XLII. CONTRIBUTIONS TO THE STUDY OF LIGNIN.

PART I. METALIGNIN, A NEW TYPE OF ALKALI LIGNIN.

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ALTHOUGH the soda process for the resolution of lignified material into cellulose, and soluble derivatives of lignin, is an important industrial process, very little evidence has been recorded as to the nature and composition of the lignin so obtained, and of the relation existing between this form of lignin and the lignosulphonic acids obtained in the bisulphite process.

Powell and Whittaker [1924, 1925], who investigated the lignins obtained from flax and a number of woods, including pine, spruce, ash, birch and poplar, employed a solution of caustic soda of 8–12 % concentration for six to ten hours at 140–160°. They considered that this process does not involve internal changes in the lignin molecule, and that the lignin so obtained is “probably closely related to lignin as it exists in the lignocellulose complex.” The results of a large number of comparative experiments showed that the lignin isolated from flax, and from the various woods under the above conditions, is of constant composition, viz. $C_{45}H_{48}O_{16}$, and the authors concluded that plant lignin is derived from a basic substance which they term “lignol,” $C_{41}H_{40}O_{16}$. Lignol contains nine hydroxyl groups and the authors assume that the lignins present in the various woody tissues differ only in the extent to which the hydroxyl groupings of the basic lignol are methylated. The lignin $C_{45}H_{48}O_{16}$ contains four methoxyl and five hydroxyl groupings and the product obtained from spruce-wood showed on analysis the composition $C = 64.0$, $H = 5.5$ %.

There is no doubt that the working conditions, the time and temperature and the concentration of alkali used influence the resulting product. Under the prolonged action of alkali at high temperatures internal changes, and probably oxidation of the lignin complex, take place [Fuchs, 1926]. The data obtained by Beckmann, Liesche and Lehmann [1923] illustrate this variability in composition.

Beckmann, Liesche and Lehmann [1921] have employed perhaps the most restrained conditions in isolating lignin fractions from rye-straw; namely, 2 % sodium hydroxide in aqueous-alcoholic solution acting in the cold for

48 hours. The alcohol prevented the solution of hemicelluloses, pentosans and other non-lignified substances, which are soluble in, and removed by, aqueous alkalis.

Their product was a yellow powder which darkened and aggregated at 50°. Its molecular weight was of the order of 800 and its composition approximated to the formula, $C_{40}H_{44}O_{15}$, this unit containing 4 hydroxyl and 4 methoxyl groupings.

The two investigations cited illustrate extreme variations in working conditions. Other products obtained from commercial alkaline black liquors have been described [see Hägglund, 1924; Holmberg, 1921].

Apart from oxidation and definite internal change brought about by the prolonged action of caustic alkali, removal of one or more methoxyl groupings of the original lignin is probable, resulting in the isolation either of a single derivative, or of a mixture of partly demethylated derivatives. In order to obtain a lignin as near as possible to its original condition, it is desirable, therefore, to reduce the severity of the alkaline attack and shorten the time as far as consistent with satisfactory resolution.

In the course of experiments having for their object the quantitative separation of lignin from lignified tissues, Mehta [1925] found that sodium hydroxide solution in a concentration of 4 % gave the best result, and that with this strength of solution at a pressure of 10 atmospheres the resolution of the wood was complete in one hour. The lignin is stated to be isolated quantitatively on acidifying the solution.

The method was used by this author for the estimation of lignin in a large number of plant products—the values obtained being very much lower than those generally found by the hydrochloric acid method of Willstätter and Zechmeister [1913]. The lignin obtained from different species of wood was found to be a brown powder with the odour of vanillin, insoluble in water, but soluble in dilute alkalis, ammonia, alcohol, acetone and glacial acetic acid. It differed from all lignins previously described in that it had a fairly definite melting point (170°). The acid value was found to be 477 and the iodine value 139.7.

The method appeared to us likely to yield a lignin with the minimum of chemical change, while the marked solubility in a range of organic solvents and the evidence of a definite melting point seemed to indicate a lignin of relatively simple composition, in agreement with our own results on jute fibre. By arrangement with Dr D. N. Nanji, therefore, we have carried out an investigation of the substance, the results of which are given below.

