by subtraction of the sulfur recovered as soluble sulfate ion from the total percentage of sulfur, and corrected for the extra amount of ash in the reprecipitated material, remained unchanged.

Hence the greater part of the chlorine introduced by the chlorine dioxide oxidation was labile to bases and was probably not attached to aromatic rings. However, chloroquinones lose all or part of the chlorine substituted in the ring on treatment with dilute alkali (94, 95, 96, 97) and there might also have been replacement of aliphatic chlorine. The lability of the chlorine in this sample was analogous to that of the chlorine in the oxylignin γ of Levitin, Thompson and Purves (57) and the material itself was probably analogous. The stability of sulfur content to alkali, was as expected of sulfonate groups attached either to the aliphatic or aromatic portions of the molecule. The results tended to eliminate the possibility that any of the

sulfur was in the form of bisulfite addition compounds would have been decomposed by base.

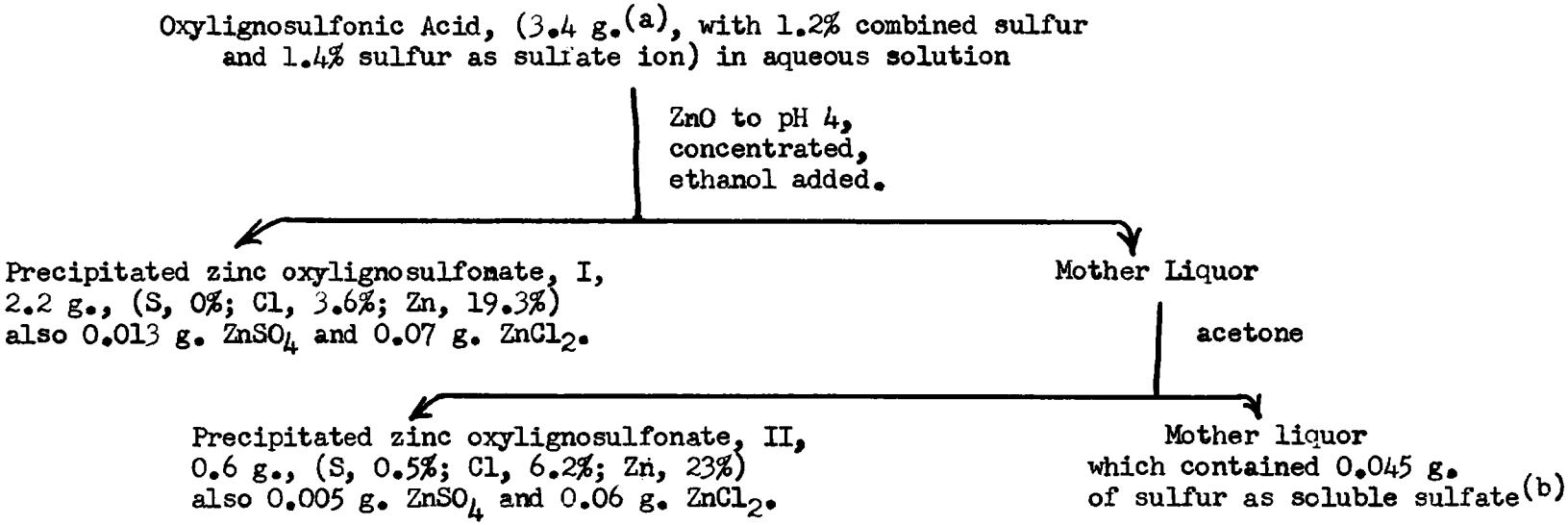
Some of this material when washed with glacial acetic acid incurred a 10% loss in weight, but no loss of sulfur, indicating that the sulfur-containing portion could be enriched in this way. This would not be a satisfactory method for removing calcium sulfate, although it would remove calcium acetate.

The following flow sheet, Figure 8, contains the results for a precipitation of an oxylignosulfonic acid with zinc oxide. The soluble material could not be isolated because the chlorate and chlorite salts present as by-products from the chlorine dioxide decomposed violently when an attempt was made to dry the residue. It was obvious that the precipitation separated fractions with no or very little sulfur, probably as basic zinc polycarboxylic acid salts.

One of the difficulties up to this point in the work had been the removal of chlorite and chlorate as well as chloride ion. This problem was solved by treating the oxidized solution with a little cold hydriodic acid, which reduced any chlorites and chlorates to chloride without introducing any new cations. The iodine formed was rapidly removed by extraction with ether. It was presumed that no iodination occurred in the strongly acid solution and that none of the lignosulfonic acid was extracted in the ether. The aqueous residue now contained hydrochloric acid, hydriodic acid, oxylignosulfonic acid

FIGURE 8

FRACTIONATION OF A ZINC OXYLIGNOSULPHONATE



(a) The concentration of the solution and therefore the weight of oxylignosulfonic acid in the volume used was determined by drying an aliquot in vacuo over P_2O_5. This dry material was analyzed for total sulfur. From another aliquot of the solution $BaSO_4$ was precipitated to give the sulfate sulfur. Combined sulfur was assumed to be the difference between total sulfur and the sulfur determined as soluble sulfate.

(b) Here, by difference from the amount of sulfur in the original lignin, 0.037 g. remained combined with organic material whose amount was estimated at about 1 g. Hence this portion must have contained more than 3% of sulfur organically combined.

and sulfuric acid from sulfonic acid groups split off during the oxidation. Treatment with silver carbonate precipitated the silver halides, but not the sulfate, because silver sulfate was soluble enough in the concentrations concerned. This assertion was verified by extracting the residue of silver halides and excess carbonate with hydrochloric acid and by testing the extract with barium chloride. Dilute hydrochloric acid was added to the original liquor to an amount exactly equivalent to the amount of silver ion present, leaving only sulfuric acid and the oxylignosulfonic acids. This was the solution used in the next two series of fractionations.

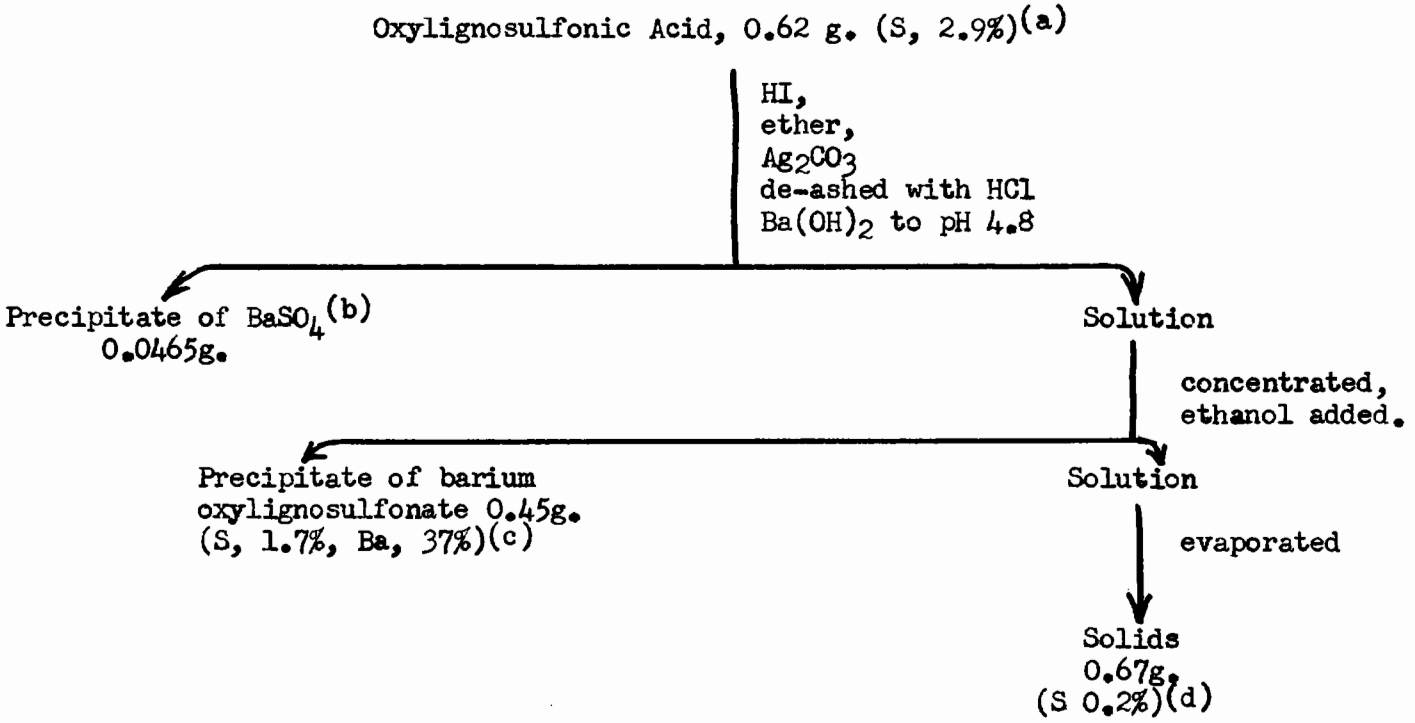
The first of these fractionations resulted in the isolation of a barium oxylignosulfonate with the analyses given in Figure 9.

When allowance was made for the barium content of 37%, the free oxylignosulfonic acid had a sulfur content of 2.7% and the weight about 45% of the 0.62 g. of lignosulfonic acid oxidized. The soluble material, isolated by concentrating the mother liquor to dryness, was practically free of sulfur. As the footnotes to Figure 8 show, 6.4/18 or 36% of the original sulfur was recovered as free sulfuric acid which was isolated as the barium salt, and 7.6/18 or 42% as the barium oxylignosulfonate. The total recovery was thus about 80%.

In the preceding precipitation as zinc salts, about 55% of the original sulfur was converted to sulphuric acid by the

FIGURE 9

ISOLATION OF A BARIUM OXYLIGNOSULFONATE



(a) Total, 18.0 mg. S.
(b) Accounting for 6.4 mg. S.
(c) Accounting for 7.6 mg. S.
(d) Accounting for 0.1 mg. S.

oxidation with chlorine dioxide. These results might be attributed either to the final breakdown of small sulfur-containing fragments, or to an oxidative attack on carbon-sulfur links which removed sulfonic acid groups directly.

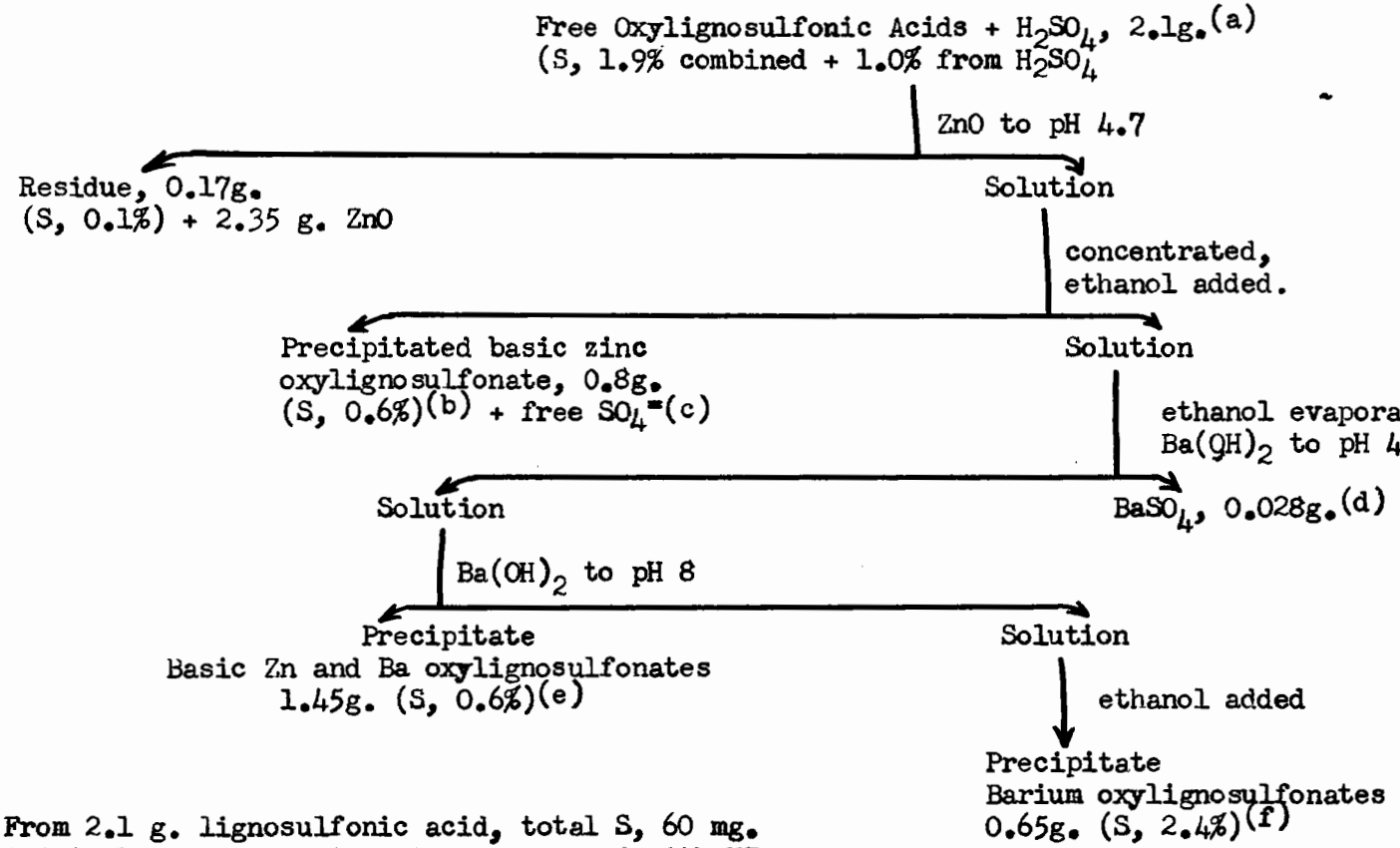
In an attempt to separate fractions richer and poorer in sulfur, a mixed precipitation with zinc oxide and then with barium hydroxide was carried out. Figure 10 and its footnotes show that the oxylignosulfonate contained 37.5% of barium, and thus the 2.4% sulfur reported represented about 4% of sulfur on the organic portion considered alone. Since free chloride ion was present at this point, even the brief treatment with barium hydroxide at pH 8 was enough to split off some of the chlorine from the molecule.

From these results, it would appear that the oxidation of a lignosulfonic acid with chlorine dioxide removed from 30 to 60% of the sulfur as sulfuric acid, and created at least two carboxylic acid groups for each sulfonic acid group left in the molecule. Since the organic products could be separated by zinc oxide precipitation into fractions containing more and less sulfur, it seemed likely that at least two different kinds of sulfonic acid group, or at least two different lignosulfonic acids, were present in the Stage II lignosulfonic acid that was oxidized.

The chlorination that occurred during the oxidation

FIGURE 10

FRACTIONATION AS ZINC AND BARIUM OXYLIGNOSULFONATES



(a) From 2.1 g. lignosulfonic acid, total S, 60 mg. Original ClO_2 oxidation mixture reduced with HI and freed of halides by Ag_2CO_3 (see Fig. 9)

(b) corresponding to 5 mg. S.
(c) corresponding to 20 mg. S.
(d) corresponding to 4 mg. S.
(e) corresponding to 9 mg. S. Free sulfate ion was absent.
(f) corresponding to 16 mg. S; Ba, 37.5%; Cl, 2.3% combined and 1.1% as chloride ion.

would also appear to have been of two different types, since some was labile to alkali, like aliphatic chloride or chloroquinones, while some was more stable. Only 20% of the original lignosulfonic acid was ready dialyzable, but on chlorine dioxide oxidation this figure was increased to 85%. Hence the oxidation reduced the average molecular weight substantially, although 1% to 3% of the sample remained as an insoluble oxylignosulfonic acid.

It would appear then that the bleaching action of chlorine dioxide on residual waste sulfite liquor or on insoluble lignosulfonic acids in a pulp might be more than just the breaking down of the lignin molecule into smaller, more soluble and less coloured fragments. It may include as well the introduction of a large number of carboxylic acid groups into the pieces, thus making them more soluble in alkaline wash waters, even though the oxidation may have removed up to 60% of the sulfonic acid groups from the lignin molecule. The concomitant chlorination would have little effect on solubility except that on alkaline washing many of the chlorine atoms might be replaced by hydroxyl groups, thus rendering the higher molecular weight fragments still more soluble in the alkali. On the other hand, condensation to larger entities might occur under the influence of base, similar in nature to the base-induced condensation of the oxylignins β and γ of Levitin, Thompson and Purves (57).

Attempts were also made to obtain a sulfur balance after oxidizing a calcium lignosulfonate with calcium hypochlor-

ite buffered to pH 11.5 with calcium hydroxide, but traces of calcium sulfate in the reagents made the determinations too inaccurate to be of significance.

Ultraviolet and Difference Spectra

The ultraviolet spectra of the lignin derivatives described in Table VII were all taken in aqueous solutions buffered to pH 7.0 with phosphate. These spectra (Figures 11, 12 and 13) were plotted with the percentage extinction coefficient", $E^{\%}_{cm.}$, as the ordinate, where $E^{\%}_{cm.} = \frac{\text{Absorbance}}{c \cdot l_c}$, c being the concentration in grams per 100 g. of solvent and l_c the cell path length in centimeters.

