

THE ACTION OF STANNOUS CHLORIDE ON LIGNIN

A Thesis

Presented to the Faculty of Virginia Polytechnic Institute
as a Partial Fulfillment of the Requirements for the
Degree of Master of Science
in Chemistry

by

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ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. R. E. Hussey, under whose supervision this investigation was carried out, for his many helpful suggestions and criticisms.

Gratitude is expressed to the Department of Chemistry of Virginia Polytechnic Institute for its cooperation and assistance.

INTRODUCTION

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This investigation was undertaken to further the work of Wagner¹ who isolated coniferyl aldehyde by the treatment of wood with stannous chloride. An attempt has been made to determine whether or not coniferyl aldehyde can be obtained by the action of stannous chloride on two different lignin preparations, and thus answer the question as to whether Wagner's coniferyl aldehyde came from the lignin of the wood or existed free in the wood.

1 Wagner, M. S. Thesis, V.P.I. (1946)

REVIEW OF LITERATURE

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Chemists and botanists have known for many years that wood will give color reactions when treated with certain organic bases and phenols and certain inorganic reagents.

Phloroglucinol, the so-called Wiesner reagent,¹ gives with wood in the presence of hydrochloric acid a deep reddish-violet coloration; resorcinol¹ colors wood a deep blue in the presence of hydrochloric acid, and benzidine in acetic acid colors wood a deep orange.² Wood subjected to the Maule reaction³ which involves the use of potassium permanganate, dilute hydrochloric acid, and dilute ammonium hydroxide gives a distinct red coloration. This reaction, however, does not give any definite colors when applied to those woods of coniferous gymnosperms. Concentrated or fuming hydrochloric acid colors wood green.⁴

The color reactions given by wood in the presence of certain inorganic reagents have been attributed to some characteristic group of the lignin complex, possibly in the nature of syringyl groups. On the other hand, the color reactions given by wood with certain organic reagents have been attributed by many investigators to the presence in wood of a single aldehyde, coniferyl aldehyde.

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- 1 Wiesner, J., Sitzler. Akad. Wiss. Wien., 77, 60 (1878)
 - 2 Schneider, H., Z. Wiss. Mikroskop., 31, 68 (1914)
 - 3 Maule, C., Beitrage Wiss. Bot. 4, 166 (1900)
 - 4 Warnecke, H., Pharm. Ztg., 33, 574 (1888)

Probably the first attempt at isolating the substance responsible for the color reactions of wood was made by Czapek.¹ By digesting wood with stannous chloride and then extracting the reaction mixture with benzene, Czapek was able to isolate a substance he called "hadromal". "Hadromal" was a yellow crystalline substance melting at 75 - 80° C. It had phenolic and aldehydic properties and gave the various lignin color reactions. Although Czapek was unable to obtain enough "hadromal" to identify it, later investigations by Hoffmeister² and Wagner³ showed it to be coniferyl aldehyde.

Hoffmeister digested wood with stannous chloride and refluxed the mixture with benzene for about twenty hours and distilled off the benzene under a hydrogen atmosphere to prevent decomposition. He obtained a product having a molecular weight in agreement with that of coniferyl aldehyde. Oxidation of this product yielded a compound which was identified as vanillin. Hoffmeister concluded that the product he had isolated and which gave vanillin on oxidation was probably coniferyl aldehyde.

With respect to Hoffmeister's work, Pauly and Feuerstein⁴ have stated that they are so well acquainted with the possibilities of formation and properties of coniferyl aldehyde that they can assert with all certainty that Hoffmeister did not have the least trace of coniferyl aldehyde in his "hadromal".

1 Czapek, F., Z. Physiol. Chem., 27, 141 (1899)

2 Hoffmeister, Ber., 60, 2062 (1927)

3 Wagner, M. S. Thesis, V.P.I. (1946)

4 Pauly and Feuerstein, Ber., 62, 297-311 (1929)

Wagner¹ isolated "hadromal" by digesting wood with stannous chloride for five days and then extracting the reaction mixture with benzene in a continuous extraction apparatus. Subsequent treatment of the benzene extract with a saturated solution of sodium bisulfite yielded an addition product which was decomposed with sodium carbonate in the presence of iso-propyl ether. Upon evaporation of the iso-propyl ether, colorless, needle-like crystals of coniferyl aldehyde were formed, melting point, 82.5 - 83⁰ C.

Wagner's results enabled him to conclude the following:

1. There is only a single aldehyde in wood responsible for the color reactions of woody tissue and that aldehyde is coniferyl aldehyde.
2. Czapek's "hadromal" is coniferyl aldehyde.
3. Coniferyl aldehyde is present in woody tissue in only minute quantities, probably to the extent of 0.02 to 0.05 per cent.