It has been overlooked by most previous workers that caustic alkali removes from the wood not only lignin, but also resins, fat-waxes and hemicelluloses which it may be impossible to remove subsequently from the lignin and this may very well account for the variable compositions reported by different workers. The wood used throughout this investigation was spruce, which was thoroughly extracted with benzene, alcohol and water and then digested

with 5 % sodium hydroxide solution in the cold to remove hemicellulose. The lignin isolated by us was a brown powder, soluble in most organic solvents with the exception of ether, benzene and light petroleum. Its melting point was 186°. It was soluble in sodium carbonate, but not in ammonium carbonate solutions. It had the composition $C_{20}H_{20}O_6$, and determinations of the molecular weight gave the somewhat surprising result that this formula represented the molecular unit¹. We have thus, as anticipated, a compound of relatively simple composition; almost all lignins previously isolated having been assigned formulae with approximately double this number of carbon atoms. As the product is possibly a depolymerised form of the lignin as it exists in the wood and as it exhibits definite properties by which it can be identified, we propose to refer to it as *metalignin*.

Metalignin, $C_{20}H_{20}O_6$, has one free hydroxyl group, two methoxyl groups and, according to the composition of the oxime it contains, two carbonyl groups, one of which may be ketonic and the other aldehydic. The iodine value of 139.7, previously recorded, corresponds to two unsaturated linkages in the molecule (found: $C_{20}H_{20}O_6$ of molecular weight 356 absorbs iodine 498.4, $2I_2$ requires 508). It is interesting to note in this connection, that Cross and Bevan [1882] isolated a small alcohol-soluble fraction from chlorinated jute which had the composition $C_{19}H_{18}O_9Cl_4$ with one free hydroxyl grouping. These results together with those recorded for the alkali lignins are summed up in the following schematic formulae:

I. Metalignin
 $C_{20}H_{20}O_6$

II. Beckmann, Liesche and
Lehmann: alkali lignin
from rye-straw $C_{40}H_{44}O_{15}$

III. Powell and Whittaker:
lignin $C_{45}H_{48}O_{18}$

Preparation of metalignin.

Spruce-wood was employed throughout the present work as its constants are well known and the majority of the lignin derivatives previously described in the form of sulphonic acids were prepared from this wood. An analysis of the wood employed will be found on p. 299, from which it will be seen that it contains 5.8 % of extractives and 3.8 % of hemicelluloses. The purification of the wood followed generally on the lines recommended by Friedrich and Diwald [1925].

The wood, in the form of fine sawdust, was well extracted with benzene (12 hours), alcohol (12 hours) and water (12 hours) to remove resins and glucosides, and then digested with four changes of a 5 % solution of sodium hydroxide for 36 hours to remove hemicelluloses (for quantitative results see p. 299). The metalignin itself was isolated by heating the purified sawdust in an autoclave with a 4 % sodium hydroxide solution at 8 atmospheres

¹ It is interesting to note that Holmberg [1921], by the extraction of sulphite liquor with ether, has isolated a crystalline substance, M.P. 250°, of the same formula $C_{20}H_{20}O_6$, which is probably the lactone of diguaiacyltetramethylenecarbinolcarboxylic acid.

pressure for one hour¹. The dark solution of sodium metalignate was poured off and the metalignin precipitated by the addition of hydrochloric acid, washed by decantation, dissolved in 95 % alcohol and the alcoholic solution evaporated to dryness. The metalignin thus obtained was a lustrous black solid.

It was purified by solution in glacial acetic acid and precipitation with water; the precipitated product was washed with water and dried at 60°. After the first precipitation the original value for the melting point, 170°, was raised to 180°, whilst after the second and third treatment the melting point remained constant at 185–186°.

Properties of metalignin.

The purified metalignin was a light brown, odourless solid, easily soluble in pyridine, alcohol, acetone, glacial acetic acid, ethyl acetate, naphthalene, trichloroacetic acid, saturated calcium thiocyanate solution and slightly soluble in chloroform. It was insoluble in ether, benzene, ligroin, light petroleum, as well as in sodium bisulphite solution, sulphurous acid and ammonium oxalate solution. It dissolved readily in sodium hydroxide, ammonium hydroxide and sodium carbonate solutions and was precipitated from these on the addition of acids. It was insoluble in ammonium carbonate solution. The calcium and barium salts were precipitated on the addition of the soluble salts of these elements to a solution of metalignin in ammonia. In its solubility in glacial acetic acid and acetone, it differed from the product obtained by Powell and Whittaker. The dry substance contained 0.13 % ash. Analyses are calculated on ash-free material.