According to Flaig, (100) "the conditions during humification of organic substances in the soil point to the possibility that lignin might have been one of the precursors in the formation of humic acids. The first stage in the degradation of lignin was connected with the loss of methoxyl groups which resulted in the formation of phenolic substances. This was the justification for the use of polyphenols for making synthetic humic acids".

A subsequent stage in the degradation might involve the transformation of the humic acids to coals (99). Since the initial stage involved an oxidative demethylation, the product, "humic acid" might have some similarities to the oxylignins produced by chlorine dioxide or alkaline hypochlorite.

TABLE VII

SAMPLES WHOSE ULTRAVIOLET SPECTRA WERE STUDIED

1. A Calcium Lignosulfonate whose absorption spectrum was supplied by Dr. G.A. Allen of the Pulp and Paper Research Institute of Canada.

2. An Autohydrolyzed Lignosulfonic Acid, (OCH_3, 11.9%; S, 3.1%).

3. A Calcium Oxylignosulfonate, (OCH_3, 3.6%; S, 2.1%; Ca, 13.3%), the calcium salt of an autohydrolyzed lignosulfonic acid which had been oxidized with chlorine dioxide.

4. A Synthetic Humic Acid prepared by the oxidation of hydroquinone in basic solution with potassium persulfate (101).

5. A Hypochlorite Oxylignin (OCH_3, 9.3%; Cl, 5.0%) Prepared by the exhaustive oxidation of periodate lignin for 160 hours by Dr. W. Sacks (5).

6. A Chlorine Dioxide Oxylignin β, (OCH_3, 4.9%; Cl, 9.0%) Prepared by Dr. N.S. Thompson and designated Expt. 10, Table 1, Ref. (57).

7. A Hypochlorite Oxylignin Calcium Sulfonate, (OCH_3, 7.7%) S, 6.3%, Ca, 10.2%). Item 5, sulfonated and precipitated as the calcium salt.

8. A Chlorine Dioxide Oxylignin Calcium Sulfonate, (OCH_3, 4.9%; S, 8.9%; Ca, 10.4%). Item 6, sulfonated and precipitated as the calcium salt.

9. An Autohydrolyzed Lignosulfonic Acid, (OCH_3, 10.8%; S, 3.1%), which had been autohydrolyzed for 1 hour. (Table IV).

10. An Autohydrolyzed Lignosulfonic Acid, (OCH_3, 11.4%; S, 3.7%), which had been autohydrolyzed for 15 hours. (Table IV).

Figure 11, containing Items 1, 2 and 3, Table VII, indicated that the autohydrolyzed lignosulfonic acid had the characteristic peak at 280 mμ, but that oxidation of this material removed this peak (plot 3, Fig. 11). Previous workers have emphasized this effect of oxidation. For the sake of comparison a calcium lignosulfonate was included.

Figure 12, containing Items 1, 4, 5 and 6, Table VII, again showed the effect of oxidation on the peak at 280 mμ. In the case of the chlorine dioxide oxylignin (plot 6, Fig. 12) the peak was suppressed to a shoulder, but in the hypochlorite oxylignin case (plot 5) superimposed shoulders near 270 mμ and at 300 mμ overshadowed the usual peak at 280 mμ. They might be related to the slight inflections in plot 4 for humic acid at these points. Otherwise, the humic acid was apparently not closely related to the lignins with regard to the band at 280 mμ. These two figures confirm the fact that the use of the ultraviolet spectra for the determination of lignin in bleached pulps, as suggested, for example, by Bethge and co-workers, (98) cannot be valid. Oxidized lignin, although it might be present, would not give the peak at 280 mμ.

The effect of oxidation upon the ultraviolet spectra before or after sulfonation is apparent in Figure 13. In the case of the chlorine dioxide oxylignins (plots 6 and 8) sulfonation after oxidation did not appear to affect the shape of the plot, only changing the extinction coefficient. This change might have been caused by the difference between the molecular

FIGURE 11.

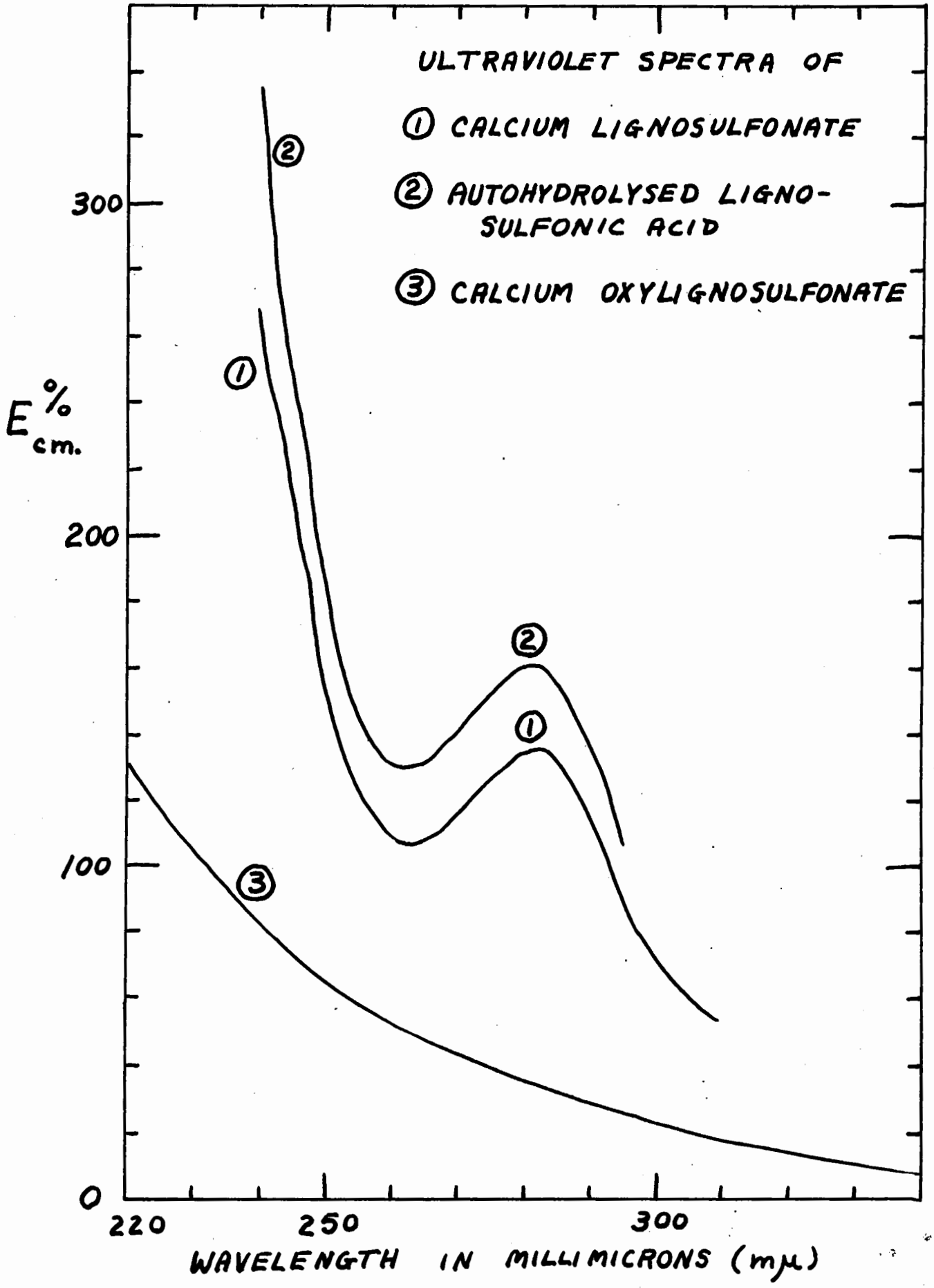

ULTRAVIOLET SPECTRA OF
① CALCIUM LIGNOSULFONATE
② AUTOHYDROLYSED LIGNO-SULFONIC ACID
③ CALCIUM OXYLIGNOSULFONATE
$E^{\%}_{cm.}$
300
200
100
0
220
250
300
WAVELENGTH IN MILLIMICRONS (mμ)

FIGURE 12.

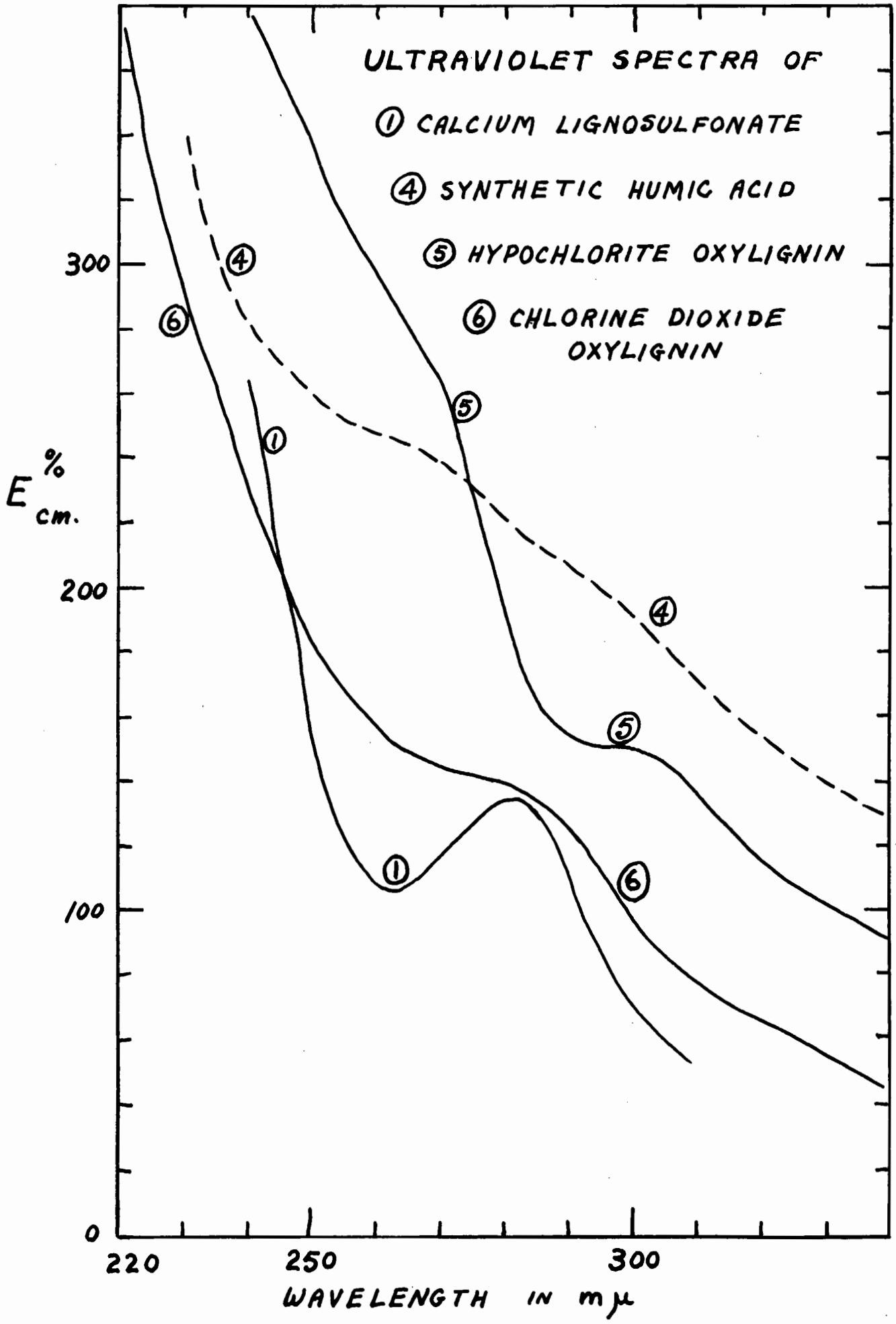
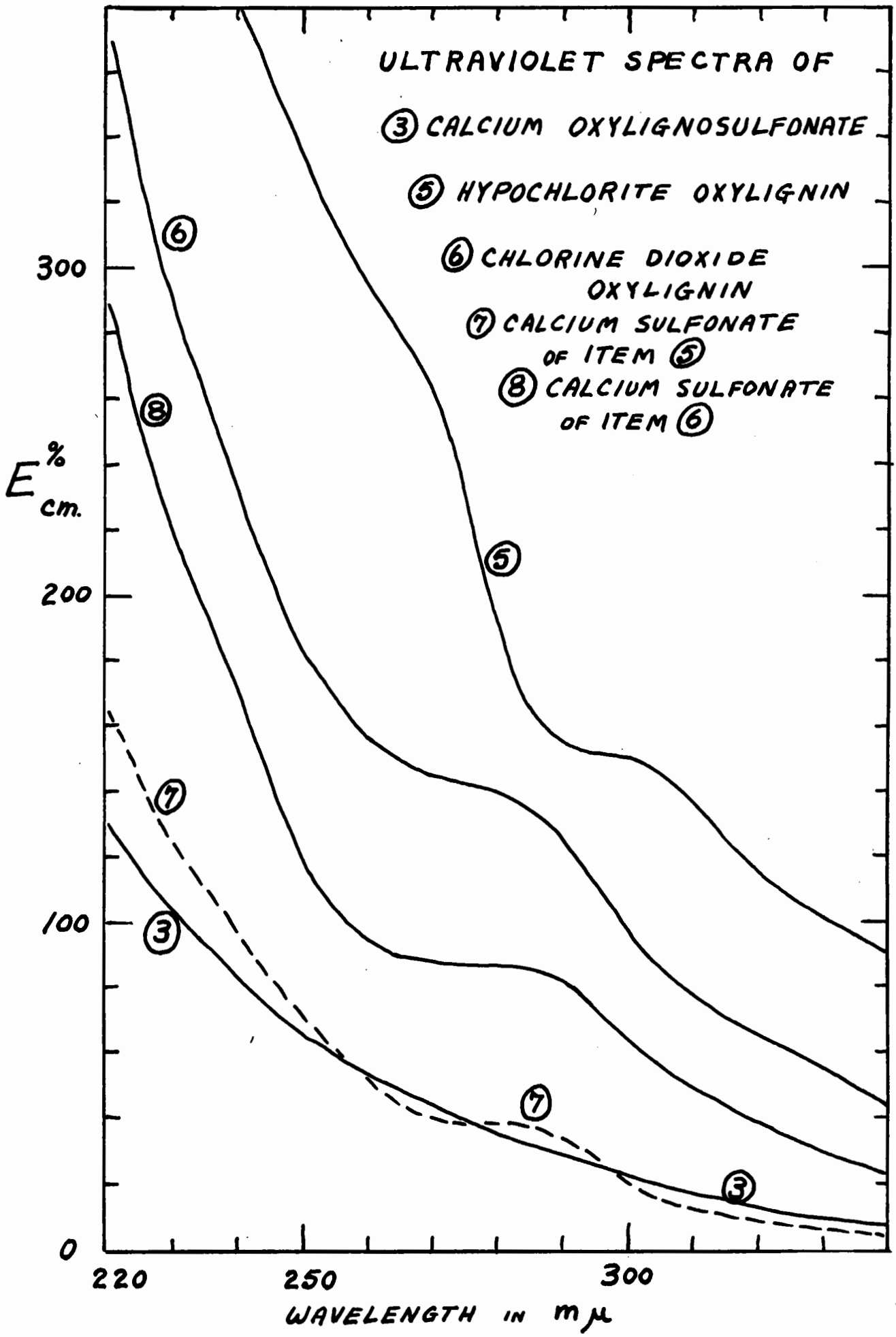

ULTRAVIOLET SPECTRA OF
① CALCIUM LIGNOSULFONATE
④ SYNTHETIC HUMIC ACID
⑤ HYPOCHLORITE OXYLIGNIN
⑥ CHLORINE DIOXIDE OXYLIGNIN
E % cm.
300
200
100
0
220
250
300
WAVELENGTH IN mμ

FIGURE 13.


