Cholesteryl Bromide.—To 20 g. of cholesterol was added 50 cc. of benzene and 6 cc. of phosphorus tribromide. The product was heated for two hours on a steam-bath, most of the benzene was distilled off and ether was added. It was shaken with water, separated and the ether was evaporated and the residue crystallized from absolute alcohol; m. p. 96°.

Cholestyl Bromide from Cholesteryl Bromide.—A solution of 5 g. of cholesteryl bromide in 50 cc. of dry ether, 500 mg. of platinum oxide catalyst and 5 cc. of glacial acetic acid was shaken for one hour with hydrogen at 45 pounds pressure. The catalyst was filtered and the product crystallized from absolute alcohol; m. p. 115°.

Anal. Calcd. for $C_{27}H_{47}Br$: C, 71.8; H, 10.4. Found: C, 71.7; H, 10.4.

Cholestyl Bromide from Epi-chloestanol.—To a solution of 3 g. of *epi*-cholestanol in 15 cc. of dry benzene was added 1 cc. of phosphorus tribromide. The product was heated on a steam-bath for two hours, most of the benzene distilled off, extracted with ether and the extract shaken with sodium carbonate solution. It was then crystallized from alcohol–ether and finally from acetone; m. p. 115°. A mixture with cholestyl bromide from the first preparation gave no melting point depression.

Anal. Calcd. for $C_{27}H_{47}Br$: C, 71.8; H, 10.4. Found: C, 71.6; H, 10.3.

Hydrolysis of Cholestyl Bromide.—This bromide was hydrolyzed by the procedure described for the hydrolysis of α-chloroandrosterone to androsterone. It was purified through its half succinic ester; m. p. 184°. Mixed with *epi*-cholestanol it gave no depression. Mixed with *beta*-cholestanol it gave a depression of 32°.

Anal. Calcd. for $C_{27}H_{48}O$: C, 83.4; H, 12.5. Found: C, 82.7; H, 12.4.

We wish to thank Mr. H. M. Crooks of this Laboratory for the micro analyses on the compounds reported in this paper.

Summary

3-Chloro-Δ^5-dehydroandrosterone has been prepared from cholesterol. This can be converted into any of the three known naturally occurring male hormones. Isoandrosterone has been converted into androsterone. The hydrolysis of cholestyl bromide gives *epi*-cholestanol.

STATE COLLEGE, PA.
DETROIT, MICH. RECEIVED DECEMBER 12, 1935

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXIII. The Preparation and Methylation of Spruce Lignin Sulfonic Acids[1]

BY GEORGE H. TOMLINSON, 2ND, AND HAROLD HIBBERT

Introduction

In the manufacture of sulfite pulp, the wood is heated under pressure with a solution of calcium bisulfite and free sulfurous acid. The essential feature of this process is the removal of the lignin from the wood as a result of the formation of water soluble lignin sulfonic acids, the latter existing as their calcium salts in the so-called waste sulfite liquor.

Since this liquor can be fractionated it has been generally conceded that it contains at least two distinct sulfonic acids. One of these, generally termed α-lignin sulfonic acid, is precipitated from the liquor by the addition of aromatic amines. Klason has stated[2] that this fraction is identical with that salted out by sodium or calcium chloride, and that it represents 65% of the total product. The β-lignin sulfonic acid remaining in the filtrate may be precipitated as the lead salt by the addition of basic lead acetate. Klason considered that the two fractions are essentially very similar, and that fractionation is rendered possible by the presence of an acrolein group in the α-lignin in contrast with an acrylic acid group in the β-lignin sulfonic acid.

Klason's experimental evidence for this is not convincing, and a critical examination by Hägglund[3] showed that the addition of an aromatic amine to waste sulfite liquor results in the precipitation of a considerably larger quantity of product than is obtained by the addition of sodium chloride. The yield of the α-fraction was also found to be dependent on the nature of the amine used. Thus β-naphthylamine gives a higher yield than quinoline, while fuchsin[4] precipitates a portion not precipitable with naphthylamine. Hägglund concludes[3] that there can be no sharp chemical nor physical distinction between two α- and β-fractions and that, on the average, the lignin sulfonic acids in the α-fraction exist in a higher de-

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(1) Abstracted from a thesis "The Formation of Vanillin from Lignin Sulfonic Acids and its relation to the Structure of Lignin" presented by George Tomlinson to McGill University in partial fulfilment of the requirements for the Ph.D. degree, April, 1935.