No definite conclusions can be drawn from Wagner's results as to whether coniferyl aldehyde is a characteristic group of the lignin complex or a minor constituent of the wood.

It is a well known fact that isolated lignin, with the exception of alkali lignin, gives the same color reactions as wood. Assuming in the case of the alkali lignin that the color-producing group has been removed by the action of the alkali, (that some color-producing

1 Wagner, M. S. Thesis, V.P.I. (1946)

group is removed will be shown to be true later in this paper), one could conclude that the color reactions are really due to the lignin itself, and not to some minor constituent of the wood present in very small quantities.

Podbreznik¹ has claimed that the color reactions of woody tissues are neither due to methylpentosans nor to other aromatic compounds, such as vanillin, coniferyl alcohol, or Czapek's "hadromal". Of a number of aromatic compounds tested, eugenol gave reactions which, on the whole, most closely resembled those of woody tissues. On the basis that extracted lignin and oxidized lignin give the same color reactions, Podbreznik concluded that the color reactions are mainly due to the lignin itself.

Wiechert² claimed that the color reactions given by phenols and amines in the case of red beech wood are not due to lignin, but may be traced to some substance accompanying lignin, possibly in the nature of coniferyl aldehyde. He has stated, however, that the Maule reaction is due to the lignin itself and depends on chlorination and oxidation. Wiechert, using Czapek's method with zinc chloride and hydrochloric acid for the isolation of coniferyl aldehyde, obtained degradation products from which only vanillin could be definitely identified. He concluded that the color reactions of lignin preparations is not due to coniferyl aldehyde, but to vanillin and that lignin isolated by reagents which destroy

1 Podbreznik, Pulp Paper Mag. Can., 27, 299 (1929)

2 Wiechert, K., Papier - Fabr. 37, 325 (1939)

or dissolve the vanillin and coniferyl aldehyde will not give the usual color reactions.

Brauns¹ claimed that the color reaction given by phloroglucinol and hydrochloric acid with native spruce lignin, isolated with ethyl alcohol at room temperature, is really due to the lignin and not to some substance accompanying lignin. Brauns and Brown² found that spruce wood methylated with diazomethane no longer gave this color reaction. Different lignin preparations, such as Willstätter, Freudenberg, and Klason lignins were tested with phloroglucinol and hydrochloric acid before and after methylation with diazomethane. All except the lignin isolated according to Klason with 72% sulfuric acid gave the color reaction before the methylation, but after methylation the color reaction failed to take place. They thus concluded that the hydroxyl group capable of methylation was responsible for the color reaction.

Crocker³ has expressed the view that the color reactions given by lignin with the various organic reagents do not indicate to any appreciable extent the composition of lignin. Spectroscopic data indicate the strong predominance of one aldehyde in wood and it is thought that this aldehyde is probably coniferyl aldehyde.

Rawlings⁴ has recently isolated coniferyl aldehyde in small amounts from wood by prolonged treatment of sawdust with a saturated

1 Brauns, F. E., J.A.C.S. 61, 2120 (1939)

2 Brauns and Brown, Ind. Eng. Chem. 30, 779 (1938)

3 Crocker, E. C., Ind. Eng. Chem. 13, 625 (1921)

4 Rawlings, B. S. Thesis, V.P.I., (Now in Progress)

solution of sodium bisulfite.

From the foregoing literature review, it can be seen that, without doubt, coniferyl aldehyde is present in wood, and it may probably exist in the wood in the free state. Previous work¹ also indicates that coniferyl aldehyde is not alone responsible for the color reactions of wood.

1 Brauns, F. E., J.A.C.S. 61, 2120 (1939)

EXPERIMENTAL

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The methods for the isolation of lignin may be divided into the following two classes: (1) Those that depend on the removal by hydrolysis of the cellulose and other components, leaving the lignin as an insoluble residue, and (2) those that depend on the removal of lignin from the cellulose and the other substances with which it is associated.

Class (1) methods make use of cuprammonium solution, sulfuric acid, fuming hydrochloric acid, and hydrofluoric acid. Class (2) methods make use of sulfites, alkalies, and alcohols.

Removal of the lignin from wood by any of the above methods, in any appreciable quantity, requires the use of heat and/or pressure, and as a consequence a lignin preparation is obtained which can no longer be considered as being identical with the lignin as it exists in the wood.

However, Brauns¹ has recently isolated from spruce wood, by the use of ethyl alcohol, a lignin which he calls "native" lignin. He defines native lignin as "that lignin isolated in such a manner that the solvent does not react with the lignin or alter it in any way". The experimental data presented by Brauns indicate that the lignin isolated from spruce wood according to his method is unchanged and behaves chemically in a

1 Brauns, F. E., J.A.C.S. 61,2120 (1939)

manner similar to the total lignin of the wood.