ULTRAVIOLET SPECTRA OF
③ CALCIUM OXYLIGNOSULFONATE
⑤ HYPOCHLORITE OXYLIGNIN
⑥ CHLORINE DIOXIDE OXYLIGNIN
⑦ CALCIUM SULFONATE OF ITEM ⑤
⑧ CALCIUM SULFONATE OF ITEM ⑥
$E^{\%}_{cm.}$
300
200
100
0
220
250
300
WAVELENGTH IN mμ

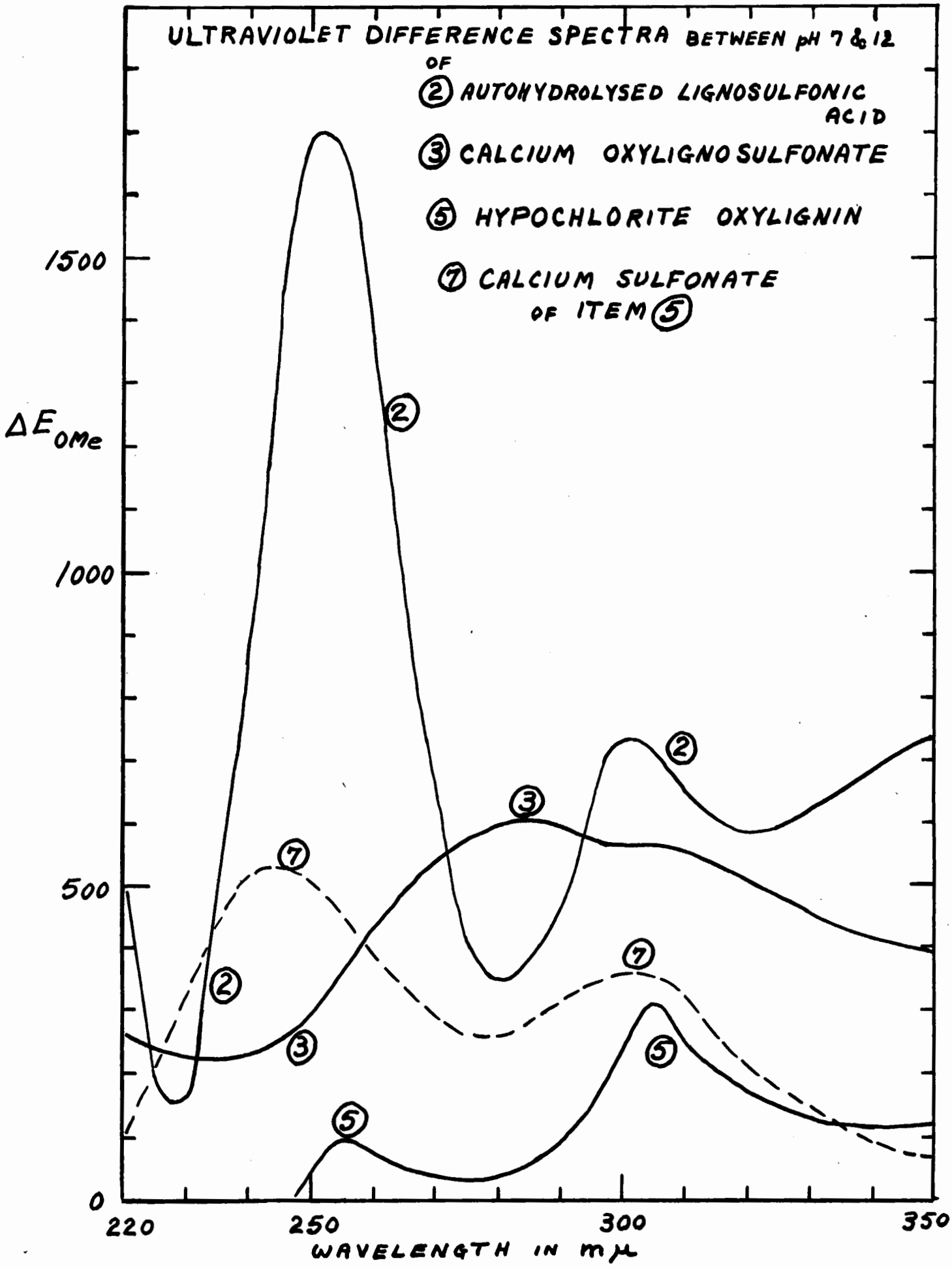
weight of the unsulfonated oxylignin and that of the calcium salt of the sulfonated material. Sulfonation of the lignin, then oxidation, changed the plot considerably by removing any trace of the peak at 280 mμ (see Fig. 11). The hypochlorite oxylignin (plot 5, Fig. 13) on sulfonation lost the subsidiary shoulders at 270 mμ and 300 mμ and became similar in shape to the other sulfonated oxylignins (plot 7). Perhaps sulfonation removed quinone-like groups which might have been responsible for the shoulders observed in the spectrum of the hypochlorite oxylignin, and left exposed the normal peak (now reduced to a shoulder) at 280 mμ. These observations confirmed those of previous workers on the change of ultraviolet spectra after the oxidation of lignins (57)(5) and the fact that sulfonation did not influence the maximum at 280 mμ to any extent (55).

Following the methods of Aulin-Erdtman (55) the differences between the extinction coefficients at pH 12 and at pH 7 were plotted against the wavelength. These plots are given in Figures 14, 15, 16 and 17. In the first three of these figures, however, the extinction coefficients were calculated to Aulin-Erdtman's "methoxy molar" concentration (77) which she defined as

$$\frac{(\%\ \text{Methoxyl in sample})\ (\text{Grams of sample per litre})}{\text{Mol. wt. of } OCH_3}\ .$$

In Figure 14, the difference plots for Items 2, 3, 5 and 7 of Table VII are given. The hypochlorite oxylignin (plot 5) was dissimilar to the difference spectra of the lignin

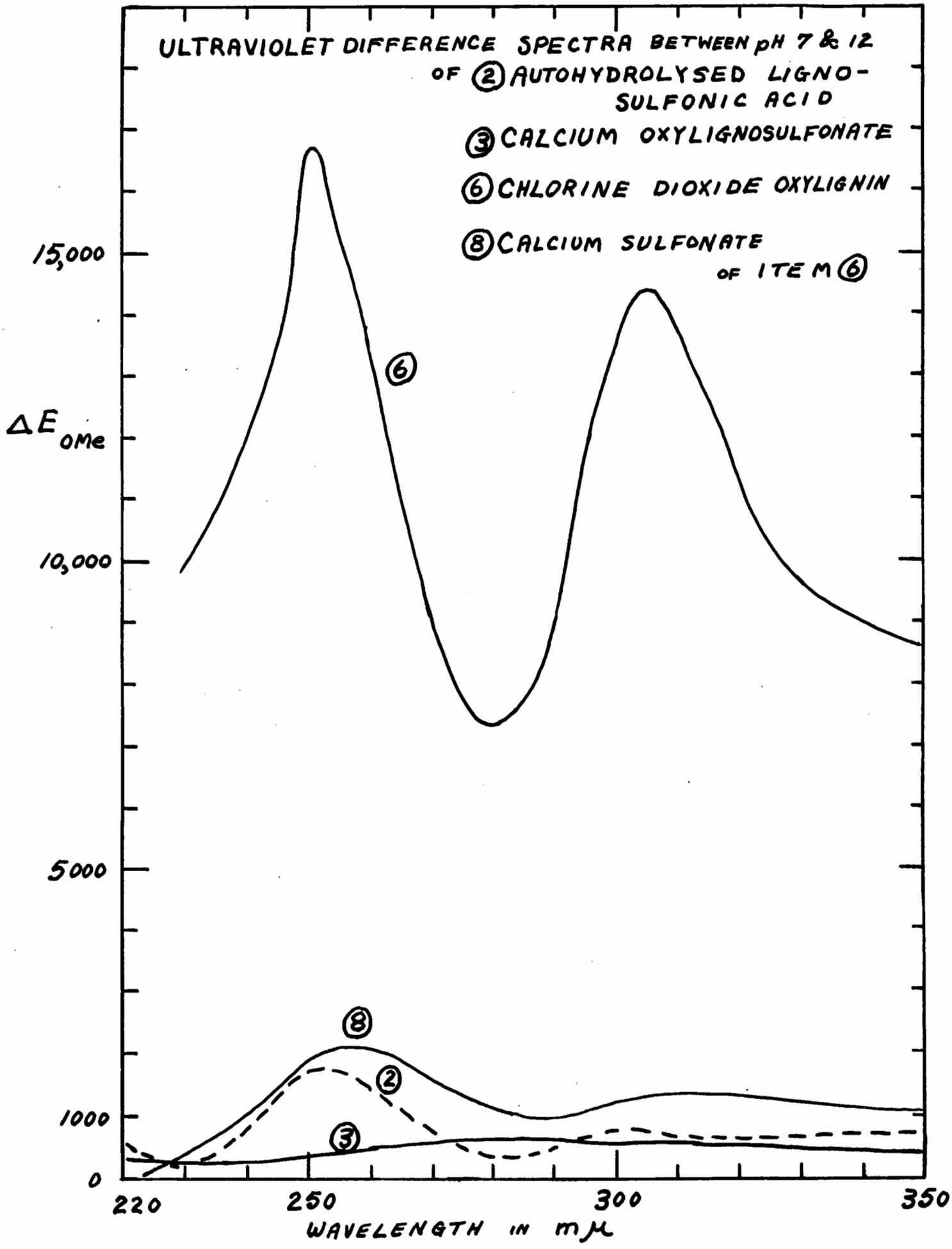
FIGURE 14.


ULTRAVIOLET DIFFERENCE SPECTRA BETWEEN pH 7 & 12 OF
② AUTOHYDROLYSED LIGNOSULFONIC ACID
③ CALCIUM OXYLIGNOSULFONATE
⑤ HYPOCHLORITE OXYLIGNIN
⑦ CALCIUM SULFONATE OF ITEM ⑤
ΔE OMe
1500
1000
500
0
220
250
300
350
WAVELENGTH IN mμ

model substances used by Aulin-Erdtman (81), but on subsequent sulfonation (plot 7) the difference spectrum resembled those obtained for most lignins. A possible explanation would be that hypochlorite oxylignin existed as a quinone-like modification yielding sulfonated hydroquinone-type units, which then would act toward base in a fashion analogous to the phenolic model compounds. The lignosulfonic acid which had been oxidized with chlorine dioxide (plot 3) apparently was oxidized in a different fashion than the hypochlorite oxylignin.

From Figure 15, embodying Items 2, 3, 6 and 8 from Table VII, and with a different ΔE_{OMe} scale, it was apparent that the salt of a chlorine dioxide oxidized lignosulfonic acid (plot 3) was not at all similar to the chlorine dioxide oxylignin (plot 6, Fig. 15) nor to the same oxylignin after it had been sulfonated (plot 8). Perhaps, then, oxidation with chlorine dioxide occurred in a different way with the sulfonated lignin than with the lignin itself. Another interpretation would be that the oxidation of the lignosulfonic acid had been more severe. This material (Item 3, Table VII) indeed was more analogous to the extensively oxidized oxylignin γ of Thompson (57) than to the oxylignin β with which it was being compared here. Sulfonation of the chlorine dioxide oxylignin did not change the peaks of the ΔE_{OMe} (plot 6) very much, although the difference coefficients of the resulting plot (plot 8) were very much less.

FIGURE 15.

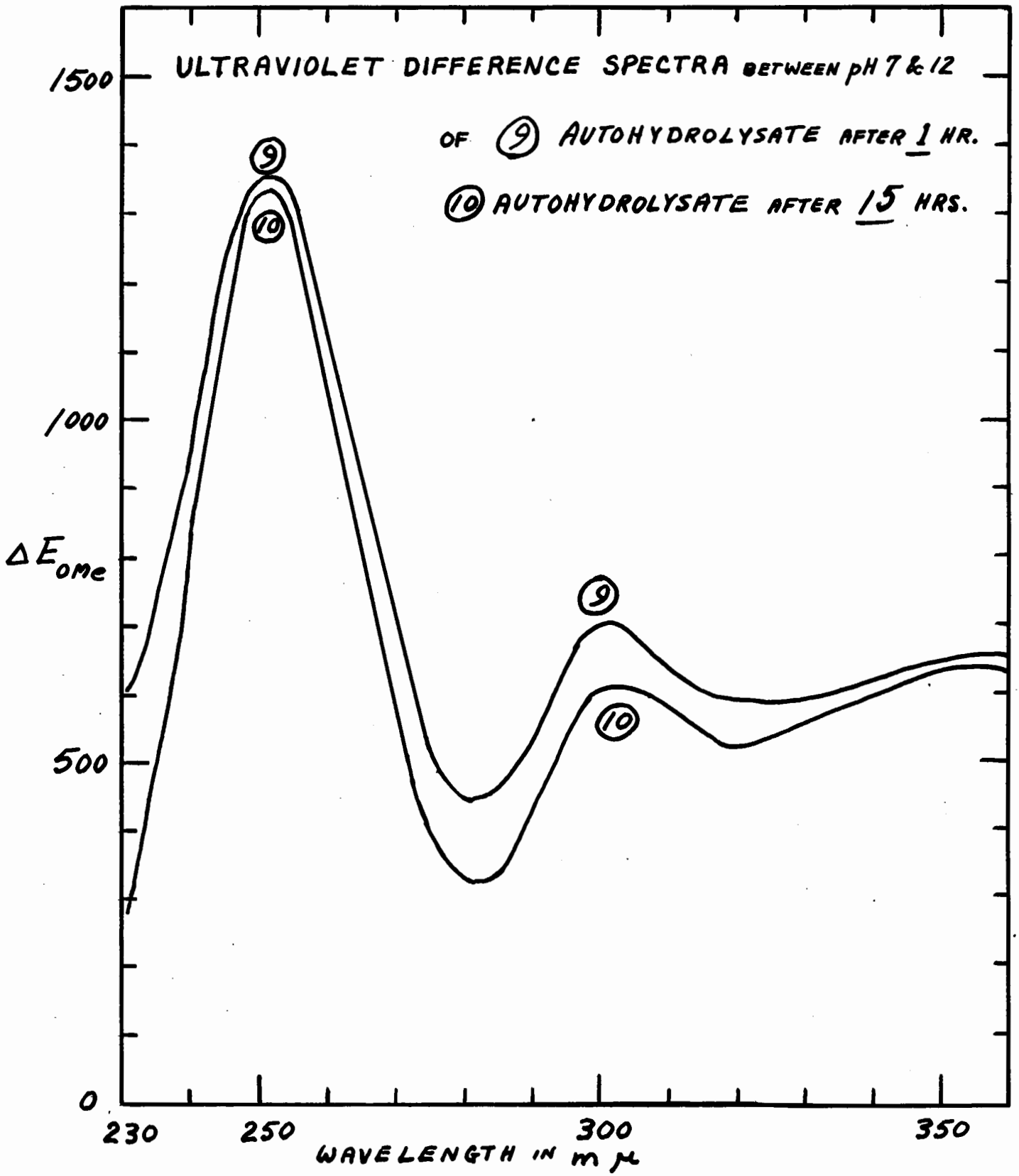

ULTRAVIOLET DIFFERENCE SPECTRA BETWEEN pH 7 & 12
OF ② AUTOHYDROLYSED LIGNO-SULFONIC ACID
③ CALCIUM OXYLIGNOSULFONATE
⑥ CHLORINE DIOXIDE OXYLIGNIN
⑧ CALCIUM SULFONATE OF ITEM ⑥
15,000
10,000
5000
1000
0
ΔE 0me
220
250
300
350
WAVELENGTH IN mμ

Plots 3 (Figs. 14 and 15) for the lignosulfonic acid oxidized with chlorine dioxide could not be used to determine the ratio of hydroxyl groups to methoxyl groups by the method of Aulin-Erdtman, since they were not similar in shape to the difference plots for the model substances used (81). Apparently, the extensive oxidation destroyed the structures which contributed phenolic hydroxyl groups ionizable between pH 7 and pH 12. These ions were capable of entering into resonance in such a way as to give the maxima observed in the ultraviolet difference spectra of the model compounds used by Aulin-Erdtman.

Plots 8 and 6 (Fig. 15) for the chlorine dioxide oxylignin, sulfonated and unsulfonated, and plot 7 (Fig. 14) for the hypochlorite oxylignin when sulfonated, were quite suitable for estimating the phenolic hydroxyl/methoxyl ratio by Aulin Erdtman's method (see below), but plot 5 (Fig. 14) for the hypochlorite oxylignin was not strictly analogous.

Figure 16, containing Items 9 and 10, Table VII, was included to illustrate the negligible difference between the Stage II lignosulfonic acids obtained after 1 hour and after 15 hours' autohydrolysis. The ratio of methoxyl groups to phenolic hydroxyl groups was also calculated for these substances. In describing the method of calculation, Aulin-Erdtman (55) stated that C, the number of ionized, non-conjugated phenolic groups per 100 methoxyl groups, was given approximately by

FIGURE 16.

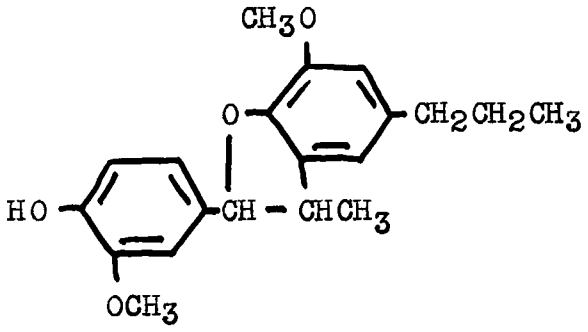

ULTRAVIOLET DIFFERENCE SPECTRA BETWEEN pH 7 & 12
OF (9) AUTOHYDROLYSATE AFTER 1 HR.
(10) AUTOHYDROLYSATE AFTER 15 HRS.
1500
1000
500
0
ΔE ome
9
10
9
10
230
250
300
350
WAVELENGTH IN mμ

$$C = \frac{100\,\Delta E_{OMe} \text{ of sample at a maximum in the difference spectrum}}{\Delta E_{OMe} \text{ at the same maximum in the model compound}}$$

The values of C calculated from the maxima were very close to those calculated from other corresponding wave lengths throughout the spectrum, but the observational errors in the difference spectra were least at the maxima. In the present thesis it was convenient to use the abridged calculation using only the maxima, and to find n, the number of methoxyl groups per phenolic element, instead of C, the value n = 100/C or

$$n = \frac{\Delta E_{OMe} \text{ for model compound at a difference maximum}}{\Delta E_{OMe} \text{ for sample at same maximum}}$$

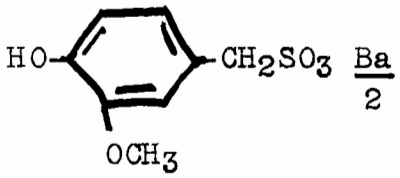
If this equation was applied to a model substance like dihydrodehydrodi-isoeugenol, (XIV), then the result was n = 1, but from the formula the number of methoxyl groups per



XIV

phenolic hydroxyl group was 2. A factor of 2 should have been introduced to adjust model compounds which had 2 methoxyl for each phenolic hydroxyl group to the same terms as those with

the ratio 1:1, such as barium 4-hydroxy-3-methoxytoluene sulfonate (XV). The present Thesis assumes that this factor had



XV

been introduced, although there was no evidence of this in the references (79, 80, 81, 55). The model substances used were XIV and XV, the difference spectra for these compounds having been given in reference (81) in Figure 1, plot I; Figure 2, plot VIII; and in reference (55) in Table III, Items A and G.