(2) Klason, *Ber.*, **53B**, 1864 (1920); **64B**, 2733 (1931).

(3) Hägglund, *Zellstoff u. Papier*, **13**, 261 (1933).

(4) Hennig, *Papier Fabr.*, **30**, Tech.-wiss. Teil, 179 (1932).

gree of molecular association than do those in the β-fraction.

Recently Freudenberg and co-workers[5] have stated that they were unable to obtain any fraction other than that precipitated with quinoline, a result contrary to that found by Hägglund and ourselves. Freudenberg and co-workers were unable to offer any satisfactory explanation for this difference in behavior.

Hägglund[3] points to certain differences in the sulfur and methoxyl content of two β-fractions prepared from the same liquor, one having been obtained after the removal of the α-fraction with quinoline, the other after the removal of the α-fraction with α-naphthylamine. No analyses are given for the α-fractions prepared by the two methods, and the variations which apparently exist in the sulfur and methoxyl contents of the different fractions obtained from the same liquor remain obscure.

It has now become apparent that the chance of a stoichiometric relationship between sulfur and lignin is quite remote for any particular fraction. The sulfur content of the isolated lignin sulfonic acid depends on the time and temperature of the sulfite cook,[6] a product having a high sulfur content being obtained on prolonged heating. Lignin sulfonic acids or their salts have been described having sulfur contents ranging from 4[7] to 12.8%.[8] Thus any fraction obtained from a liquor prepared by the use of purely arbitrary cooking conditions is unlikely to be a mono-, a di- or a tri-sulfonic acid, but a mixture of at least two.

Discussion

In connection with the study of the relationship between lignin and vanillin to be discussed in Part XXV of this series, it was found necessary to prepare lignin sulfonic acids or their salts free from other organic or inorganic matter. The lignin sulfonic acids were carefully fractionated in order to determine whether vanillin formation is characteristic of all fractions, and also to ascertain the extent that this and other chemical properties vary from fraction to fraction.

Two separate sulfite liquors were prepared from benzene–alcohol extracted wood meal using calcium and potassium bisulfite, respectively. Different cooking schedules were employed in each case to insure different degrees of sulfonation. Different methods were also used in the fractionation of the two liquors.

In the first case, the wood meal was cooked with a calcium bisulfite liquor for twelve hours at 125°, and highly sulfonated lignin sulfonic acid fractions were obtained. The calcium α-lignin sulfonates were salted out by means of calcium chloride, and the β-lignin sulfonates isolated from the mother liquor by the addition of basic lead acetate. The α-lignin sulfonates were then further separated into two fractions, the one most readily salted out being designated Ca L. S. A. α-I,[9] the one least readily, Ca L. S. A. α-II. The complete scheme of fractionation is outlined in Diagram 1. The isolated α-fractions were dissolved in water, and dialyzed. The solutions were concentrated and the calcium lignin sulfonates precipitated from aqueous alcohol into an alcohol–ether mixture. By this method products were obtained in which the atomic ratio of calcium to sulfur was less than one, due to a certain loss of calcium ions during dialysis as a result of the hydrolysis of the calcium sulfonates. The free acids were not prepared, since as found by King, Brauns and Hibbert[10] they are quite unstable in the solid state and polymerize spontaneously to form insoluble products.

The β-lignin sulfonic acids were regenerated from their lead salts by solution in dilute acetic acid, followed by the addition of sulfuric acid to precipitate the lead ions. Calcium chloride was added to supply the calcium ions and the solution was then dialyzed. The β-sulfonates were isolated in the same manner as the α-sulfonates.

TABLE I

SUMMARY OF ANALYSES OF THE CALCIUM LIGNIN SULFONATES

%	Ca L. S. A. α-I	Ca L. S. A. α-II	Ca L. S. A. β
S	9.4	9.6	10.4
SO_3H	23.8	24.3	26.3
Ca	3.5	3.8	5.0
"Lignin"[a] on Ca- and SO_3H-free basis	72.7	71.9	68.7
OCH_3	11.2	11.35	10.45
OCH_3 based on "Lignin"	15.4	15.8	15.2

[a] % "Lignin" = 100% − (% SO_3H + % Ca).