Found: C = 66.8, H = 5.6; C = 67.0, H = 5.6; $C_{20}H_{20}O_6$ requires C = 67.3, H = 5.6.

The formula $C_{20}H_{20}O_6$ for metalignin is the same as that predicted by Klason for α -lignin (see below). Determinations of the molecular weight by the cryoscopic method in glacial acetic acid gave the average value 341.

0.4410 g. in 31.3 g. glacial acetic acid $\Delta = 0.164^\circ$ M.W. = 336

0.8770 " " = 0.314° " = 341

1.3186 " " = 0.473° " = 347

The molecular weight was also determined in naphthalene and gave the average value 342.

The molecular formula is therefore equal to $C_{20}H_{20}O_6$. Two methoxyl groups were found to be present.

Found: OMe = 18.6 % and 17.4 %; $C_{18}H_{14}O_4(OCH_3)_2$ requires OMe = 17.4 %.

Monobenzoyl-metalignin $C_{20}H_{18}O_6(CO.C_6H_5)$. Metalignin reacted with benzoyl chloride in alkaline solution with great ease.

The monobenzoyl-metalignin was a pale yellow, almost white solid, M.P. 184°. It was very soluble in pyridine, less so in alcohol and insoluble

¹ A 10 % solution of sodium hydroxide at 4 atmospheres pressure for 1 hour also gave good results.

in ether, benzene, ligroin and light petroleum. The crude benzoyl derivative was dissolved in pyridine and precipitated with 95 % alcohol. After three such treatments the melting point became constant at 184°.

Found: C = 70.1 %, H = 5.1 %, OMe = 13.8 %; $C_{27}H_{24}O_7$ requires C = 70.4 %, H = 5.2 %, OMe = 13.4 %.

Monoacetyl-metalignin $C_{20}H_{19}O_6$ (CO.CH₃). The acetyl derivative was prepared according to the description given by Powell and Whittaker [1924]. 5 g. metalignin and 20 g. acetyl chloride were mixed and a few drops of concentrated sulphuric acid added. The metalignin rapidly went into solution with evolution of a considerable amount of heat, the mixture being heated for one hour at 80°. The acetyl derivative was precipitated by pouring the hot solution into ice-water with vigorous stirring. The acetyl-metalignin was very soluble in pyridine, alcohol and acetone, insoluble in ether, benzene, ligroin and light petroleum. It was purified by dissolving in acetone and precipitating with brine, washing with water and drying at 60°. Unlike the acetyl derivative described by Powell and Whittaker it was quite stable.

Found: C = 66.0 %, H = 5.5 %; $C_{22}H_{22}O_7$ requires C = 66.3 %, H = 5.5 %.

Methyl-metalignin $C_{18}H_{13}O_3(OCH_3)_3$. 5 g. metalignin were dissolved in 12 cc. of 10 % caustic soda solution and dimethyl sulphate was added drop by drop with constant shaking. The methylated derivative was slowly precipitated. Purification was effected by dissolving the crude product in pyridine and precipitating with 45 % alcohol. The methylated derivative was a pale, almost canary yellow compound, very soluble in pyridine, acetone and alcohol, insoluble in ether, benzene and light petroleum.

Found: OMe = 25.4 %; $C_{18}H_{13}O_3(OCH_3)_3$ requires OMe = 25.1 %.

Metalignin dioxime $C_{20}H_{22}O_6N_2$. The metalignin contains active carbonyl groupings, which was shown by the fact that it reduced Fehling's solution and ammoniacal silver nitrate solution and by the preparation of the dioxime. This compound was prepared by the method described by Brady and Dunn [1913]. 3 g. metalignin were mixed with 3 g. hydroxylamine hydrochloride and an 8 % solution of sodium hydroxide was added gradually to the mixture. The solution was filtered and the oxime precipitated by the addition of ammonium chloride solution.

The oxime was a pale brown solid, soluble in pyridine and acetone, but only slightly soluble in alcohol. It was insoluble in ether, light petroleum and benzene. It was purified from alcohol solution.

Found: N = 6.7 % and 6.9 %; $C_{20}H_{22}O_6N_2$ requires N = 7.2 %.

Metalignin-phenylhydrazone. The preparation of a phenylhydrazine derivative proved unsatisfactory. The metalignin did not react with the phenylhydrazine at all readily, and it seemed doubtful if the compound finally obtained was the true hydrazone. With the exception, perhaps, of the compound obtained by Dorée and Hall [1924] from their lignosulphonic acid, the phenylhydrazones obtained from the various lignins do not stand in any definite relationship to the parent substance.