The data for the calcium lignosulfonate of Item 2, Table VII, for which the difference spectrum was given in plot 2, Figure 14, have been used to illustrate the calculation.

Using XIV as the model compound:

At the maximum at 250 mμ, n = 14,900/1,700 = 8.8

At the maximum at 300 mμ, n = 5,370/730 = 7.4

Using XV as the model compound:

At the maximum at 250 mμ, n = 10,500/1,700 = 6.2

At the maximum at 300 mμ, n = 3,910/730 = 5.4

The conclusion was that the number of methoxyl groups per phenolic hydroxyl group was between 5 and 9. This value was within the

limits found for a representative barium lignosulfonate in Aulin-Erdtman's work, namely, n = 5 to 7 (55). Table VIII summarizes the data for all samples whose difference spectra resembled those of the two model compounds.

The ordinary lignosulfonic acids had a range of ratios of methoxyl to phenolic hydroxyl groups which was essentially the same as the range obtained by Aulin-Erdtman. As Figure 14 showed, the difference plot for the chlorine dioxide oxylignosulfonic acid did not bear enough resemblance to the plots of the other substances for the method to be applied. The hypochlorite oxylignin (Table VII, Item 5) was not closely analogous to the model compounds in difference spectrum, but it had maxima at about the same places and appeared to have only a small number of phenolic groups (n = 10 - 150). When sulfonated to give Item 7, the plot was closer to the usual shape, and the figures for n (10 - 30) suggested an increase in phenolic groups, although the number was still low, in relation to the methoxyl content. The deficiency would have been still more pronounced if the methoxyl content of the oxylignin (7.7%)had been as large as that (12%) of the parent lignosulfonic acid. These observations were consistent with the formation of quinone type groups from phenolic groups in the oxidation and this view was supported by the slight shift to longer wave length of the maxima in the difference spectra, a shift which also showed up in certain model compounds (81) when the ionized phenols were in a conjugated system. The difference ultraviolet spectrum

TABLE VIII

VALUES OF n, THE NUMBER OF METHOXYL GROUPS PER PHENOLIC HYDROXYL GROUP FOR CERTAIN COMPOUNDS IN TABLE VII

Item Number in Table VII	2	5	6	7	8	9	10
Value for n, using XIV as model							
At 250 mμ	8.8	149	0.9	28.2	7.3	11.0	11.2
At 300 mμ	7.4	17.3	0.4	15.1	4.1	7.7	8.8
Value for n, using XV as model							
At 250 mμ	6.2	105	0.6	19.8	5.1	7.8	7.9
At 300 mμ	5.4	12.6	0.3	11.1	3.0	5.6	6.4
Range of values for n	5-9	10-150	0.25-1.0	10-30	2-8	5-11	6-12

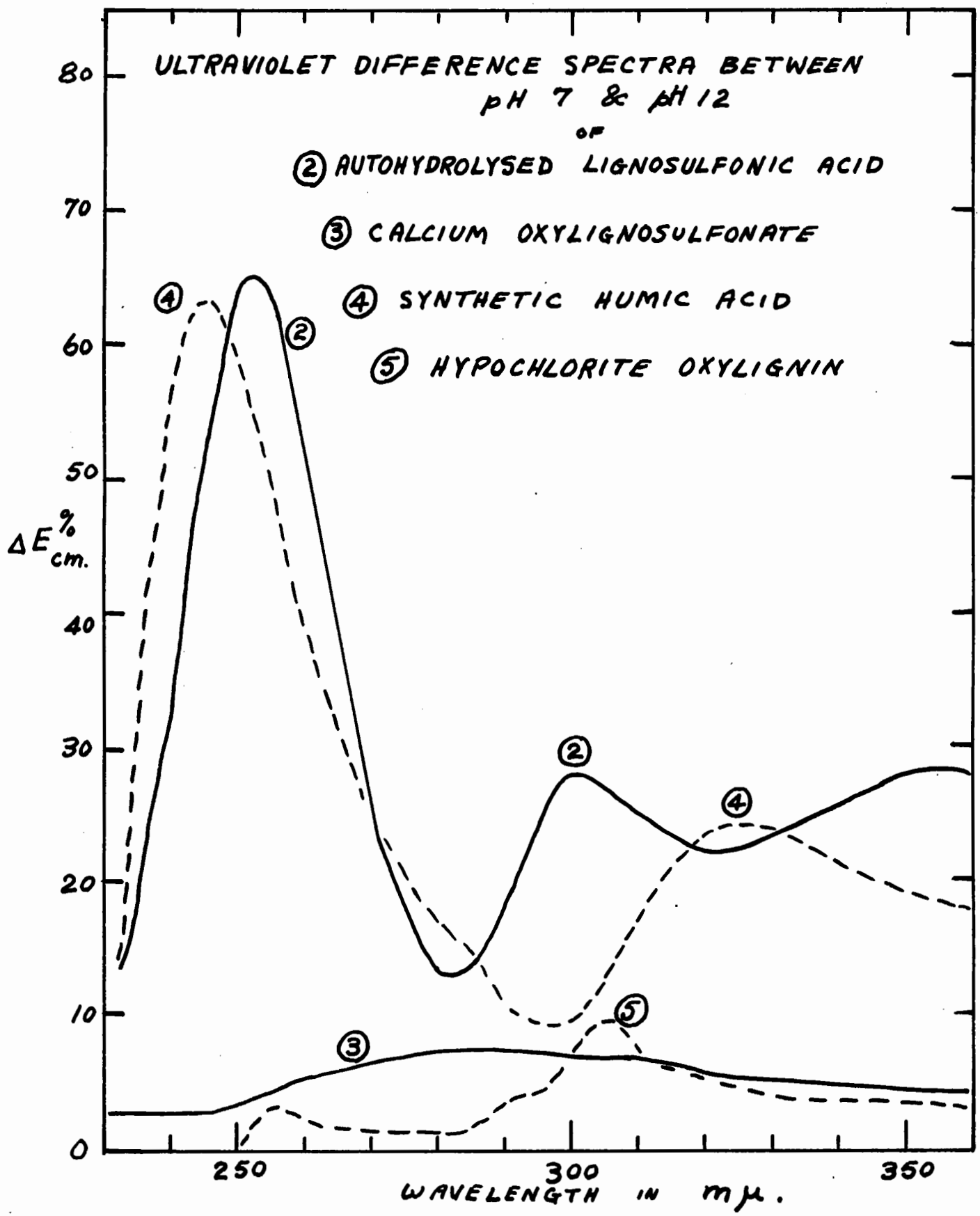
of this hypochlorite oxylignin was more analogous to those of such conjugated systems than to those of the regular model compounds, but sulfonation appeared to reverse the situation, again confirming the idea expressed earlier, that sulfonation of the hypochlorite oxylignin was the reduction and perhaps sulfonation of quinone-like rings.

On the other hand, the chlorine dioxide oxylignin (Item 6) showed a very low ratio of methoxyl to hydroxyl groups, (n = 0.25-1.0), there having been probably more phenolic than methoxyl groups. Even after sulfonation (Item 8) the value for

n (2-8) was small, although nearer the normal ratio. The analogy to the model compounds still held, indicating that the aromatic rings were still preserved, although extensively demethoxylated.

In Figure 17, the difference plots for synthetic humic acid are compared with those of hypochlorite oxylignin, autohydrolyzed lignosulfonic acid and the calcium salt from its oxidation with chlorine dioxide, (Items 4, 5, 2 and 3, respectively, from Table VII). The "percentage" extinction coefficient, $E^{\%}_{cm}$ was used here because the humic acid had no methoxyl content from which to calculate a E_{OMe} value. The comparison showed the resemblance between the synthetic humic acid (plot 4) and the normal type of difference curve obtained for lignins and lignosulfonic acids (plot 2). The contrast with the strongly altered hypochlorite oxylignin (plot 5) and with the lignosulfonic acid after oxidation with chlorine dioxide was marked. In other words, this humic acid, which resembled the polyhydroxy quinone in formula XIII, possessed phenolic hydroxyl groups similar to those of the lignins, since these groups were capable of causing a similar shift in the ultraviolet spectrum with change in pH. Erdtman (91) said that the hydroxyl groups in formula XIII were very acidic. Thus it might be that some of them would be ionized even at a pH as low as 7 and would only reveal themselves in difference spectra taken between, say, pH 2 and pH 7. Spectra were accordingly taken of all the items in Table VII at pH 2, and the difference spectra determined between pH 2 and pH 7 to

FIGURE 17.


ULTRAVIOLET DIFFERENCE SPECTRA BETWEEN
pH 7 & pH 12
OF
② AUTOHYDROLYSED LIGNOSULFONIC ACID
③ CALCIUM OXYLIGNOSULFONATE
④ SYNTHETIC HUMIC ACID
⑤ HYPOCHLORITE OXYLIGNIN
80
70
60
50
40
30
20
10
0
ΔE% cm.
250
300
350
WAVELENGTH IN mμ.

see if such ionization occurred and also contributed to resonance.

The difference spectra between pH 2 and pH 7, (Figure 18) for most of the oxylignins appeared to be a reprise of the difference spectra between pH 7 and 12. Apparently there were a few strongly acidic groups, either carboxylic or highly acidic phenols, which ionized between pH 2 and pH 7 and could contribute to the resonance enough to cause the observed difference in spectra. The hypochlorite oxylignin was a definite exception. As related before, it might have been a special quinone-type case, for its wide variance in difference spectrum from that of the other oxylignins between pH 2 and pH 7 was removed upon sulfonation (c.f. plots 5 and 7). The humic acid also showed the presence of some groups ionizable in this pH range (plot 4).

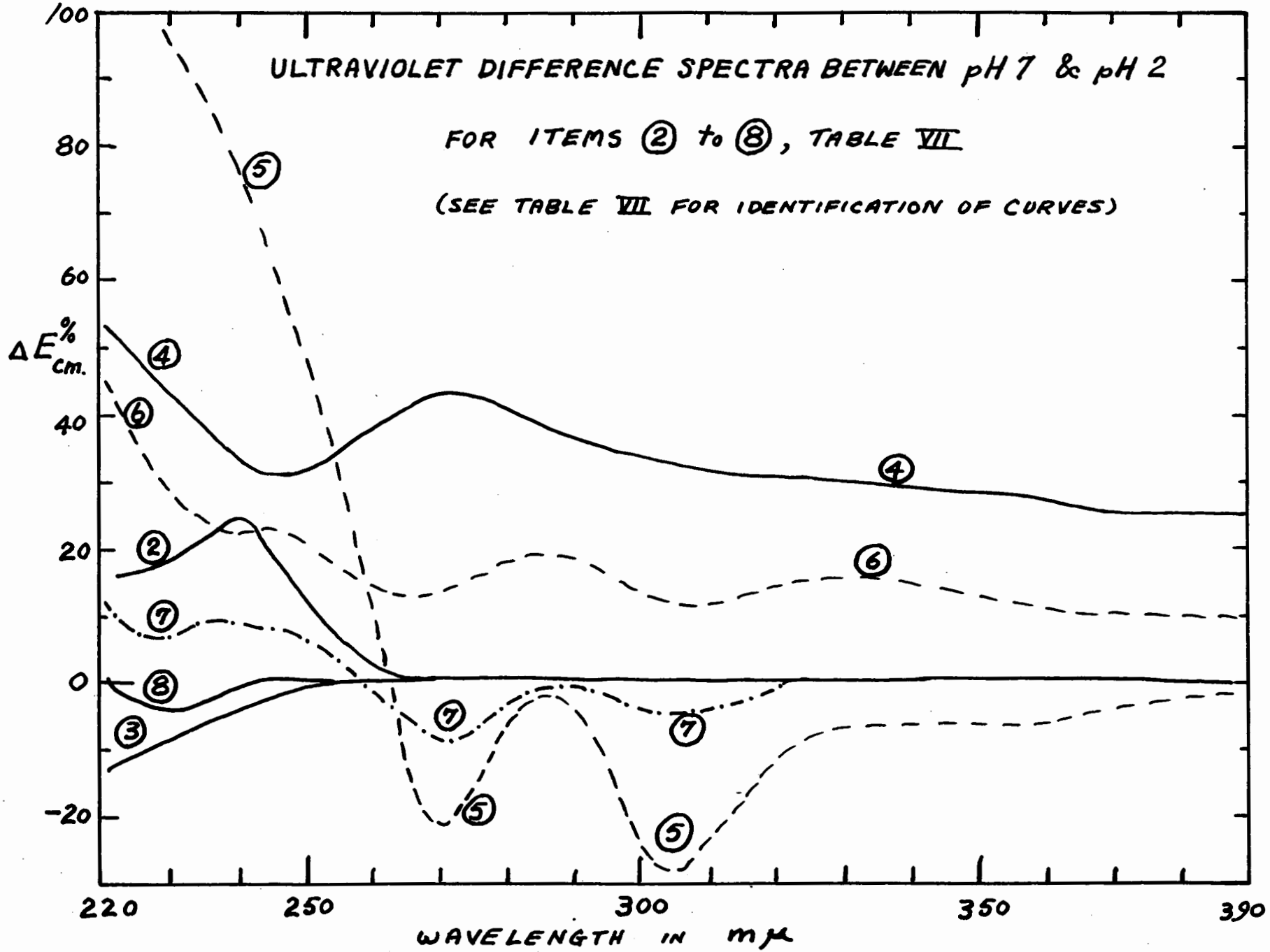
Infrared Spectra

Infrared spectra were kindly made for us by Miss Goodspeed of the Fuels Branch, Bureau of Mines, Ottawa, as mentioned in the Experimental Part, using the potassium bromide pellet technique, and apparent extinction coefficients, 1%, 1 cm., were calculated using the following formula

$$(E)^{\%}_{cm.} = \frac{\text{Absorbance}}{\text{Pellet length (cm.)} \cdot \text{Concentration (\% solid in KBr pellet)}}$$

where absorbance = $\log_{10}$(% transmission or transmittance)

FIGURE 18.


ULTRAVIOLET DIFFERENCE SPECTRA BETWEEN pH 7 & pH 2
FOR ITEMS ② to ⑧, TABLE VII
(SEE TABLE VII FOR IDENTIFICATION OF CURVES)
100
80
60
40
20
0
-20
$\Delta E^{\%}_{cm.}$
220
250
300
350
390
WAVELENGTH IN mμ
②
③
④
⑤
⑥
⑦
⑧

The following comments were based on the assumption that spectra taken on the same machine at almost identical concentrations (just under 1% in a potassium bromide pellet of just under 0.1 cm. length) and under almost identical conditions were comparable. The difference in the apparent extinction coefficient which was considered significant was one of 10% below $(E)^{\%}_{cm}$ = 150 and 20% above that value, where there was greater inaccuracy in reading transmittance and changing it to absorbance via logarithms. Table IX gives descriptions and analyses of the materials upon which infrared spectra were determined. Tables X and XI give the apparent extinction coefficients for various peaks as calculated from Figures 19 to 21. Table XII gives possible assignations of spectra according to Colthup (117), including those to which reference was made in the Historical Section of this thesis.

Some new spectral correlations for lignins and lignin-like substances have been made recently. In a paper by D.C.C. Smith (118) it was said that aromatic aldehydes and ketones related to lignin had carbonyl stretching bands as follows: methyl p-hydroxybenzoate, 1694 $cm.^{-1}$; acetovanillone, 1657 $cm.^{-1}$; 4-hydroxy-3-methoxycinnamaldehyde, 1660 $cm.^{-1}$; 3,4-dimethoxycinnamaldehyde, 1661 $cm.^{-1}$. Thus the band at 6.1 μ may be due to aromatic aldehydes or ketones. A recent paper by Brown and Wyss (119) reported a band at 1600 $cm.^{-1}$ (6.25 μ) in certain coals, which they interpreted (120) as having arisen, in part at least, from carbonyl groups chelated to hydroxyl groups,

TABLE IX

MATERIALS FOR WHICH THE INFRARED SPECTRA WERE GIVEN IN FIGURES 19 TO 21, AND TABULATED IN TABLES X AND XI

I. Spruce Periodate Lignin, Extracted with Water, as prepared by Sacks (5). (OCH_3, 12.3%; Klason lignin, 90.1%; ash, 1.8%.)

II. Spruce Periodate Lignin, Alkali Extracted, as prepared by Sacks (5). (OCH_3, 12.2%; Klason lignin, 93.9%; ash, 6.2%.)

III. Spruce Periodate Lignosulfonic Acid, Autohydrolyzed, as prepared by this author from a lignin analogous to II. (OCH_3, 11.5%; S, 3.0%; ash, 2.0%.)

IV. Hypochlorite Oxylignin from II, prepared by Wiekowski according to the method of Sacks (5). (OCH_3, 8.8%; Cl, 5.2%.)

V. Chlorine Dioxide Oxylignin-β, prepared by Thompson. (Sample β-10 in Table I of ref. (57)). (OCH_3, 4.8%; Cl, 8.8%.)

VI. Zinc Oxylignosulfonate, prepared by oxidizing a lignosulfonic acid (III) with chlorine dioxide. See Fig. 8. (S, 0.6%; Cl, 2.0%; Zn, 19%.)