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(5) Freudenberg, Sohns and Janson, *Ann.*, **518**, 62 (1935).

(6) Hägglund, *Biochem. Z.*, **158**, 350 (1925).

(7) Freudenberg and Sohns, *Ber.*, **66B**, 262 (1933).

(8) Klason, *ibid.*, **58**, 1761 (1925). Actually the naphthylamine salt was prepared. This gave on analysis S, 8.34; N, 3.5; which corresponds to S, 12.8, for the lignin sulfonic acid, calculated on a naphthylamine-free basis.

(9) Ca L. S. A. α-I = calcium salt of α-lignin sulfonic acid fraction I.

(10) King, Brauns and Hibbert, *Can. J. Research*, **13**, 88 (1935).

The three fractions α-I, α-II and β were obtained in yields of 19, 44 and 37%, respectively.

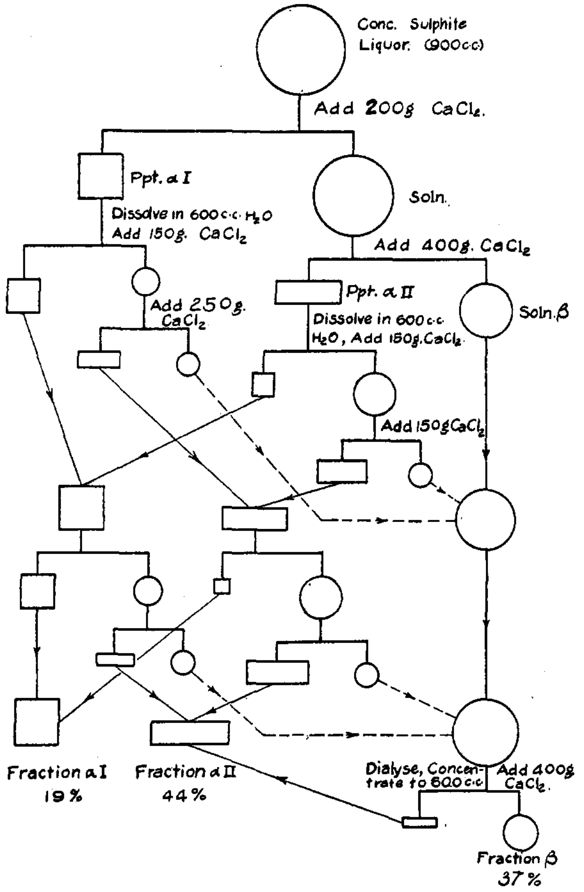

Diagram 1.—Fractionation of calcium lignin sulfonates.

In the second cook a potassium bisulfite liquor was used, and the temperature was maintained at 110° instead of 125° as in the previous experiment, in order to have the lignin less highly sulfonated. The observation of Hägglund that the ratio of the α- to the β-fraction is dependent on the precipitating reagent was confirmed. It was found that the degree of efficiency of the various reagents as precipitants increased in the following order: sodium chloride, calcium chloride, quinoline and *i*-amylamine, β-naphthylamine and finally lead acetate. It is quite apparent from this that the old nomenclature of α- and β-lignin sulfonic acids is quite inadequate for so complex a mixture.

The potassium lignin sulfonates from this liquor were separated into the fraction precipitated with quinoline, designated K L. S. A. I[11] and that recovered from the mother liquor designated K L. S. A. (II + III). From another portion of the liquor those lignin sulfonates not precipitated with quinoline were separated into fractions K L. S. A. II and K L. S. A. III, the former representing the portion precipitated with β-naphthylamine, and the latter that remaining in solution and recovered by treatment with lead acetate. The fractionation scheme is outlined in Diagram 2. The sulfonic acids were all regenerated from their respective insoluble salts, converted into their potassium salts, and further purified by dialysis and precipitation in organic solvents.

The four K L. S. A. fractions I, (II + III), II and III were obtained in yields of 70, 30, 16 and 14%, respectively.