From the results recorded above, the formula

is given to metalignin. It will be seen that all the oxygen atoms, except one, are accounted for, leaving a nucleus of 16 carbon atoms.

It was hoped that on oxidation some definitely recognisable cleavage product would result. This was not the case.

Oxidation of metalignin.

(a) 5 g. metalignin were heated with 100 cc. of 5 % nitric acid on the water-bath for six hours, when an insoluble orange-red compound slowly formed, which proved to be soluble in all the solvents for metalignin itself. From its general reactions it appeared to be similar to the compound $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_{17}\cdot\text{OCH}_3$, isolated by Dorée and Hall [1924] by the oxidation of lignosulphonic acid with 5 % nitric acid. It gave ammonia on warming with sodium hydroxide and could be reduced with zinc dust and acetic acid to a brown substance. It was more acidic in character than metalignin, dissolving readily in alkalis and ammonium carbonate, from which solutions it could be precipitated on the addition of acid.

(b) 6 g. metalignin oxidised for 4 hours with 10 % nitric acid gave 3 g. oxalic acid. Dorée and Hall also discovered that when lignosulphonic acid was oxidised with strong nitric acid, oxalic acid was obtained in considerable yield.

(c) Metalignin was oxidised with sulphuric acid in the presence of mercuric sulphate at 165°. By this method a minute amount of the mercury salt of an acid was obtained, which was very soluble in ether, alcohol and water, slightly soluble in benzene and insoluble in light petroleum. It was, however, obtained in too small a yield to be identified.

The relation between the lignins isolated by different methods and the original lignin of the plant.

In Table I are collected data relating to some of the better defined types of lignin that have been described. As these vary in the number of methoxyl groupings they contain and some are sulphonic acids and others acetyl derivatives, the empirical formula for the basic "lignol" has been calculated in each case for purposes of comparison. This "lignol" represents the hydroxylated compound, sulphonic, acetyl and methyl groupings being eliminated. A certain general similarity will be observed among all these lignols. The number of carbon atoms approximates to 36 and the number of carbon and hydrogen atoms present is approximately equal. The number of oxygen atoms varies and in this connection we have noticed that isolated lignin has a remarkable capacity for fixing oxygen (under the action, for example, of nitric acid or hydrogen peroxide) which may account for this irregularity.

The fact that, using a particular method of isolation, e.g. that of No. 7, identical products are obtained from different woods, flax, etc., seems fairly

strong evidence for the assumption that the same lignin substance is present throughout the plant world. According to Friedrich and Diwald [1925] it would appear that in the wood tissue it exists as a methylated derivative. By the action of 17 % hydrochloric acid in the cold they claim to have isolated a lignin without hydrolysis of hydroxyl groupings or subsequent condensation changes which take place under the action of the 40 % hydrochloric acid used by Willstätter.

Table I.

Method of isolation*	Author	Em- pirical formula	No. of OH groups	No. of OMe groups	Corre- sponding basic "lignol"	Lignol	
						% C	% H
1. 17 % HCl cold	Friedrich and Diwald [1925]	$C_{39}H_{48}O_{14}$	1	5	$C_{24}H_{38}O_{14}$	60.8	5.6
2. 3 vol. HCl (d. 1.18) and 1 vol. H_3PO_4 (d. 1.7)	Urban [1926]	$C_{43}H_{48}O_{16}$	5	4	$C_{39}H_{40}O_{16}$	61.2	5.2
3. H_2SO_3 aq. at 110°	Dorée and Hall [1924]	$C_{26}H_{30}O_{12}S$	3 or 4	2	$C_{24}H_{24}O_9$	63.2	5.26
4. Ditto	Klason [1925]	$C_{30}H_{32}O_{12}S$	3 (?)	2 (?)	$C_{28}H_{26}O_9$	66.1	5.1
5. Calcium bisulphite liquor—computed	Klason α -lignin [1920]	$C_{22}H_{22}O_7$	1	2	$C_{18}H_{16}O_6$	65.85	4.84
6. 4 % NaOH at 10 atmos. pressure 1 hour	Dorée and Wright Metalignin	$C_{20}H_{20}O_6$	1	2	$C_{18}H_{16}O_6$	65.85	4.84
7. 8–12 % NaOH at 140 – 160° for 6–10 hours	Powell and Whittaker [1925]	$C_{45}H_{48}O_{16}$	5	4	$C_{41}H_{40}O_{16}$	62.4	5.07
8. 2 % alcoholic NaOH in cold on rye-straw	Beckmann, Liesche and Lehmann [1921]	$C_{40}H_{44}O_{15}$	4	4	$C_{36}H_{36}O_{15}$	61.01	5.08

* Spruce-wood or allied soft wood unless otherwise stated [Fuchs, 1926, p. 281].