VII. Barium Oxylignosulfonate, prepared similarly to VI from III, removing VI and then precipitating with barium hydroxide. See Fig. 10. (S, 2.4%; Cl, 2.3%; Ba, 37.5%.)

VIII. Klason Lignin from spruce, spectrum from the Alberta Research Council. Mean of 2 plots for pellets of different thickness.

IX. Natural Humic Acid from Ellerslie Lignite, a spectrum from the Alberta Research Council.

X. Synthetic Humic Acid, prepared from hydroquinone according to the directions of Eller (101).

XI. Synthetic Humic Acid, similar to X, spectrum from Alberta Research Council.

TABLE X

APPARENT EXTINCTION COEFFICIENTS $(E)^{\%}_{cm}$ IN THE INFRARED FOR THE SAMPLES DESCRIBED IN TABLE IX

Wavelength (microns)	2.9-3.0	3.45-3.5	5.8-5.85	6.1	6.25	6.65	6.85	7.05	7.90	8.25	8.8	Other notable peaks with notation of wavelength followed by $(E)^{\%}_{cm}$ and strength
Wave number (cm^{-1})	3300-3500	2850-2900	1710	1650	1600	1500	1460	1420	1270	1210	1130	
Samples in Table IX.												
I	112s	85s	71k	93k	138s	185s	138s	145s	200b	178b	185b	9.7, 196b; 11.7, 63b; 12.2, 62i; 12.9, 55i.
II	115s	81s	53h	104i	155s	190s	143s	150s	222s	182s	198b	9.7, 220b; 11.7, 70b; 12.3, 65i; 12.8, 61i.
III	101s	80s	98s	58h	104s	167s	137s	127s	gen. absn. 7.9-8.9, 200			9.7, 200b; 11.7, 84b; 12.3, 76i.
IV	70b	78s	192s	48h	90s	112s	111s	123s	200b	192b	178b	9.7, 146b; 12.9, 62b.
V	88s	58s	211s	78h	83s	72s	90s	gen. absn.	160i	gen. absn. 7.9-9.7 max. 8.55, 170b		7.2, 108b; 12.9, 54
VI	147s	56k,i	77k	gen. absn. 6.0-6.4 max. out of range		53h	h	gen. absn.	h	8.2-9.3 max. 8.55, 118b		9.6, 145b; 7.15, 197b.
VII	99s	43k	58s	6.1-6.5 max. 6.3, 195b		h	h	gen. absn.	h	8.1-8.6 max. 8.3, 93b		9.6, 114s; 7.15, 154b; 14.8, 54i.

Symbols: s = sharp peak; b = blunt peak; k = knee or shoulder on curve;
i = point of inflection; h = hollow or no inflection.

TABLE XI

APPARENT EXTINCTION COEFFICIENTS $(E)^{\%}_{cm}$ IN THE INFRARED FOR THE SAMPLES DESCRIBED IN TABLE IX

Wavelength (microns)	2.9-3.0	5.8	6.2	6.65	6.85	8.4	Other notable peaks with notation of wavelength followed by $(E)^{\%}_{cm}$ and strength
Wave Number (cm^{-1})	3300-3500	1710	1610	1500	1460	1190	
Sample in Table IX.							
I	112s	71k	....	185s	138s	....	3.5, 85s; 6.1, 93k; 6.25, 138s; 7.05, 145s; 7.9, 200b; 8.25, 178b; 8.8, 185b; 9.7, 196b; 11.7, 63b;
VIII	203s	h	78s	140s	125s	....	3.5, 130s; 7.05, 104s; 7.9, 155s; 8.25, 138s; 9.7 240b.
IX	250s	204s	234	h	....	184	6.9, 112k; 7.15, 132b.
X	139s	146s	153	132	146	253	12.3, 95.
XI	245s	127s	160	169	160	240	12.3, 117.

Symbols: s = sharp peak; b = blunt peak; k = knee or shoulder on curve;
h = hollow or no inflection.

TABLE XII

POSSIBLE AND LIKELY ASSIGNATIONS OF SPECTRA
(according to Colthup (117))

Wave Number ($cm.^{-1}$)	Wavelength (μ)	Correlated Structure (1)
3400	2.95	-OH (s); sulfonic acid (m)
2900	3.45 - 3.50	-CH in methyl; aldehydes (m)
1710	5.85	carboxylic acids (s); esters (s); anhydrides (s); aldehydes (s); ketones (s)
1640	6.1	benzenes, monosubstituted; p-di-substituted; 1,3,4 tri-substituted. C=C; quinones (s) (2); aromatic aldehydes and ketones (3)
1650-1550	6.1 - 6.5	carboxylate anion (s)
1600	6.25	carboxylate anion and all possible mono-, di-, and tri-substituted benzenes; chelated hydroxy quinones (4)
1500	6.65	all possible mono-, di-, and tri-substituted benzenes
1460	6.85	benzenes, 1,2,3 and 1,3,5 trisubstituted.
1420	7.05	carboxylic acid (m); carboxylate anion (s) any R-OH; methyl or methylene ketone; C=C; sulfate (organic); sulfonate
1270	7.90	aromatic ethers (s); phenols (s); carboxylic acids (s); esters of aromatic acids (s); acetates (s); aromatic aldehydes (m); primary alcohols (w)
1210	8.25	benzenes, o- and p- di-substituted and 1,3,4 tri-substituted; aromatic ethers (s); phenols (s); tertiary alcohols (s); aromatic aldehydes and ketones (w); aliphatic esters (s); sulfonic acids (s); sulfonate anion (s); sulfate esters.

(1) s = strong; m = medium; w = weak band.
(2) See ref. 121. (3) See ref. 118. (4) See refs 119, 120.

FIGURE 19.

INFRARED SPECTRA OF I, II, III & IV, TABLE IX

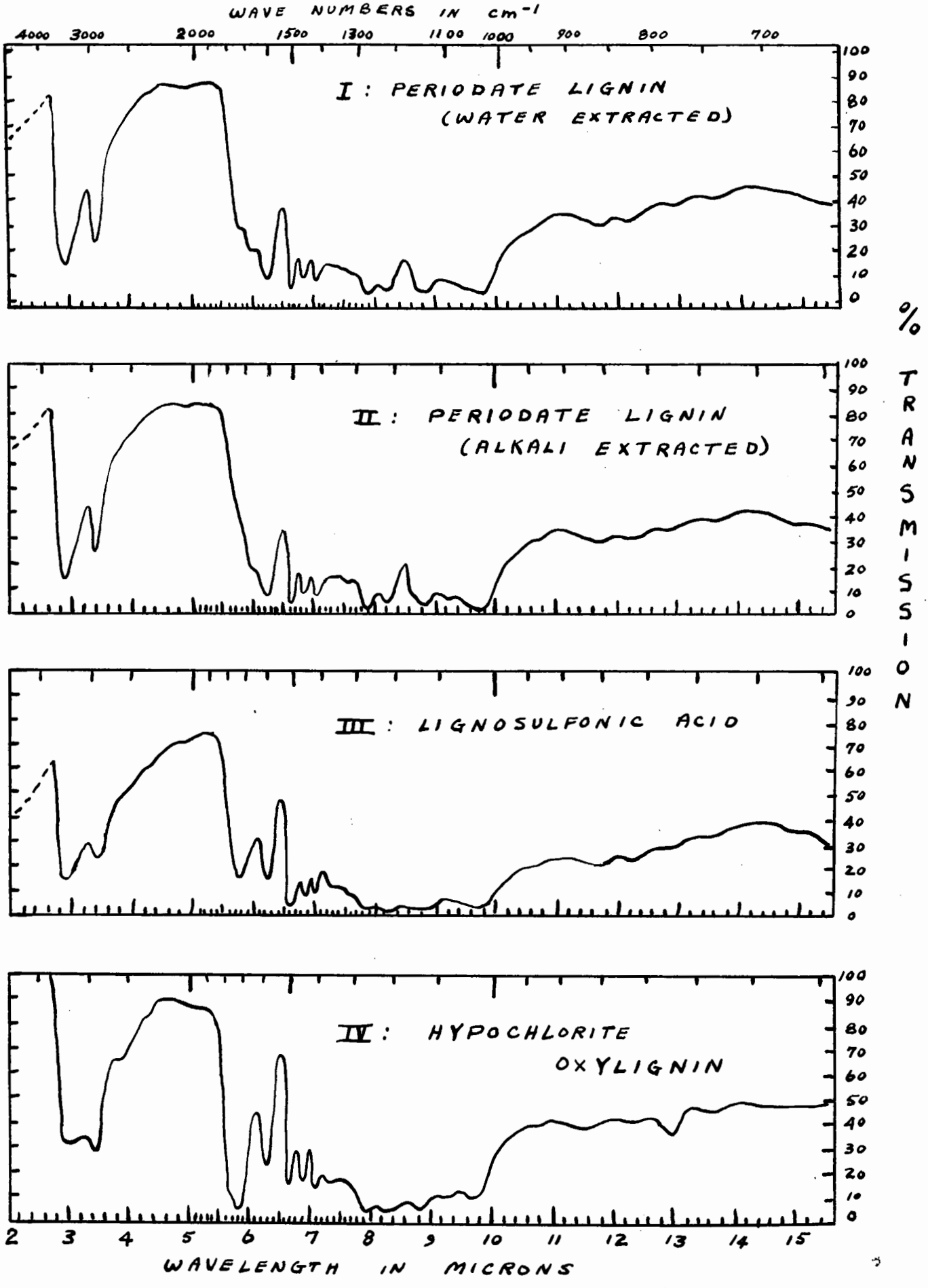


FIGURE 20.

INFRARED SPECTRA OF IV, V, VI & VII, TABLE IX.

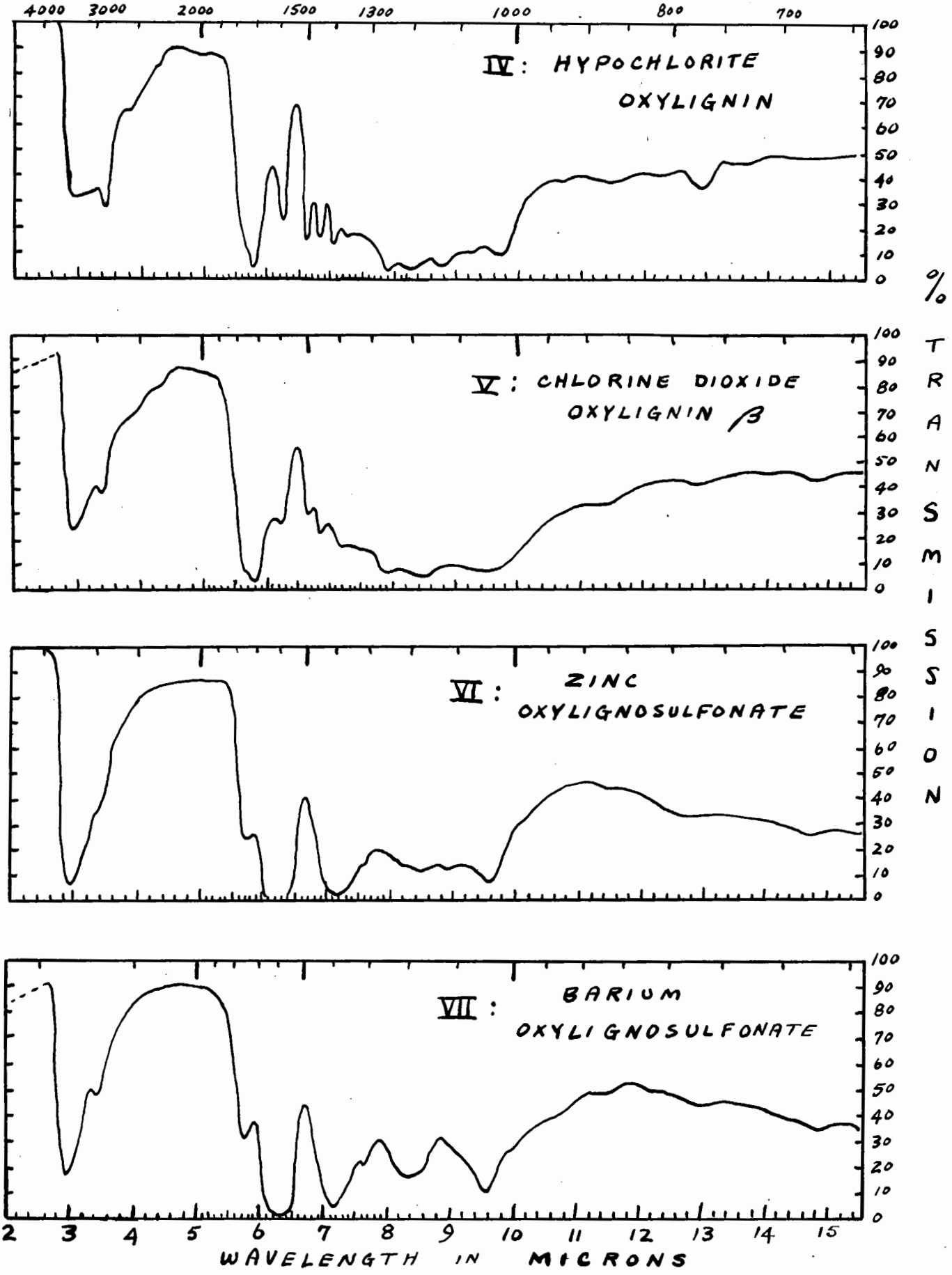


FIGURE 21.

INFRARED SPECTRA OF I, VIII, IX, X, TABLE IX.

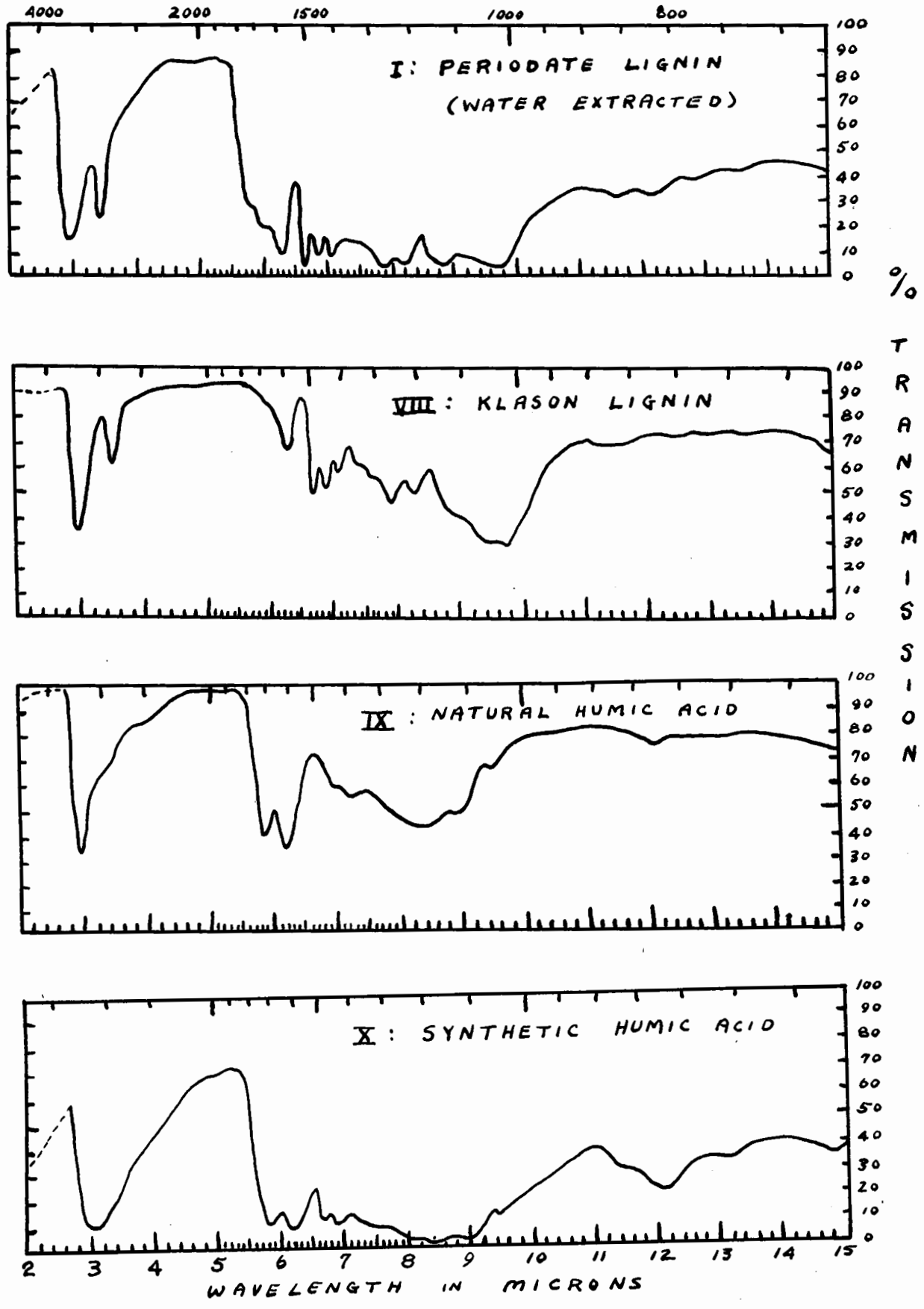
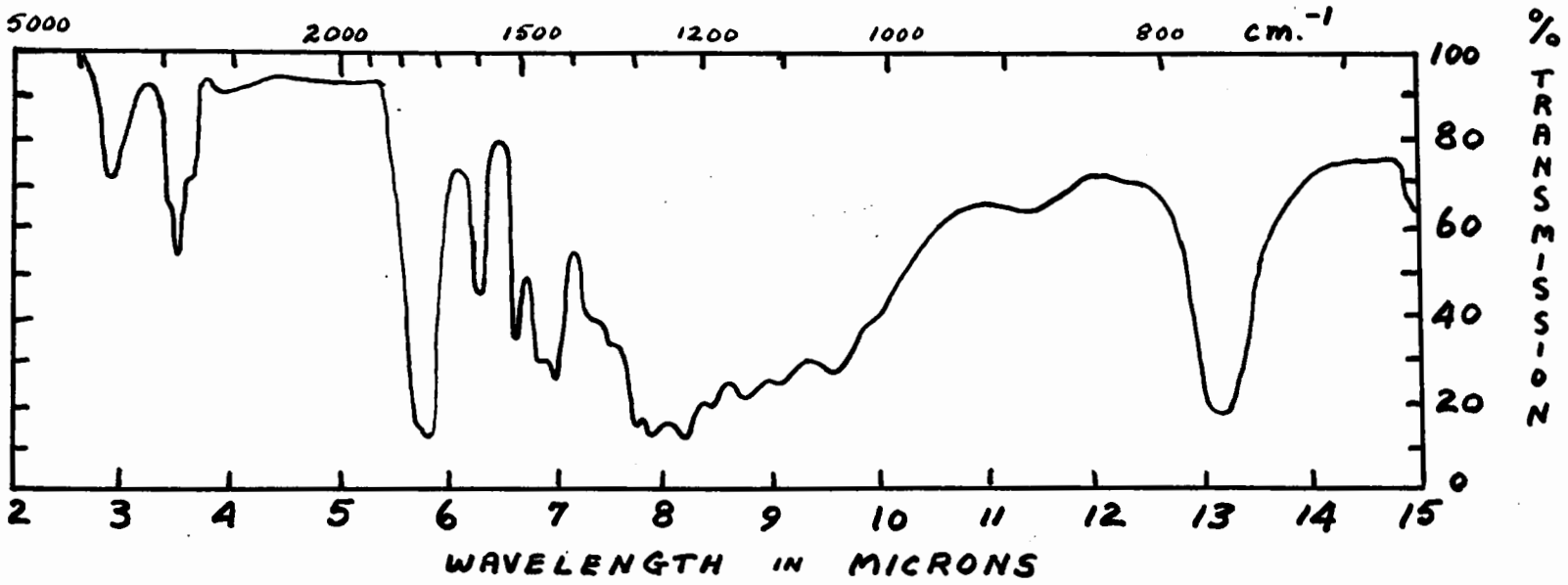