TABLE II

SUMMARY OF ANALYSES OF THE POTASSIUM LIGNIN SULFONATES

%	K L. S. A. Fractions I	(II + III)	II	III
S	5.4	..	6.6	5.6
SO_3H	13.7	..	16.7	14.2
K	3.7	2.7	5.0	5.8
"Lignin" on K- and SO_3H-free basis	82.6	..	78.3	80.0
OCH_3	12.8	10.8	12.0	9.2
OCH_3 based on "Lignin"	15.5	..	15.3	11.5

The effect of the cooking conditions on the sulfur content of the lignin sulfonates is quite pronounced, and even the different fractions from the same liquor show considerable variations. Since an increase in sulfur content is accompanied by a decrease in methoxyl content due to the change in molecular weight, this latter value has been calculated on a metal- and SO_3H-free basis. When so calculated the methoxyl contents show moderate agreement in the case of those fractions capable of being precipitated by reagents other than lead acetate.

A considerable portion of the lignin sulfonic acid was lost during dialysis, a phenomenon previously observed by Fuchs[12] and Hennig.[4] After correcting for the increase in molecular weight due to sulfonation, it was found that about 60% of the lignin that passed into solution during the sulfite cook was actually recovered. The quinoline method of fractionation is considered by the authors to be more satisfactory than the calcium chloride method.

Although lignin sulfonic acids have been methylated by numerous investigators, in all previous

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[11] K L. S. A. I = potassium salt of lignin sulfonic acid fraction I.

[12] Fuchs, "Die Chemie des Lignins," Springer, 1926, p. 35.

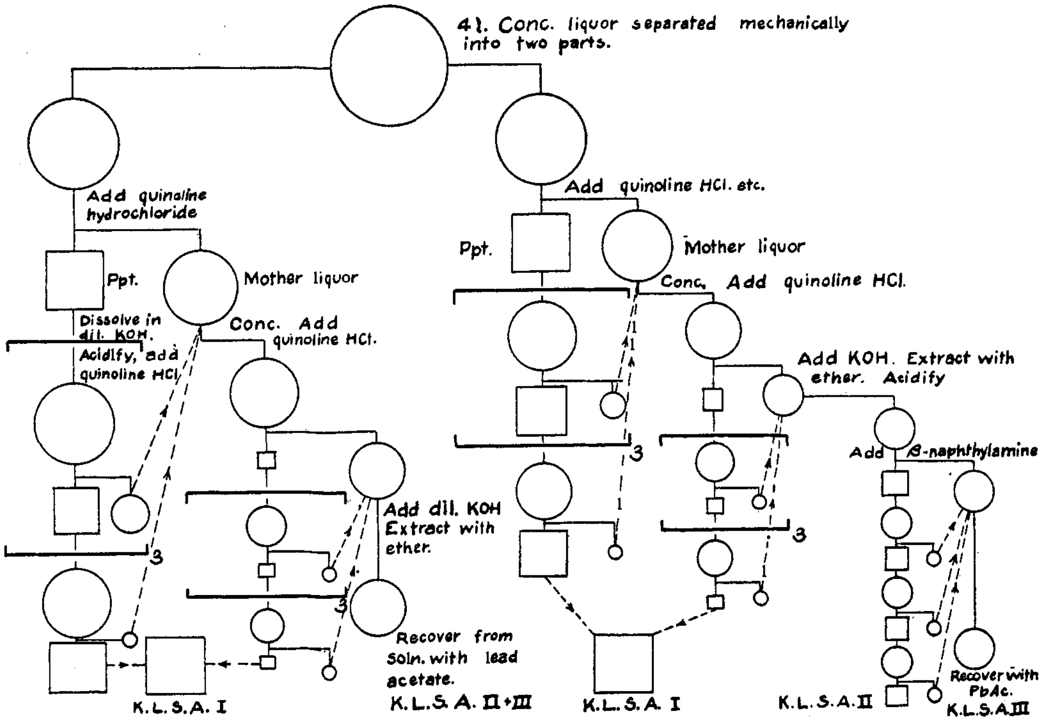

Diagram 2.—Fractionation of potassium lignin sulfonates.

cases where the sulfur content of the methylated product had been determined, it was found that the methylation was accompanied by a partial loss of sulfur.[10,13] By maintaining the temperature and alkali concentration at a minimum, it has been found possible to obtain methylated products in which no loss in the sulfur content has occurred other than is to be expected from the increased molecular weight. Fraction K L. S. A. I, after repeated methylation to constant value, contained OCH_3, 26.2%; S, 5.3%; while methylated K L. S. A. (II + III) contained OCH_3, 27.4%; S, 5.7% calculated on a potassium-free basis. When calculated on a potassium- and SO_3H-free basis the former contained OCH_3, 30.0%; the latter OCH_3, 31.6%.