As will be seen (No. 1), this lignin contains 5 methoxy-groupings, of which two are readily removed on saponification and are believed to be ester methoxyl, whilst the remaining three are ether methoxyl.

Metalignin (No. 6) is characterised by melting point and solubility range and it differs from the others in possessing the molecular formula corresponding to a C_{20} unit, the others approximating to a C_{40} unit complex. It is interesting to note that Klason had previously deduced that an α -lignin of the same formula constituted (in the form of its sulphonic acid) one component of the lignin isolated in the calcium bisulphite process. Later [1925], in order to explain the existence of the acid $C_{26}H_{30}O_{12}S$ (No. 3) which is obtained by the action of sulphurous acid solution at 110° , Klason has doubled the formula for α -lignin and considers that the acid C_{26} is a mixture of a mono- and a dibasic sulphonic acid $2C_{20}H_{20}O_6 \cdot 2H_2SO_3$ and $2C_{20}H_{20}O_6 \cdot H_2SO_3$ respectively, while in a later communication he states that the simplest acid obtainable by the action of sulphurous acid solution on wood has the composition

There is thus a connection between the product obtained from spruce by sulphurous acid, and by the action of dilute alkali for a minimum time. It

may be that metalignin, C_{20} , is the unit upon which the natural lignins are based and that, whilst the usual type isolated is of the order C_{40} , it may exist in the plant in an even more polymerised form. In this way its resistance to oxidation in the living tissue and its susceptibility when isolated may be explained.

With regard to the constitution of metalignin, we do not assume the presence of the acidic (carboxyl) grouping. The fully methylated derivative is insoluble in sodium hydroxide, so that the solubility in alkali hydroxides appears to be due to the one free (phenolic?) hydroxyl group. From the evidence of the oxime we assume the presence of one carbonyl-group and one aldehydo-group in agreement with the results of Powell and Whittaker, who postulated two carbonyl- and one aldehydo-groupings in the C_{45} unit complex. The extended formula thus becomes: $C_{16}H_{12}O(OCH_3)_2.OH.CO.CHO$.

We have obtained a certain amount of evidence which makes it probable that the unassigned atom of oxygen exists in a pyrone ring and that the $CO-CH_2$ group is also present. It will be remembered that Klason regards α -lignin as derived from 2 molecules of coniferyl aldehyde, giving the following formula:

in which two aromatic nuclei are present. It seems impossible, with such a constitution, to explain the fact that on oxidation no aromatic products are obtained. The Klason formula closely resembles that of the anthocyanins, *e.g.* quercetin:

and the tetramethyl ether of this on oxidation with alkaline potassium permanganate yields veratric acid $C_6H_3(COOH)(CH_3)_2$, and probably phloroglucinol dimethyl ether. With metalignin on the other hand gentle oxidation, *e.g.* with dilute nitric acid, results in complete breakdown to oxalic and carbonic acids with the intermediate formation of non-aromatic nitro-compounds. We therefore prefer to regard metalignin as based upon hydro-aromatic nuclei in some such way as shown in the following ideal formula:

in which the two double linkages and the benzo-pyrone ring are readily opened up on oxidation tending to the disruption of the entire complex.

Alkali resolution as a method for the estimation of lignin.

Mehta [1925] has developed the following process for the quantitative estimation of lignin in wood. 5 g. dry wood in the form of fine sawdust are treated with 100 cc. of 4 % sodium hydroxide solution at 10 atmospheres pressure in a Pyrex glass tube for one hour. The lignin is said to be removed quantitatively as a sodium derivative leaving a pure α -cellulose. The solution is acidified, and the precipitate dissolved in 95 % alcohol. The alcohol is removed and the residue dried to constant weight at 100°.

The figures arrived at, compared with those obtained on the same samples by the Willstätter process, show marked differences, as will be seen in Table II.