FIGURE 22.

INFRARED SPECTRUM OF THE METHYL ESTER OF THE HYPOCHLORITE OXYLIGNIN OF SACKS (5)



hydroxy-quinonoid structures having been put forward as one possibility. On reductive acetylation the intensity of this band was markedly reduced and those of the bands for phenolic acetates were increased over that observed for the product of normal acetylation. These workers also presented polarographic evidence in the form of a wave at 0.5 to 0.6 volt (reference zero, mercury pool anode) which could only be obtained from quinone-like groups in the coal. Previously Josen and Fuson (121) has reported maxima for the quinone grouping of around 1660 $cm.^{-1}$, with values ranging to 1730 $cm.^{-1}$ for certain condensed conjugated ring systems. Thus the peaks at 6.1 μ (1650 $cm.^{-1}$) and even the one at 5.85 μ (1710 $cm.^{-1}$) in the lignins might have been correlated to the presence of quinone groupings.

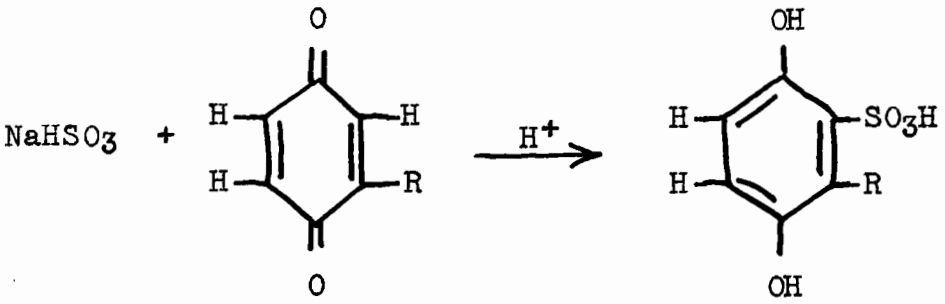
When the spruce periodate lignins prepared by the old and by Sack's process were compared, there was no great difference in the spectra. (See Fig. 19, plots I and II, also Table X, items I and II). The periodate lignin which had been boiled with water (item I, Table X) to remove oxycellulose had perhaps slightly more of whatever caused the inflection at 5.85 μ. From Table XII this inflection might be due to carboxylic acid or ester groups, which might be less plentiful in lignin II, because this sample had been subjected to the milder treatment with weak alkali.

The bands at 5.85 μ, 6.1 μ and 6.25 μ also seemed to be present in other lignins, for the three steps in the overall band which were observed by this author, indicating three over-

lapping bands, were also observable in the spectra of Brauns' "native lignin" from maple as determined by Kudzin and Nord (122). The infrared spectra obtained by D.C.C. Smith (118) on Brauns' "native lignin" from aspen also showed these three bands. Hydrolysis of this aspen lignin with aqueous normal sodium hydroxide removed the band at 1694 cm.$^{-1}$ (corresponding to our band at 5.85 μ) leaving the other two bands only somewhat diminished, while sodium borohydride removed the band at 1658 cm.$^{-1}$ (corresponding to our band at 6.1μ) leaving the bands at 1694 cm.$^{-1}$ and at 1600 cm.$^{-1}$ (6.25μ). His interpretation was that the band at 1694 cm.$^{-1}$ was due to carbonyl stretching of an ester group which was hydrolyzed by the sodium hydroxide, and the band at 1658 cm.$^{-1}$ was caused by the carbonyl stretching of an aldehyde or ketone, such as coniferaldehyde or acetovanillone, with maxima at around 1660 cm.$^{-1}$, which had been reduced by the sodium borohydride. In lignins from other woods the structures causing these three bands were present in different proportions and the three bands did not show up distinctly.

A comparison of the lignin (II) with the lignosulfonic acid (III), obtained from it by the mild treatment outlined earlier in this discussion, showed them to be similar in most respects, the notable exception being a peak at 5.8μ in the lignosulfonic acid which was pronounced because of the concurrent diminution of the absorption at 6.1μ and at 6.25μ. (Table X, Items II and III). A possible explanation of this change would

be the removal of carbonyl units in the quinone type rings by the reaction. In this event the sulfonation might eliminate



the absorption at 6.1 μ, but leave that at 5.85 μ, which might be due to other carbonyl groups as in an ester, aldehyde or ketone. At the concentration used, there was almost complete absorption in the region 7.9 to 8.9 μ, which was one in which the sulfonic acid groups would be expected to absorb.

When the spectra of the lignin (II) and the hypochlorite oxylignin (IV), were compared, the most notable difference was in the magnification of the peak at 5.85 μ (Table X, items II and IV) accompanied by a disappearance of the peak at 6.1 μ and a diminution in the peaks at 6.25, 6.65, 6.85 and 7.05 μ. These changes could be explained by the known production of carboxylic acid groups, which would absorb at 5.85 μ, together with the destruction of some aromatic units as indicated by the decrease in the intensity in the maxima between 6.2 and 7.1 μ. These maxima are correlated to aromatic substitution. The removal of certain carbonyl groups, either by the destruction or condensation of quinone rings, or by the oxidation of aldehydes or ketones to acids, might account for the disappearance of the 6.1 μ peak.

The small peak at 12.9 μ for the oxylignin (IV) might be related to the presence of $-CCl_2$ linkages.

The spectra of lignin (I) was compared with the chlorine dioxide oxylignin-β, obtained by Thompson (57) from lignin (I) after removing soluble material from the crude product with acetone (Tables IX and X, Items I and V). The large maximum at 5.8 μ, indicative of carboxylic acid groups was again observed. As well, there appeared to be extensive destruction of the aromatic material, as indicated by the much lower intensities of the bands from 6.2 to 7.2 μ, which were correlated to aromatic substitution. This observation was in accordance with the view that chlorine dioxide would attack aromatic rings preferentially.

Both the hypochlorite and chlorine dioxide oxylignins (IV and V) had a smaller methoxyl content than the parent lignin, therefore the 3.5μ band was lower. The ratio of methoxyl group to phenolic hydroxyl group content, as indicated roughly by the difference spectra in the ultraviolet, was large in the hypochlorite oxylignin and small in the chlorine dioxide oxylignin-β. In the hypochlorite oxylignin, the methoxyl band at 3.5μ had a larger apparent extinction coefficient than the hydroxyl band at 2.9μ, a circumstance which was only repeated in the case of the spectrum of the methyl ester of the hypochlorite oxylignin. In all the other lignins and their derivatives the hydroxyl band was greater than the methoxyl band, and much greater for chlorine dioxide oxylignins. The above remark was in agreement with Freudenberg's observations on methylated and unmethylated

lignins (86). As had been expected, the methyl ester prepared by Sacks (5) from his hypochlorite oxylignin showed difference between the peak at 3.5μ and the one at 2.9μ greater than the difference displayed by the free acid. The complete spectrum of this methylated sample was reproduced in Figure 22, the incomplete spectrum having been given in Sacks' thesis (5), p. 42. Sacks' spectrum had been obtained by evaporation of a chloroform solution of the methylated oxylignin upon a salt plate; the thickness and concentration were not given, and thus the apparent extinction coefficients could not be calculated. In addition to the effects of methylation, there appeared to be a much larger band for the $-CCl_2$ grouping at 13.1μ, perhaps caused by residual chloroform.

The zinc and barium oxylignosulfonates (Tables IX and X, Items VI and VII) were made from a lignosulfonic acid which had been more extensively oxidized by chlorine dioxide than the chlorine dioxide oxylignin-β (V), and consequently the aromatic band at 6.65μ appeared diminished even further. The other aromatic bands were masked by very strong absorption in the regions of 6.0 to 6.5 and 6.9 to 7.4μ, which was characteristic of the ionized carboxylic acid groupings expected in these salts. In spite of this ionization, there was still absorption at 5.85μ, lessened of course because of the transformation of un-ionized carboxylic acid groups to the ionized form, but still as large in intensity as the same band in the parent lignin. This band at 5.85μ was slightly lower in intensity in the case of the

barium oxylignosulfonate, for this salt was completely neutralized (precipitated from solution at pH 8) and it was hard to see how any carboxylic acid group could be the cause of this absorption. A possible explanation would be the re-formation of quinone-type linkages upon the loss of sulfur occurring during the oxidation of the lignosulfonic acid with chlorine dioxide. The absorption characteristic of sulfonic acid salts was observed in both cases as a broad band centered on 8.3μ.

In the barium oxylignosulfonate there was a small broad band at 14.8μ which might be due to C-Cl bonds. This band was more diffuse in the zinc oxylignosulfonate and in the chlorine dioxide oxylignin (V). It may have been spurious.

For the sake of direct comparison the spectrum of a Klason lignin was obtained from Dr. Wood of the Alberta Research Council. The data for this material were given in Table IX and XI. The peaks at 5.85μ and 6.1μ were missing, but otherwise the spectra of periodate and Klason lignins seemed to be essentially the same, the only other significant difference being in the peak for aromatic substitution at 6.25μ.

The infrared spectrum was also determined for a synthetic humic acid, prepared according to Eller's directions (101), and was compared with data for a natural humic acid isolated from a lignite, by Dr. Elofson and Dr. Wood of the Alberta Research Council (Table IX, Items X and IX). In both natural and synthetic humic acids the peak in the apparent extinction coeffi-

cients (Table XI) at 3.45μ due to methyl groups was missing, but that for hydroxyl groups was present and quite strong. The peak at 5.85μ was pronounced, but may have been due, in part at least, to carboxylic acid groups in the case of the natural humic acid. This peak most probably was caused by quinone-type carbonyl groups in the case of the synthetic humic acids, if Erdtman's formula (XIII) was correct. Missing in the natural humic acid, but present in lignin and the synthetic humic acids, were the bands at 6.65μ and 6.9μ, correlated to aromatic substitution. The band at 8.4μ was very strong in both cases, and probably originated in the phenolic hydroxyl groups whose presence was indicated by the ultraviolet difference spectra. The work carried out by the author on a synthetic humic acid (Item X, Table IX) had been duplicated at the Alberta Research Council. A comparison with their data (Item XI, Tables XI and IX) was included to illustrate the variation between synthetic humic acids prepared in a similar way in different laboratories and examined on different infrared spectrometers.

The foregoing account shows that many similarities exist between the infrared spectra of the natural and synthetic humic acids and the lignins. The humic acids, however, differed in yielding no band at 3.5μ (lack of methyl groups), at 6.1μ and 7.05μ (lack of aldehyde, ketone and carboxyl groups), and in having a large absorption at 7.8 to 9.8μ (maximum at 8.4μ) which obliterated all detail. If anything, the Klason lignin, rather than the periodate lignin, had the greater resemblance to the

synthetic humic acid in its general band structure. When the fine structures in the region 6.25μ to 6.85μ were compared, it appeared that the samples exhibited an increase in the number and type of aromatic substitution in the approximate order: natural humic acid, synthetic humic acid, periodate lignin and Klason lignin. As expected, the Klason lignin appeared to be more condensed than the periodate lignin, and, presumably, than lignin *in situ*.

As for the modified lignins, hypochlorite oxylignin retained the aromaticity of the parent lignin, and in neither case did sulfonation produce a marked change in the spectra. Oxidation of the periodate lignosulfonic acid with chlorine dioxide, however, greatly reduced the apparent aromaticity and the product yielded a spectrum close to that of natural humic acid, with the exception of the methyl band at 3.5μ and the band at 5.85μ caused by carboxylic acid groups. Since sulfonation in the other cases caused little change in the spectra, this comparison was probably valid for chlorine dioxide oxylignin itself. This similarity between one type of oxylignin and a natural humic acid supported, but by no means confirmed, Flaig's view (100) that the biochemical degradation of lignin in the soil resulted in humic acids. Whether humic acids are the only materials that undergo coalification and thus make lignin the only source of coal is a question which is in the purview of other investigators.

EXPERIMENTAL PART

Analytical Methods

Most of these methods were given in complete detail in the thesis of Brickman (4) and Sacks (5). Here these procedures are only outlined, but any modifications made by this author are described in detail. Analyses reported in this Thesis were the mean of 2 or more determinations, given usually to the number of significant figures justified by the variations between duplicates.

Samples were dried *in vacuo* over phosphorus pentoxide before analysis, and the results furnished the dry basis on which yields were reported for the various steps in the sulfonation and autohydrolysis. The drying process used was justified by the recent work of Newcombe (102), which showed that there had been no decomposition on the air drying and vacuum drying of lignosulfonic acids or of calcium lignosulfonates.

Klason lignin was determined according to the standard method for lignin in wood, using 72% sulfuric acid and 1 gm. samples (103), with the modification that the coarse sintered-glass crucibles were equipped with a mat of asbestos fibres, to aid in the filtration of the almost colloidal material.

Moisture was determined by heating the samples overnight at 100°; ash by heating 10 to 20 mg. samples in a micro-

muffle furnace (104) with, instead of a "Pyrex" ignition tube, one of "Vycor" to withstand the temperatures used without bending. Sulfated ash was determined on calcium and barium salts by adding 2 to 3 drops of 10% sulfuric acid to the ash in the platinum ignition boat, and by slowly fuming off the sulfuric acid, finally igniting the boat in a micromuffle furnace for 15 minutes with the flame full on, the temperature inside being estimated at about 800°. The entire procedure was repeated until the weight of the boat plus sulfated ash remained constant. These determinations were used as the basis for calculation of calcium or barium contents.

Analyses for sulfur were made by fusion with sodium peroxide (105) in a Parr micro bomb, using 10 to 30 mg. samples. After the ignition, the solution of the melt was neutralized with 5 ml. of hydrochloric acid; 2 ml. of 2.5% barium chloride solution was added and the liquor was evaporated to dryness in the apparatus described by Niederl (105). The solid residue in the evaporating tube was moistened with 1N hydrochloric acid and the evaporation was repeated. The final solid residue was then dispersed in 25 ml. of distilled water and next day the supernatant liquid was decanted through weighed filter crucibles. The barium sulfate precipitate in the evaporation tube was washed with warm 1:20 hydrochloric acid and the washings were decanted through the filter as before. After being transferred into the crucibles by means of alternate ethanol-water washes, as recommended by Pregl (107), the barium sulfate precipitate was dried

in an oven, ignited at 700°-800° and weighed.