The formation of vanillin and veratric aldehyde from the lignin sulfonic acid fractions and their methylated derivatives, respectively, is described in Part XXV of this series.

Experimental

Preparation of Calcium Lignin Sulfonates.—Two hundred grams of alcohol–benzene extracted spruce wood meal (180.2 g. on water-free basis) was digested in an autoclave (Alleghany metal) with 1800 cc. of a calcium bisulfite liquor containing 5.97% "total" and 1.2% "combined" sulfur dioxide. The temperature was maintained at 100–110° for two hours, then increased to 125° and maintained at that temperature for twelve hours.

The general method of fractionation is outlined in Diagram 1 and the yield and analyses are recorded in Table I. For further details the reader is referred to the original thesis.

Preparation of Potassium Lignin Sulfonates.—825 g. of alcohol–benzene extracted spruce wood meal (788 g. on water-free basis) was digested in a stainless steel autoclave with 12 liters of a potassium bisulfite liquor containing 5.0% "total" and 1.2% "combined" sulfur dioxide. The temperature was raised to 100° in two and one-half hours, and maintained at that temperature for an additional twenty-one hours.

The light-yellow colored liquor was filtered from the pulp, the filtrate and washings concentrated under reduced pressure and the solution divided into two equal portions which were worked up separately.

Preparation of Fraction K L. S. A. I.—One-half of the total solution was dialyzed for four days in a cellophane sack against running distilled water, and concentrated to 1.5 liters. Five hundred cc. of a 5% quinoline hydrochloride solution was added slowly with vigorous stirring. A voluminous cream-colored precipitate formed which became gummy and settled in a few minutes to form a cake. The liquor was decanted and the precipitate dissolved in 1.5 liters of 0.2 *N* potassium hydroxide solution. This solution was made slightly acid and 200 cc. of 5% quinoline hydrochloride solution added, the procedure resulting in complete reprecipitation of the lignin sulfonate. The mother liquor was decanted, and the precipitate redissolved and reprecipitated as before. This precipitation was carried out five times in all.

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(13) Hägglund and Carlsson, *Biochem. Z.*, **257**, 467 (1933).

The mother liquors from the five precipitations were combined, made slightly alkaline, concentrated and dialyzed for twenty-four hours. The solution (400 cc.) was made slightly acid, and a quinoline hydrochloride solution added until no further precipitate formed. This precipitate (about one-tenth of that previously obtained) was dissolved and reprecipitated four times in the same manner as previously described, except that the volume of the solutions from which it was precipitated was only 200 cc. This product was added to the main α-fraction obtained from dilute solution, and the combined material was dissolved in dilute potassium hydroxide, extracted with ether to remove the quinoline, made slightly acid and dialyzed for five days. The solution so obtained contained 53.4 g. of the fraction designated K L. S. A. I. A portion of this fraction was evaporated to dryness under reduced pressure at 30°, and the residue dissolved in dioxane containing 5–10% water. The solution was filtered, and then added dropwise to 10 volumes of absolute dioxane from which the lignin sulfonate precipitated. The product was centrifuged off, washed with absolute dioxane and dried in a vacuum desiccator.

Anal. K, 3.68, 3.61; S, 5.41, 5.35; OCH_3, 12.80, 12.87. On potassium-free basis: S, 5.6; OCH_3, 13.3.

Preparation of Fraction K L. S. A. II.—The mother liquors from the quinoline precipitations were combined, made slightly alkaline, concentrated under reduced pressure to 500 cc. and extracted with ether. The solution was made slightly acid, and a saturated solution of β-naphthylamine hydrochloride added until no further precipitate formed. The precipitate was centrifuged off, dissolved in 0.2 *N* potassium hydroxide, acidified and reprecipitated as before. This was carried out four times in all. The potassium lignin sulfonate was regenerated, extracted with ether, dialyzed and precipitated in dioxane in the same manner as K L. S. A. I.; yield 11 g.

Anal. K, 4.96; S, 6.60, 6.69; OCH_3, 11.92, 12.04. On potassium-free basis: S, 7.0; OCH_3, 12.8.