Braun's method¹ for the isolation of native lignin is as follows:

Black spruce wood meal (100-150 mesh) is extracted first with cold water, then with ether, and finally with 95% ethyl alcohol at room temperature in a percolator until the alcohol drains off colorless. The alcohol solution is distilled off under reduced pressure, whereupon a finely divided, creamy precipitate separates out in addition to a resinous material. This is washed with water and ether until the material becomes solid and powdery. It is filtered, dissolved in dioxane, and precipitated by pouring the solution into distilled water. The precipitate is filtered again, dried, and redissolved in dioxane to give a 10% solution, and then centrifuged and the filtered dioxane solution dropped slowly into absolute ether with vigorous stirring. This precipitation process is repeated until the methoxyl content remains constant. The product is washed after each purification with ether and finally with petroleum ether. The lignin so obtained is a very light cream-colored powder. It is soluble in 4% sodium hydroxide, ethyl alcohol, methyl alcohol, pyridine, and dioxane, and insoluble in water, ether, benzene, and petroleum ether.

In this investigation lignin was isolated by two methods: (I) with 95% ethyl alcohol according to the method of Brauns, with some modification, and (II) with a 10% solution of sodium hydroxide at 150° C. and two atmospheres pressure.

Method I - 250 grams of 100 mesh white pine sawdust were washed with three liters of distilled water, air dried, and then washed with ether in a continuous extraction apparatus until the ether washings were colorless. The ether-wet sawdust was dried under vacuum and

1 Brauns, F. E., J.A.C.S. 61,2120 (1939)

extracted in the same apparatus with 95% ethyl alcohol at room temperature until the alcohol washings were colorless, or nearly colorless. The alcohol extracts obtained in this manner from four 250-gram portions of sawdust were combined and distilled under diminished pressure at a temperature of 30 - 40° C. until the lignin separated out as a resinous-like material. The filtered material was washed with water, dried, and dissolved in dioxane and reprecipitated by pouring the dioxane solution into distilled water. The precipitate was again filtered, washed with distilled water, and allowed to dry in air.

The lignin was then precipitated with ether from its solution in dioxane a number of times until the filtrate was a very light yellow in color. Finally, the lignin was washed with ether until the ether washings were colorless. The yield was approximately 0.18% of the weight of the air-dried sawdust.

The lignin obtained in this manner was a light brown powder, soluble in 4% sodium hydroxide, ethyl alcohol, methyl alcohol, pyridine, and dioxane; insoluble in water, ether, benzene, and ligroin. Its solution in ethyl alcohol gave color reactions with phloroglucinol, resorcinol, benzidine, and aniline sulfate which were almost identical with those given by wood and these organic reagents. It reduced Fehling's and Tollen's solutions, but did not give a red color with Schiff's

reagent. Its solution in dioxane gave a light brown color with ferric chloride.

Method II - 200 grams of the white pine sawdust previously washed with water, ether, and extracted with ethyl alcohol were treated with 1500 ml. of a 10% solution of sodium hydroxide in an autoclave at 150° C. and two atmospheres pressure for thirty minutes. After cooling, the reaction mixture was filtered and the dark brown filtrate was acidified with concentrated hydrochloric acid. After standing over night the filtered lignin was washed with distilled water, dissolved in 10% solution hydroxide solution, filtered, and again precipitated by acidification with concentrated hydrochloric acid. The filtered lignin was washed with distilled water until the washings no longer gave a cloudiness with silver nitrate made acid with nitric acid. Finally, the precipitate was washed with ether until the ether washings were colorless.

The lignin obtained in this manner was a brown colored powder, insoluble in the usual organic solvents. It did not give any color reactions with the organic reagents to which reference has already been made. It is of interest to note here that although the lignin isolated in the foregoing manner did not give any color reactions, there was recovered from the acid filtrate, by extraction with ether, a red, oil-like substance which did give color reactions. This substance can also be isolated when wood is treated with alkali at room temperature.

It is improbable that these color reactions are due to the presence of vanillin in the oil. Only traces of vanillin,¹ if any at all, can be obtained by the action of alkali on lignin or wood at high temperatures.

This substance was not further investigated during the course of this work, and it is mentioned here as a possible subject for future investigation.

Treatment of Alcohol Lignin - One gram of the native lignin isolated according to Method I was intimately mixed with approximately three grams of a stannous chloride paste. This lignin-stannous chloride mixture was placed in a modified soxhlet extraction flask and extracted with hot benzene. The hot benzene extract was continuously drawn off into a flask cooled by immersion in cold water. After one hundred hours of extraction, the extract was distilled to a small volume under diminished pressure at a temperature of 30 - 35° C.