Free sulfate was determined by dissolving samples of 20 to 50 mg. in 20 ml. of water, and then adding enough normal hydrochloric acid to give a solution which would be 0.1 N. Two millilitres of 2.5% barium chloride solution was added and the resulting precipitate was allowed to digest at room temperature overnight. The next day the supernatant liquid was decanted through weighed filter crucibles. The barium sulfate precipitate was washed with warm 1:20 hydrochloric acid and the washings were decanted through the filter. After having been transferred into the crucibles by alternate ethanol-water washes, the barium sulfate precipitate was dried in the oven, ignited at 700°-800° and weighed. This procedure was designed to eliminate interference by the co-precipitation of some barium lignosulfonate.

Analyses for chlorine were made in the usual manner by fusion of the sample with sodium peroxide in a Parr micro bomb (108) using 10-40 mg. and the gravimetric precipitation of silver chloride. Free chloride was determined by dissolving samples in 1% nitric acid solution and by carrying out the gravimetric precipitation of silver chloride in a customary manner.

For the determination of yields, samples were always centrifuged, never filtered. For rougher measurements the precipitates were dried as described above in the centrifuge tubes, which were weighed. The dry contents of the tube were removed and their weight obtained by difference. For accurate work, and

to avoid the occasional "bumping" out of the contents from the tubes, on the application of the vacuum, weighed glass micro sulfur evaporating dishes were used. The slurry was washed out of the centrifuge tube into the dish, and the dish and contents were dried as above and weighed. This procedure was also applied to the drying of aliquots of solutions or slurries to obtain yields.

The methoxyl content of samples was determined by the method of Viebock and Schwappach (109) as modified by Peniston and Hibbert (110) using 10 to 20 mg. samples and the apparatus of Clark (111).

Sodium paraperiodate was analyzed by treating an aliquot, buffered with sodium bicarbonate to pH 8, with a known excess of 0.1 N arsenious acid followed by an excess of potassium iodide. After 10 minutes, the unreacted arsenious acid was titrated with 0.1 N iodine solution, using starch as an indicator (112).

Chlorine dioxide solutions were analyzed by diluting a 5 or 10 ml. aliquot to 50 ml. in a volumetric flask. Ten ml. of this solution was transferred to an Erlenmeyer flask with a little water, and 10 ml. of 10% potassium iodide and 20 ml. of 20% sulphuric acid were added. This mixture was then titrated with 0.1 N sodium thiosulphate, using 2 ml. of starch solution as an indicator. The work of Husband (58) indicated that very little chlorine passed through the trap containing saturated sodium

chlorite solution, and since only an estimate of the amount of chloride dioxide used was needed, this modified procedure was employed. The relevant equation was

$$4\ ClO_2 + 6\ I^- + 16\ H^+ \longrightarrow 3\ I_2 + 4\ Cl^- + 8\ H_2O.$$

The buffers from pH 2 to pH 10 used in this Thesis were the standard Clark and Lubs mixtures made up according to the directions of Kohthoff and Laitinen (113). The buffer for pH 12 was the trisodium phosphate solution of Ringer as quoted in Britton (114), made up from 0.15 M disodium hydrogen phosphate and 0.1 M sodium hydroxide.

Preparation of Spruce Periodate Lignin

Spruce periodate lignin was prepared according to the procedure outlined by Ritchie and Purves (53) and modified by Sacks (5). Air-dried, unextracted black spruce meal, 1250 gm., of a 60 to 100 mesh fineness, was used in this process. This wood meal had 7.2% moisture, 0.12% ash and 28.4% Klason lignin on an ash-free, moisture-free basis.

The oxidation-hydrolysis cycle was carried out in a 10 gallon (45 litre) stoneware crock as follows. The wood meal, or the moist, washed filter cake from the preceding step, was stirred for 24 hours in 10 litres of a 3.5 to 4.5% solution of paraperiodic acid, buffered to pH 4. This solution was made up by adding glacial acetic acid to a suspension of sodium paraperiodate in 10 litres of water until pH 4 was reached and the

solid had all dissolved. The sodium paraperiodate was made from sodium iodate by oxidation with chlorine according to the procedure of Langlois (88) and Hill (89). The slurry of oxidized material was filtered in the normal way through large, coarse-grained sintered glass filter funnels. After having been concentrated, the filtrate deposited some of the by-product iodate, which was recovered. The residual filter cake of partially oxidized wood was then washed by stirring for 24 hours in 40 litres of water; and the suspension allowed to settle overnight, after which time the clear liquor was decanted. There was an inevitable loss of fines in the decantation steps and this might account for the fact that the yield was only moderate. Washing and decantation were repeated. Coarse-grained sintered-glass filters, connected by rubber tubing from the stems to large suction flasks, were then immersed upside down in the slurry. Suction was applied to remove water from the slurry until only a moist filter cake remained. Filtration was slow because the filters became plugged with fines. In later steps the slurry was extremely gelatinous, which further increased the difficulty of filtration.

To hydrolyze the oxycellulose, 25 litres of 0.1 N sodium hydroxide was added to the moist mixture of lignin and partially oxidized cellulose. The resulting suspension was stirred for 24 hours, and the residue was recovered on a filter and washed in the same fashion as after the oxidation. The washing and decantation were repeated until the alkalinity of

the liquid was reduced to pH 9. The procedure for the filtration after this step was the same as that used after the washing of the oxidized material. Great difficulty was encountered in these filtrations because of the gelatinous, glue-like nature of the alkaline preparation. Acidification of the wash water with acetic acid was helpful in the second, third and fourth cycles, but it was not thought advisable to acidify before at least the greater part of the base-soluble fragments of the hydrolyzed oxycellulose were removed. Thus acetic acid was not used until after pH 9 had been reached by washing with tap water, but the subsequent inverted filtration was still difficult for the same reasons. The slightly acid, moist filter cake was then used in the next cycle of oxidation and hydrolysis. This oxidation hydrolysis cycle was repeated four times.

At the end of the fourth cycle, the slightly acid filter cake was washed with tap water until neutral, then washed with distilled water and recovered on a filter. The moist, neutral lignin preparation was dried in the air, giving a lignin which was an extremely hard, dense, brittle, resinous material. The yield was 207 gr. of air-dry lignin. Found: moisture 7.0%; ash (on a moisture-free basis) 4.3%; Klason lignin (on a moisture-free, ash-free basis) 89.6%. These data corresponded to a 50% yield of Klason lignin based on the Klason lignin in the wood.

The hard, resin-like material was ground in a coffee mill, and then by hand in a mortar, so that all passed through an 80 mesh screen, and about half was a fine powder which passed

through a 200 mesh screen. This was the "spruce periodate lignin" used in the subsequent work.

Preparation of Lignosulfonic Acids

The preliminary work to discover the mildest conditions of both sulfonation and autohydrolysis necessary to give completely soluble lignosulfonic acids was done on a small scale. For the sulfonation, a uniform suspension of 2% by weight of the air-dry lignin in a solution of 9% sodium bisulfite was divided into aliquots which were sealed in small tubes holding 5 or 20 ml. These tubes were then heated at various temperatures and for various periods of time. In the case of the 20 ml. tubes, this heating was done in the special thermostatted oil bath used by Cabott (3) and Brickman (4), with agitation provided by the rotation of the steel bomb which contained the tubes. With the small samples the heating was in a constant temperature apparatus, no agitation being used.

After the cooking, the contents of the tubes were centrifuged. The liquors in one case were dialyzed against tap water through cellophane for two days and an aliquot of the non-dialyzed portion was evaporated to dryness *in vacuo* over phosphorus pentoxide and weighed. The insoluble lignosulfonate in the centrifuge tube was washed with an equal volume of distilled water and centrifuged again, this process being repeated five times to ensure complete removal of all bisulfite. If a determination of the yield of the sodium lignosulfonate was desired,

the water was removed from the sample by solvent-exchange through dioxane, to benzene. The sample was then vacuum dried over phosphorus pentoxide overnight and weighed.

Undried, moist sodium lignosulfonate was changed into the free lignosulfonic acid by a brief immersion in 1 N hydrochloric acid, centrifuging, replacing the liquid with fresh 1N hydrochloric acid, and later centrifuging again. The solid lignosulfonic acid was then washed free of chloride ion with distilled water. In an earlier procedure, if a determination of the yield of lignosulfonic acid was required, the water in the sample was replaced first by dioxane, then by benzene, before drying in vacuo. Further investigation showed that this method entailed a considerable loss of material due to the solubility of the lignosulfonic acid in dioxane. Other water-miscible solvents were worse in this respect. Recourse was eventually had to drying the centrifuged residue directly from water over phosphorus pentoxide under vacuum.

The moist, solid lignosulfonic acid was autohydrolyzed as a suspension of not more than 2% by weight. This suspension was heated in sealed tubes at various temperatures and for various times in the same apparatus which was used in the sulfonation process. The solution was centrifuged, and the residue was washed with fresh distilled water until the washings remained colourless. This residue of lignosulfonic acid and other debris which had not been autohydrolyzed was dried in vacuo over phosphorus pentoxide and weighed. Some of the dried samples were

analyzed for sulfur and ash content.

The following larger scale experiments were based on the results of these tests. Eighteen grams of air-dry lignin was cooked in 900 ml. of 9% sodium bisulfite for 50 hours at 100°. This cook was accomplished by sealing the charge in a large glass liner fitting inside the steel bomb which rotated in the thermostatted oil bath. This apparatus was described in the theses of Cabott and Brickman (3, 4). After the usual washing, the free lignosulfonic acid was liberated by stirring the centrifuged precipitate of sodium lignosulfonate with 1N hydrochloric acid. This de-ashing with hydrochloric acid was repeated, the insoluble lignosulfonic acid was washed free of chloride ion, and was made up into a slurry with distilled water. An aliquot of this slurry was analyzed for lignosulfonic acid content by evaporating the water and by drying in the usual manner. On this basis, the rest of the original slurry was made up to 2% solids content, and autohydrolyzed for 50 hours at 100°. in the same large bomb and bath as in the sulfonation just described. The amount of autohydrolyzed lignosulfonic acid was determined by evaporating and drying an aliquot in a tared dish.

A further modification which obviated the use of sealed bombs and a special bath was developed. A three-necked round bottomed flask of suitable volume was fitted with a mechanical stirrer, a reflux condenser and a thermometer dipping well into the flask. After 2 parts of lignin and a solution of 100

parts of water and 16 parts of reagent grade sodium bisulfite had been added, the apparatus was heated on a steam bath for 50 hours, the temperature measured on the thermometer immersed in the reaction mixture varying between 96° and 98°. Measurements of the hydrogen ion concentration were taken at regular intervals, and were found to vary between pH 4.8 and pH 5.3. The product was washed and changed into the free lignosulfonic acid in the usual fashion, determinations of yield being made on aliquots of slurries. The autohydrolysis of this insoluble lignosulfonic acid was carried out in the same apparatus, using 2 parts of lignosulfonic acid for 100 parts of water, and heating on the steam bath for 50 hours. The amount of residual unautohydrolyzed lignosulfonic acid was determined by the method outlined in the previous Section.

The same modification was applied to determine the optimum conditions for both the sulfonation and the autohydrolysis. Exactly 10 g. of +200 mesh lignin was cooked in a solution of 80 g. of sodium bisulfite dissolved in water to make up 500 ml. of solution. At regular intervals, 20 ml. samples of the slurry were taken, centrifuged and washed five times to free them of bisulfite ion. These samples were then dried in tared dishes under vacuum over phosphorus pentoxide and weighed to give the yield of Stage I sodium lignosulfonate. The results gave the effect of time of sulfonation on the solubility in this cooking liquor. The filtrate and first wash water from each sample were taken and diluted to 50 ml., of which a 1 ml.

sample was diluted 10:1 with 9% sodium bisulfite solution for the determination of the absorbance on a Beckman Model DU spectrophotometer. From the absorbance at 280 mμ, corrected for a blank containing only 9% sodium bisulfite solution, the fraction of the lignosulfonate which was dissolved could be determined. The results, together with the yields were presented in Figure 1.

Each of the dried samples of Stage I lignosulfonate was then soaked in 15 ml. of potassium chloride-hydrochloric acid buffer at pH 2 overnight. The sample now re-hydrated, was sealed with its buffer in a tube which was heated for 24 hours at steam bath temperature. The contents of the individual tubes were then centrifuged separately and the precipitates were washed with water, dried and weighed as usual. In this way, the amount of insoluble, unautohydrolyzed lignosulfonic acid remaining after various times of sulfonation could be determined. The filtrate and washings up to a volume of 50 ml. were saved and a 1 ml. aliquot was diluted 10:1 with water. Of this, 2 ml. was diluted to 10 ml. (5:1) with the buffer at pH 2 for the determination of absorbance on the Beckman spectrophotometer at 280 mμ against a blank of pH 2 buffer. This determination provided another measure of the yield of autohydrolyzed lignosulfonic acid obtained with varying sulfonation times. The results, also those for the corresponding yields were given in Figure 2.

The original sulfonation liquor remaining after the 20 ml. samples had been taken, was centrifuged, the insoluble

lignosulfonate was washed and acid exchanged as before, and was autohydrolyzed at a concentration of 2.2% in distilled water. Samples of 5 ml. were taken at intervals, centrifuged, washed with 50 ml. of water and dried as before, in order to determine the effect of time of autohydrolysis on the yield of undissolved residue. The filtrate and washings from the 5 ml. samples up to the amount of 25 ml. were reserved. One millilitre of this liquor was diluted to 10 ml. in pH 2 buffer and the absorbance was taken as before. The results of this absorbance determination and of the immediately previous yield determination were summarized in Figure 3.

The procedure in the last paragraph was repeated for another sulfonation cook of only 20 hours, the autohydrolysis being carried out at a concentration of 1.4% in distilled water. Samples of 25 ml. were taken at the beginning of the autohydrolysis and 1, 2, 4, 12 and 15 hours later, the reaction being concluded at 15 hours. The samples were centrifuged and the precipitate of unautohydrolyzed residue was washed thoroughly, the washings being added to the autohydrolysate until the total volume was 50 ml. This solution was used for absorbance measurements in a 1:125 dilution in various buffers, difference spectra for some of these samples being taken according to the directions given later under the heading "Ultraviolet Spectra". (Figure 16 and Table VIII) From some of the 50 ml. samples, 25 ml. was taken and dried, as described earlier, in evaporating dishes, direct yields of the dissolved material thus being de-

termined. These dried autohydrolysates and the corresponding dried unautohydrolyzed residues were analyzed for sulfur, methoxyl and ash contents, the results of these analyses being given in Table V.

Mild Sulfonation and Autohydrolysis of the Lignin in a Wood

Spruce wood meal extracted with ethanol-benzene, was cooked in 200 ml. of the approximately 16% sodium bisulfite solution on the steam bath for 50 hours and was then washed free of bisulfite ion. The suspension was centrifuged and acid exchanged with normal hydrochloric acid to convert the sodium lignosulfonate in the wood to lignosulfonic acid. The wood residue was autohydrolyzed for 20 hours in 200 ml. of McIlvain's citrate-phosphate buffer of pH 2.5 (93). When the insoluble residue was dried in the usual fashion and weighed, the yield was about 50%.

Sulfonation of Oxylignins

In order to compare spectra, sulfonated oxylignins were made in the following manner. Approximately 0.4 g. of the oxylignin, suspended in 20 ml. of 9% sodium bisulfite solution, was sealed in a small tube. This tube and its contents were heated for 42 hours in the steam bath at about 98°. The solutions from the individual tubes were dialyzed against frequently changed volumes of 50 ml. of distilled water, the progress of the dialysis being followed by an iodine titration

of the bisulfite ion which dialyzed through the membrane. After 5 changes of water during 18 hours of dialysis, most of the bisulfite ion seemed to have migrated through the membrane. The contents of the dialysis sacks were each evaporated to dryness, taken up in 10 ml. of 0.1 N hydrochloric acid and neutralized to pH 5 with calcium hydroxide. The small amount of calcium sulfate which precipitated at this point was removed and the solution was evaporated to dryness to recover the calcium salt of the oxylignosulfonic acid in 50 to 60% yield from the parent oxylignin.

Oxidation of the Autohydrolyzed Lignosulfonic Acid with Chlorine Dioxide

The soluble autohydrolyzed Stage II lignosulfonic acids were concentrated to 4% solids content, and an equal volume of an approximately 0.4 M aqueous solution of chlorine dioxide was added. The chlorine dioxide solutions were prepared by absorbing the gas, generated in a blackened, all-glass apparatus, in 150-200 ml. of ice-cold distilled water contained in an amber bottle. Chlorine dioxide was made by the method first proposed by Calvert and Davies (115) and modified by Schacherl (116), by heating slowly from 30° to 60° a mixture of 25 g. of potassium chlorate (C.P.), 20 g. of oxalic acid (C.P.) and 80 ml. of cold 33% (by volume) sulfuric acid. The ensuing reaction was described as

$$2\ KClO_3 + (COOH)_2 + 2\ H_2SO_4 \rightarrow 2\ ClO_2 + 2\ CO_2 + 2\ H_2O + 2\ KHSO_4.$$

Before the gas was absorbed, it was scrubbed with a saturated solution of sodium chlorite to replace any chlorine dioxide, in accordance with the equation

$$2\ NaClO_2 + ClO_2 + Cl_2 \longrightarrow 3\ ClO_2 + 2\ NaCl.$$

The freshly made solution was approximately 0.4 molar in chlorine dioxide. In the preliminary work, the oxidation mixture was allowed to stand at room temperature and in the dark until no green gas was observed above the liquid, which usually took two to four days. The solution was then cooled and was used to dissolve more chlorine dioxide, made from the same quantities of reagent as before. This time it usually required a week before the green gas had disappeared from above the liquid.