Preparation of Fraction K L, S. A. III.—The combined mother liquors from the β-naphthylamine precipitations were made slightly alkaline and extracted with ether. The solution was made neutral to litmus, and a solution of 10% basic lead acetate was added slowly with stirring. The precipitate was centrifuged off, and washed four times by suspending in 1.5 liters of distilled water. The lignin sulfonic acid was liberated from its lead salt by the addition of 1% acetic acid, and the lead ions removed by the gradual addition of 5% sulfuric acid. The lead sulfate was centrifuged off, and the solution made alkaline with potassium hydroxide. The solution was dialyzed and the K L. S. A. III portion precipitated in dioxane as described for the other fractions; yield 10.1 g.

Anal. K, 5.79; S, 5.51, 5.74; OCH_3, 9.22, 9.11. On potassium-free basis: S, 5.95; OCH_3, 9.75.

Preparation of Fraction K L. S. A. (II + III).—Following the removal of fraction K L. S. A. I (yield 53.1 g.) from the second half of the original liquor by precipitation with quinoline, the remaining lignin sulfonic acids were recovered directly by precipitation with lead acetate, as described above, but without the preliminary precipitation of fraction K L. S. A. II with β-naphthylamine. The fraction obtained in this way was designated K L. S. A. (II + III); yield 22.6 g.

Anal. K, 2.66; OCH_3, 10.88, 10.78. On potassium-free basis: OCH_3, 11.1.

Methylation of Fraction K L. S. A. I.—A solution of 10.0 g. of fraction K L. S. A. I in 100 cc. of water was diluted with 100 cc. of acetone, and placed in a 1-liter 3-necked flask fitted with a mechanical stirrer and two graduated burets. The flask was maintained at 20° during the course of the reaction.

One hundred and seventy-six grams of dimethyl sulfate (130 cc.) and 86 g. of potassium hydroxide (286 cc. of a 30% solution by volume) were used for each methylation, *i. e.*, a ratio of 1 mole of the former to 1.1 of the latter. The reagents were added during the course of five hours, one-fifth of the total quantities being added each hour. At the beginning of each of these five additions, 5.2 cc. of the potassium hydroxide solution was added to give the solution an initial alkalinity, and then the remaining 52 cc. was added simultaneously with the 26-cc. portion of dimethyl sulfate at a rate of 2 cc. of the former to 1 cc. of the latter. After the five hours required for the addition of all the reagents the solution was dialyzed for thirty-six hours, concentrated to 100 cc., diluted with 100 cc. of acetone and remethylated in a manner identical to that already indicated.

A small sample was withdrawn following the fourth methylation, dialyzed an additional thirty-six hours and evaporated to dryness. The residue was dissolved in absolute methyl alcohol and precipitated in ether. The cream-colored precipitate was centrifuged, washed with ether and dried in a vacuum desiccator.

Anal. K, 5.97; OCH_3, 24.68, 24.72. On potassium-free basis: OCH_3, 26.2.

The bulk of the solution from the previous methylation was remethylated similarly for a fifth time, and dialyzed for thirty-six hours in alkaline solution, then thirty-six hours in slightly acid medium. The product was precipitated for analysis as before; yield 8.5 g.

Anal. K, 3.64; S, 5.02, 5.09; OCH_3, 25.31, 25.25. On potassium-free basis: S, 5.3; OCH_3, 26.2.

Methylation of Fraction K L. S. A. (II + III).—A solution containing 10.0 g. of K L. S. A. (II + III) was methylated by the same method as used with K L. S. A. I; yield 5.2 g.

Anal. (Following fourth methylation) K, 5.69; OCH_3, 26.01. On potassium-free basis: OCH_3, 27.6%. (Following fifth methylation) K, 2.93; S, 5.46, 5.60; OCH_3, 26.56, 26.56. On potassium-free basis: S, 5.7; OCH_3, 27.4.

Summary

1. Metallic salts of lignin sulfonic acids have been prepared using two different cooking schedules in order to obtain products of different degrees of sulfonation.

2. A comparison of various suggested methods of fractionation has been made. Quinoline was found to precipitate only a portion of the lignin

sulfonic acids, a result in agreement with the work of Hägglund but in contradiction to the later research of Freudenberg and co-workers.