This concentrated extract gave none of the typical wood color reactions. Four hours treatment of the benzene extract with a saturated solution of sodium bisulfite and subsequent decomposition of the bisulfite portion with sodium carbonate in the presence of iso-propyl ether, yielded only a small amount of a light resinous material which gave none of the typical color

1 Freudenberg, K., Lautsch, W., and Engler, K., Ber., 73, 167 (1940)

reactions with the usual organic reagents. There was no evidence of any crystalline substance.

After the purification of the native lignin, there was recovered from the ether-dioxane filtrate upon evaporation, approximately ten grams of a resinous material which gave color reactions identical with those given by the native lignin. It reduced Fehling's and Tollen's solutions, and its solution in dioxane gave with ferric chloride a dark red color, and with ceric ammonium nitrate a black, flocculent precipitate. It gave no color reactions with Schiff's reagent.

Coniferyl aldehyde is soluble in ether and alcohol¹ and ligroin.² Therefore, any free coniferyl aldehyde removed from the wood during the extraction with ethyl alcohol and not lost during the purification of the native lignin would be in this ether-dioxane filtrate. The assumption is made here that coniferyl aldehyde might possibly be present in the wood in the free state. A portion of the resinous material was dissolved in benzene and treated with a saturated solution of sodium bisulfite. Decomposition of the bisulfite portion was affected with sodium carbonate in the presence of iso-propyl ether. No crystalline substance was obtained upon evaporation of the iso-propyl ether.

The bisulfite-treated benzene portion after purification gave

1 Beilstein, Organische Chemie., Vol. III, p. 106

2 Wagner, M.S. Thesis, V.P.I. (1946)

the usual color reactions, but they were not as intense as those given by the material before treatment with the saturated solution of sodium bisulfite.

To make certain that no coniferyl aldehyde was in the ether-dioxane filtrate, a portion of the dried material was refluxed with ligroin, in which it was insoluble, for ten minutes. Upon evaporation of the ligroin, a small amount of a light colored resinous material was obtained which gave no color reactions.

Three grams of this same material were intimately mixed with approximately three grams of a stannous chloride paste. After four days on a steam bath, the reaction mixture was extracted with benzene. This extract also failed to give color reactions, and its treatment with a saturated solution of sodium bisulfite in a manner analogous to the treatment of the other benzene extracts failed to yield any crystalline products.

Treatment of Alkali Lignin - Ten grams of the alkali lignin isolated according to Method II was mixed with ten grams of a stannous chloride paste. After being heated on a steam bath for five days, the reaction mixture was extracted with benzene. The benzene extract was treated with a saturated solution of sodium bisulfite. Decomposition of the bisulfite portion in the presence of iso-propyl ether and subsequent evaporation yielded only a small amount of a resinous material which did not give any color reactions.

DISCUSSION OF RESULTS

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This investigation was undertaken in an effort to determine whether or not coniferyl aldehyde could be obtained by treating lignin isolated from wood with stannous chloride, and also to determine whether the coniferyl aldehyde isolated by Wagner¹ existed free in the wood or came from the action of stannous chloride on the lignin in the wood.

The results of this investigation indicate that coniferyl aldehyde cannot be obtained by the treatment of lignin, as isolated here, with stannous chloride in the manner described.

This work, along with that of Wagner¹ and Rawlings², would seem to indicate that the coniferyl aldehyde isolated by Wagner in his treatment of wood with stannous chloride, existed free in the wood.

The lignin isolated during this investigation with ethyl alcohol at room temperature gave color reactions almost identical to those of the original wood. Tests made indicated that this lignin preparation was free of aldehydes. The residue recovered after treatment of the alcohol lignin with stannous chloride failed to give any color reactions. This fact is in agreement with the statement made by Wagner that his sawdust, after treatment with

1 Wagner, M. S. Thesis, V.P.I. (1946)

2 Rawlings, B. S. Thesis, V.P.I. (Now in progress)

stannous chloride and subsequent extractions with benzene, failed to give color tests characteristic of woody tissues.

However, on the basis of the experimental evidence presented here, it cannot be stated with certainty that Wagner's coniferyl aldehyde did exist free in the wood. The lignin isolated here with ethyl alcohol at room temperature represents approximately one per cent of the total lignin in the wood. The ease with which it is removed from the wood indicates that it is loosely, or not at all, combined with any of the other constituents of the wood. No definite evidence has as yet been presented that this type of lignin is chemically the same in every respect as the total lignin in the wood. However, this lignin is the least degraded of any lignin which has thus far been isolated from wood.

No definite conclusions can be made regarding the treatment of the lignin isolated by the use of alkali. That it was highly degraded is shown by the fact that it gave no color reactions and was insoluble in the usual organic solvents.

CONCLUSIONS

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1. It is unlikely that white pine lignin will yield coniferyl aldehyde when isolated and treated with stannous chloride according to the methods described in this investigation.
2. It is probable that Wagner's coniferyl aldehyde existed free in the wood.