In two later runs exactly 200 ml. of chlorine dioxide solution and 200 ml. of autohydrolyzed lignosulfonic acid solution were mixed. The progress of the oxidation was then followed by diluting 2 ml. samples 1:5 and taking 2 ml. of the diluted solution for estimation. The estimation for residual chlorine dioxide was that of Husband (58) who added acidified potassium iodide and titrated the iodine liberated with standard sodium thiosulfate solution. The oxidation was allowed to continue until most of the chlorine dioxide was consumed. The solution was then cooled, saturated as before with more chlorine dioxide, and the titration of aliquots resumed. This process was repeated three or four times, and similar run was made with a blank of diluted chlorine dioxide solution. The results were were given in Figure 4.

The excess chlorine dioxide was removed by bubbling air through the solution until a piece of moist starch-iodide paper no longer turned blue when held in the current of air rising from the liquid. In the earlier experiments chloric acid, formed as a by-product in the reaction, was reduced to hydrochloric acid by cooling the solution and bubbling sulfur dioxide through it for about 15 minutes. This method of reduction was abandoned because the sulfate produced interfered with attempts to establish a sulfur balance for the isolated fragments. In some experiments, samples were dialyzed against tap water overnight and the amount of undialyzed material was determined by the evaporation and drying of the contents of the dialysis sack. The amount of undialyzed material was taken as an inverse measure of the effectiveness of a given oxidation.

Precipitations with Calcium Hydroxide

A flow sheet for this procedure was given in Figure 6 (see Discussion). Solid calcium hydroxide was added with stirring to the solution from the oxidation until pH 5 was reached. The precipitate of calcium sulfate was removed on the centrifuge and washed with a small volume of water. The remaining solution, plus the washings, were concentrated to about 10% solids on the basis of the material going into the oxidation. Any calcium sulfate which precipitated at this stage was removed. The solution was then diluted with ethanol until no further cloudiness was observed when more ethanol was added to the clear centrifu-

gate. This amount was usually about five times the volume of the original solution. The precipitate (I) was then recovered, washed with ethanol and dried.

The alcoholic extract was evaporated, the residue was taken up in the minimum volume of water and shaken with a large excess of silver carbonate. A mixed precipitate of silver chloride, calcium carbonate and silver carbonate was removed on the centrifuge, and the solution was treated with just enough calcium chloride to precipitate as silver chloride any silver ion which might remain. This balance was achieved by centrifuging samples after successive increments of calcium chloride until cloudiness was obtained on the addition of silver nitrate solution to a test sample of the clear solution above the silver chloride precipitate. The whole solution was then centrifuged until clear, and evaporated to dryness.

The dried precipitate (I) from ethanol was treated briefly with a volume of water which was half of that which had originally dissolved it. This suspension was then centrifuged and the solution was fractionally dialyzed through a cellophane membrane against twice its volume of distilled water, first for four hours, then for 17 hours, then for 65 hours. The three dialysates were then separately fractionated by evaporation to a small volume, and by the addition of alcohol in two stages. At the first stage the volume of alcohol was twice that of the original concentrate, and after the separation of

the precipitate, ethanol was added to the filtrate until nothing further precipitated. This suspension was also separated into precipitate and solution. These precipitates were kept separate, but the alcoholic solutions were combined, evaporated and the residue taken up in water. The calcium chloride was removed by treatment with silver carbonate as above and the solution remaining was evaporated to dryness. The material remaining behind in the dialysis sack after the 65 hours was also dried.

Another calcium oxylignosulfonate was precipitated as outlined in Figure 7. Five hundred milliliters of a solution containing 8.1 g. of oxylignosulfonic was bubbled free of excess chlorine dioxide with air, but was not otherwise treated to remove chlorite or chlorate. The suspension was centrifuged to remove the precipitate of insoluble oxylignosulfonic acid, here 0.2 g. The clear solution was neutralized to pH 5 with solid calcium hydroxide, but the precipitate of calcium sulfate which formed was partially soluble in N hydrochloric acid. Excess calcium hydroxide was therefore present.

The solution of the calcium oxylignosulfonate plus some calcium sulfate in solution was evaporated to 50 ml. To this concentrate was added 250 ml. of ethanol which precipitated the calcium oxylignosulfonate and the calcium sulfate together. This precipitate was washed again with ethanol, then with benzene and dried as usual under vacuum over phosphorus pentoxide. The material at this stage was a soft, light buff powder, the analysis being given in Figure 7.

A sample of this calcium oxylignosulfonate, 1.00 g., was suspended for one week in 150 ml. of a solution containing 50 g. of sodium hydroxide and 10 g. of sodium carbonate in one litre, which was the buffer Sacks (5) used in his hypochlorite oxidations of periodate lignin. This suspension which had a final pH of 11.8, was neutralized with glacial acetic acid to pH 7, evaporated, and the residue extracted with ethanol. The insoluble portion was twice taken up in 15 ml. of water and reprecipitated with ethanol, and the powder was dried by solvent-exchange through benzene and then under vacuum over phosphorus pentoxide. Yield 0.82 g., or 82% by weight. Anal.: Total S, 2.7%; Cl, 0.6%; Ca, 22.5%. The sulfur analysis broke down into 0.8% present as free sulfate ion, and 1.9% present as combined sulfur. The calcium content, determined from sulfated ash was not strictly accurate for there was some sodium in this precipitate.

Another 1 g. sample of the calcium oxylignosulfonate was treated with 150 ml. of a saturated solution of calcium hydroxide for one week. The suspension, of a final pH of 11.6, was treated with about 7 ml. of glacial acetic acid which brought the pH to 6.6. A precipitate of essentially the same composition and one fifth of the quantity of that described below was removed at this point. The mother liquor was concentrated on the steam bath until solids appeared and was then diluted with ethanol to precipitate the calcium lignosulfonate (together with some calcium acetate). The calcium acetate was leached away

with glacial acetic acid, and the residual calcium lignosulfonate, representing four-fifths of the product, was dried as before. This powder, yield 0.7 g., contained 1.8% organically combined sulfur and 6.1% sulfur from sulfate present as the calcium salt. Hence, calcium sulfate accounted for 0.18 g. of the precipitate. The remainder was calcium lignosulfonate.

In another test, 1.051 g. of the calcium lignosulfonate, of which 0.0325 g. was sulfur by analysis, was extracted with 100 ml. of glacial acetic acid and then with benzene. The residue, 0.933 g., was found on analysis to contain the equivalent of 0.0317 g. of sulfur, so that the recovery was nearly (97%) complete.

Precipitation with Zinc Oxide

The precipitation of a zinc oxylignosulfonate was carried out as outlined in Figure 8. Zinc oxide, 5.076 g. was added to 200 ml. of a solution containing 3.36 g. of oxylignosulfonic acid to bring the solution to pH 4.9. After standing overnight, excess zinc oxide, 0.321 g., was removed as a precipitate on the centrifuge. Hence the net consumption was 4.755 g., most of which went to neutralize the hydrochloric acid formed during the oxidation. The clear solution of zinc oxylignosulfonate, zinc chloride and other zinc salts was evaporated to less than 50 ml. and was added to 200 ml. of ethanol. The precipitate of zinc salts was washed twice with 200 ml. acetone, and after being dried amounted to 2.4 g. with the analysis given

in Figure 8. The acetone washings and the ethanolic solution were combined, and the precipitate which formed was removed on the centrifuge and dried. Weight 0.71 g. Aliquots of the mother liquor were analyzed for free sulfate. Found, 0.045 g. S, or about 94% of the sulfate sulfur. The material in this solution could not be dried sufficiently for analysis of the total sulfur present because the mixed salts, mostly zinc chloride, zinc chlorate and zinc chlorite deliquesced strongly on contact with any air more moist than the air above powdered phosphorus pentoxide in the desiccator. The residue exploded on any attempt at evaporation using heat.

Precipitation with Barium Hydroxide

The precipitation of barium oxylignosulfonate after removal of anions other than oxylignosulfonate and sulfate was summarized in Figure 9. A solution of 0.62 g. of oxylignosulfonate in 30 ml., from which the excess chlorine dioxide and precipitated oxylignosulfonic acid had been removed, was mixed with 10 ml. of cold 47% hydriodic acid solution. The iodine formed was removed by extraction with ether. The aqueous solution was then shaken with 10 g. of freshly prepared silver carbonate (an excess) to precipitate all halides. After filtration, the solution of silver salts of oxylignosulfonic acid was treated with an exactly equivalent amount of 1N hydrochloric acid, here about 2.7 ml., to precipitate silver as the chloride and to leave in solution the oxylignosulfonic acids and sulfuric

acid. To this solution was added a concentrated solution of barium hydroxide to give a final pH of 4.5. Barium sulfate precipitated during this addition. Yield, 0.0465 g. after filtering and igniting in the usual procedure for sulfate analysis. The solution was evaporated to 5 ml., and 50 ml. of ethanol was added to precipitate 0.45 g. of a material containing 1.7% sulfur. The ethanolic solution was allowed to evaporate to dryness, giving 0.67 g. of salts of 0.2% sulfur content.

Precipitation with Both Zinc Oxide and Barium Hydroxide

A mixed precipitation of the zinc and barium salts of an oxylignosulfonic acid was carried out. Analyses, yields and a graphic summary of these products are in Figure 10. A solution containing 2.07 g. of oxylignosulfonic acid in 100 ml. was treated with hydriodic acid and then silver carbonate as in the previous precipitation to remove extraneous anions (except sulfate) from the solution of oxylignosulfonic acids. Correspondingly larger quantities of reagents were used. To this solution of oxylignosulfonic acid and sulfate ion was added 2.42 g. of zinc oxide to bring the pH to 4.75. Excess zinc oxide was removed on the centrifuge and dried. The product, 2.52 g., when ignited yielded 2.35 g. of zinc oxide, while 0.17 g. was organic material. The clear solution was concentrated to 45 ml. and 500 ml. of ethanol was added, to precipitate 0.80 g. of zinc oxylignosulfonate. The ethanolic solution and washings were combined and 50 ml. of water was added before evaporation on the steam bath to leave 25 ml. of an aqueous

solution containing the zinc salts soluble in ethanol. When a concentrated solution of barium hydroxide was added to this solution to bring the pH to 4.0, barium sulfate was precipitated, and was ignited to constant weight (0.028 g.). More barium hydroxide solution was added until pH 8 was reached, and the voluminous, gelatinous precipitate which separated was recovered on the centrifuge, was washed with acetone and benzene and dried as usual. This precipitate was probably a mixture of the basic zinc and the barium oxylignosulfonate together with zinc hydroxide. The mother liquor was then treated with ethanol and a final precipitate of barium oxylignosulfonate was obtained. This precipitate was washed and dried in the usual fashion.

The Preparation of Synthetic Humic Acid

The synthetic humic acid was made according to the method of Eller (101) by dissolving 1 g. of hydroquinone in excess 0.1N sodium hydroxide and by adding, with stirring, 5 g. of potassium persulfate over a period of one hour. The clear brown solution was neutralized with N hydrochloric acid and the resulting precipitate was separated on the centrifuge, was washed free of chloride ion, and was air-dried. The hard, resin-like product was ground and dried, under vacuum, over phosphorus pentoxide.

Ultraviolet Spectra

Ultraviolet spectra were determined for solutions of the various materials, mentioned in Table VII, on a Beckman Model DU spectrophotometer. The wavelength range covered was from as low as possible, usually between 210 and 230 mμ, to 400 mμ. Spectra were usually observed at 5 mμ intervals, but with smaller intervals at the peaks. Solutions were made up, usually at concentrations of 0.5%, and were diluted usually 1:100 so that the absorbance maxima fell within the range of 0.7 to 1.5. For a given set of comparable spectra, the same serial dilution was followed, although the criterion with respect to absorbance at the maximum might have to be violated. The last two stages in the serial dilution employed one of the buffers described in the section on analytical methods, but the buffer was omitted from all but the last stage in some cases where precipitation of a calcium phosphate might occur unless the solution was very dilute. Such precipitation was avoided because any turbidity would have invalidated the ultraviolet measurements. A blank solution composed of the corresponding buffer was present in the compensating cell.

Infrared Spectra

Infrared spectra were very kindly made for us by Miss F.E. Goodspeed of the Fuels Division, Mines Branch, Department of Mines and Technical Surveys, Government of Canada, Ottawa, through the courtesy of Dr. D.S. Montgomery. She used a Perkin-

Elmer double beam infrared recording spectrometer and the potassium bromide pellet technique, with a potassium bromide pellet as a blank. The samples were micronized in a ball mill and were made into pellets of known concentration with the potassium bromide. The pellets were then dried in an oven for one hour and cooled under vacuum over phosphorus pentoxide overnight, measurements being taken the next day.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. Spruce periodate lignin, prepared according to the modified process of W. Sacks, which used a very mild alkaline hydrolysis to remove the oxycellulose, was cooked in 9% aqueous sodium bisulfite for various times and temperatures. Steam bath temperature (about 98°) and one to two days time was found to be sufficient for the sulfonation to Hägglund's insoluble Stage I lignosulfonic acid, and also for the autohydrolysis near pH 2 to the soluble Stage II acid. These conditions were much milder than those hitherto used.

2. The sealed tubes to carry out the above reaction proved to be unnecessary, and a more convenient open cook at atmospheric pressure could be used with a stronger sodium bisulfite solution (16%) so that it still acted as a buffer at pH 5.2 over the period of the cook in spite of the loss of some sulfur dioxide. This open cook, with both sulfonation and autohydrolysis taking place successively in flasks equipped with mechanical stirring and a reflux condenser, had the advantage that aliquots could be taken to follow the progress of the reaction. The method was applied to obtain data from which could be estimated the optimum times for both steps in the reaction. Sulfonation for 20 hours, followed by acid exchange and autohydrolysis at 2% solids concentration for 12 to 15 hours, caused the solution of about 90% of the lignin.

3. A 2% aqueous solution of the soluble autohydrolyzed lignosulfonic acid obtained under the above optimum conditions was saturated with chlorine dioxide four times, over a period of two weeks. Even after this drastic oxidation, the rate of consumption of chlorine dioxide was still greater than its rate of decomposition in water, and over 15% of the lignosulfonic acid was not sufficiently degraded to dialyze through a cellophane membrane immersed in running tap water overnight. The oxidation with chlorine dioxide, then, did not reach a limit and stop as did that with alkaline hypochlorite. Although a slower agent than hypochlorite, chlorine dioxide oxidized in a different fashion, and a combination of the two oxidants should be more effective than either alone.

4. Calcium, barium and zinc salts were prepared in aqueous solution by neutralization of the chlorine dioxide oxylignosulfonic acid, and were then precipitated by the addition of various organic liquids. These salts could not be purified by reprecipitation. They were analyzed and their spectra were taken and studied. Indications were that they were very extensively oxidized polyelectrolytes, containing many carboxylic acid groups per sulfonic acid group, retaining very little aromatic structure and probably no phenolic units.

5. Quantitative analyses of the original autohydrolyzed lignosulfonic acid, the oxylignosulfonic acid and the final precipitated oxidation products indicated that from one-third to one-half of the original combined sulfur had been split off

during the oxidation as sulfate ion, probably by a direct attack on the carbon to sulfur bonds. In view of the almost complete material balances obtained, few if any small sulfur-containing fragments were formed, and a gradual breakdown to sulfate ion and carbon dioxide could not be considered probable.

6. Ultraviolet spectra of the above oxidized products and of those obtained by Dr. W. Sacks and Dr. N.S. Thompson, confirmed the fact that oxidation removed the peak at 280 mμ wavelength considered typical of lignins and their derivatives. Thus an estimation of lignin based on the absorption at 280 mμ in the ultraviolet would be in error when applied to bleached pulp.

7. Ultraviolet difference spectra were obtained by plotting the difference between the spectra of the samples in buffer at pH 7 and in one at pH 12. The results showed that the ratio of methoxyl groups to ionizable phenolic groups capable of entering into resonance, calculated according to a modification of the method used by Aulin-Erdtman, varied depending on the oxidant and the extent of the oxidation. This method was also applied in a new way, by measuring the difference between the spectra at pH 2 and at pH 7. It was anticipated that any ionizable groups capable of entering into resonance in this range, such as very strongly acidic phenolic hydroxyl groups would be revealed. The polyhydroxy hydroquinone (the synthetic humic acid) and, most strongly, the hypochlorite oxylignin did

appear to possess groups which ionized in this pH region to resonating forms.

8. Infrared spectra were kindly provided by other workers for a number of the above substances. The lignins yielded infrared plots similar to those already in the literature, and in the oxidized lignins varying degrees of attack on the aromatic structure were revealed by the diminution of bands associated with aromaticity. Variation in the phenolic hydroxyl to methoxyl ratio, as determined from the ultraviolet difference spectra, was also evident in the infrared. Oxidation with chlorine dioxide was more destructive of aromatic units than hypochlorite oxidation, as had been anticipated.

9. The ultraviolet difference spectra showed the presence of some similarities between lignin derivatives and a humic acid synthesized from quinone, both between pH 12 and 7 and between pH 2 and 7. Certain bands strongly present in the infrared spectrum of the humic acid and correlated to quinone-type carbonyl groups (5.85 μ and 6.2 μ) were also found in the oxylignins, but many other bands were absent. Even so, the synthetic humic acids appeared to give a more complicated infrared spectrum than that of a natural humic acid obtained from a lignite coal. The natural humic acid also bore a resemblance to the most strongly oxidized chlorine dioxide oxylignins in the lack of aromatic absorption in the infrared.

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