3. A technique has been developed whereby lignin sulfonic acids may be methylated without the simultaneous partial loss of sulfur observed by previous investigators.

MONTREAL, CANADA RECEIVED NOVEMBER 4, 1935

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, PULP AND PAPER RESEARCH INSTITUTE, McGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXIV. The Formation of Vanillin from Waste Sulfite Liquor[1]

BY GEORGE H. TOMLINSON, 2ND, AND HAROLD HIBBERT

Introduction

During the last seven years a number of papers[2–7] have appeared describing the formation of vanillin from waste sulfite liquor by the action of hot alkalies. The highest vanillin yields recorded in each of these papers are shown in Table I. In most cases no analysis of the sulfite liquor was given so that it has been impossible to correlate vanillin yield with lignin content of the original liquor. Different methods of extraction of the vanillin from the acidified reaction mixture have been employed by the various investigators. However, except in those experiments described in Kürschner's original paper,[2] the yield of vanillin has been determined by modifications of the gravimetric method of Pritzker and Jungkuntz[8] which involves the precipitation of the vanillin with *m*-nitrobenzoic hydrazide. No analyses of the original condensation product have been recorded, but Hönig and Ruziczka[6] found that the analysis of their recrystallized product corresponded to that of vanillin *m*-nitrobenzoylhydrazone. Melting point determinations formed the only criteria for the identity of Kürschner's product.[3,4,5] Recently Shoruigin and Smolyaninova[7] have prepared 2 g. of vanillin (no analysis given) from 6 liters of liquor.

Pauly[9] has stated, but without giving any experimental details, that vanillin may be obtained from lignin and a wide variety of lignin-containing materials by the use of his "chromic acid acetic acid oxidation technique," claiming a yield of 1.9% from spruce and even higher yields from other woods. Following the directions stipulated in the patent of Pauly and Feuerstein,[10] Shoruigin and Smolyaninova[7] in the course of thirty-four experiments obtained a yield of only 0.16% (based on the weight of the wood) when determined by their method of analysis, although considerably higher values were obtained when less accurate methods were used.

Discussion

The present investigation has been confined to the action of alkali on waste sulfite liquor and lignin sulfonic acids. An experiment was carried out following the directions given by Kürschner[3,4] for obtaining the maximum vanillin yield. Waste sulfite liquor was boiled with alkali, acidified, extracted with trichloroethylene and this extract shaken with *m*-nitrobenzoic hydrazide. The precipitate so formed was found to contain only one-third the methoxyl content calculated for vanillin *m*-nitrobenzoylhydrazone. Recrystallization of this product resulted in the isolation of the pure condensation product (as determined by analysis), but it was found impossible to carry out the purification quantitatively. As the calculation of vanillin yield from the weight of original product would involve serious error it was necessary to develop a new extraction technique. It was found that the chief error involved in the authors' application of Kürschner's method[11] was due to some side reaction between the trichloroethylene (or some persistent impurity in it), and the *m*-nitrobenzoic hydrazide. Extrac-

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(1) Abstracted from a thesis "The Formation of Vanillin from Lignin Sulfonic Acids and its Relation to the Structure of Lignin" presented by George Tomlinson to McGill University in partial fulfilment of the requirements for the Ph.D. degree. April, 1935.

(2) Kürschner, *J. prakt. Chem.*, **118**, 238 (1928).

(3) Kürschner and Schramek, *Tech. Chem. Papier-Zellstoff-Fabr.*, **28**, 65 (1931).

(4) Kürschner and Schramek, *ibid.*, **29**, 35 (1932).

(5) Kürschner, *ibid.*, **30**, 1 (1933).

(6) Hönig and Ruziczka, *Z. angew. Chem.*, **44**, 845 (1931).

(7) Shoruigin and Smolyaninova, *J. Gen. Chem.* (U. S. S. R.), **4**, 1428 (1934).

(8) Pritzker and Jungkuntz, *Chem.-Ztg.*, **52**, 537 (1928).

(9) Pauly, *Ber.*, **67B**, 1177 (1934).

(10) Pauly and Feuerstein, English Patent 319,747 (1929).

(11) Kürschner's vanillin yields are based on the weight of the crude hydrazone (without recrystallization) and no analyses are reported