Table II.

	4 % NaOH	H ₂ SO ₄ .aq.	Difference
Lignum vitae ...	38.39	47.99	9.6 %
Teak ...	31.07	45.80	14.7
Larch ...	21.33	32.80	14.7
Spruce ...	17.80	30.55	12.7

The higher values obtained by the Willstätter method are ascribed to the presence of impurities and to combination with SO₄H residues. The presence of impurities to the extent of 14.7 % is certainly high, and it is doubtful if the discrepancy can be due to this cause.

In the present work a quantitative examination was made of the spruce sawdust employed, to see if the difference in the values obtained by the two methods could be accounted for in any way. About 20 g. spruce wood, after extraction with benzene and alcohol and 5 % sodium hydroxide, were heated with 4 % sodium hydroxide in an autoclave for one hour at 10 atmospheres pressure. The sodium lignate was filtered off and the residual "cellulose" examined. This was at first red in colour, but quickly oxidised in the air to brown and finally to a dull green. After washing and drying this colour was still retained. It was never "snow white" or "exceptionally light" in colour as described by Mehta. Treatment of this "cellulose" with hydrochloric acid (d. 1.2) for twelve hours showed that it contained 5.4 % of lignin.

An examination was also made of the filtrate after precipitation of the lignin with hydrochloric acid. This was of a pale yellow colour which deepened to brown on the addition of alkali. The filtrate did not give a precipitate with a solution of calcium chloride, a result at variance with that of Powell and Whittaker. After neutralisation with ammonia, the liquid was evaporated almost to dryness on the water-bath, when a dark solid was obtained which was removed by extraction with alcohol. The alcoholic extract gave a brown

residue, soluble in water, pyridine, alcohol, and alkalis. It had an odour of ω -hydroxy-methylfurfural.

A more exact quantitative experiment was also carried out: 5 g. spruce sawdust, after extraction for eight hours with benzene and alcohol and with water for four hours, were finally digested with a 5 % solution of sodium hydroxide for twelve hours to dissolve the hemicelluloses present. The purified sawdust was then autoclaved for one hour with 100 cc. of 4 % sodium hydroxide at 10 atmospheres pressure. The following values were obtained:

Metalignin (precipitated by acid)	18.6 %
Residue from filtrate (not precipitated by acid) ...	7.3
Lignin remaining in the cellulose	3.7
Total	29.6

In a further effort to ascertain the cause of the difference between the values obtained by Mehta's method and the hydrochloric acid method all the constituents of the wood were estimated by the methods of Dore [1920] (with the exception of the lignin). The following values were obtained (calculated on the original dry spruce sawdust, which contained 10 % of natural moisture):

Extraction with benzene	1.7 %
„ alcohol	1.6
„ water	2.5
„ sodium hydroxide (5 %)	3.8
Cellulose	55.0
Mannan	7.6
Galactan	0.1
Total	72.3

The difference (27.7 %) should be lignin, which agrees with the usual figure of 28–30 % found for spruce by direct estimation with hydrochloric acid. It is obvious, therefore, that Mehta has isolated only a fraction of the lignin present in the wood.

Part of the deficiency in total lignin-content can be accounted for by the retention of a portion of the lignin in the cellulose residue after heating with caustic soda, and the remainder is to be found in the water-soluble body present in the acid filtrate after precipitation of the lignin, which may be a decomposition product of lignin. The hemicellulose portion (3.8 %) was found to be separable into two parts, a part precipitated by acid, and a water-soluble fraction, precipitated by the addition of 95 % alcohol. These results are in agreement with those of O'Dwyer [1926], who found that there were two hemicelluloses present in beech-wood.

SUMMARY.

1. By the action of 4% caustic soda at 10 atmospheres pressure for 1 hour on purified wood, a new type of lignin has been obtained and characterised, for which the name *metalignin* is proposed.

2. This lignin has the formula $C_{20}H_{20}O_6$ with molecular weight 356. It melts at 186° and is soluble in a range of organic solvents, differing in these respects from lignins previously described.

3. The preparation of derivatives indicates the presence of one hydroxyl, two methoxyl and two carbonyl groups. Two double linkages are apparently present.

4. Metalignin agrees in composition with the α -lignin of Klason [1920] existing as a sulphonic acid in bisulphite liquors.

5. The technique described in (1) above does not, as has been claimed [Mehta, 1925], give a quantitative separation of lignin.

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