

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.

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Studies on Lignin and Related Compounds. XXIV. The Formation of Vanillin from Waste Sulfite Liquor¹

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Introduction

During the last seven years a number of papers²⁻⁷ have appeared describing the formation of vanillin from waste sulfite liquor by the action of hot alkalis. 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 Jungkuntz⁸ which involves the precipitation of the vanillin with *m*-nitrobenzoic hydrazide. No analyses of the original condensation product have been recorded, but Hönig and Ruziczka⁶ 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 Shorugin and Smolyaninova⁷ have prepared 2 g. of vanillin (no analysis given) from 6 liters of liquor.

Pauly⁹ 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 Shorugin and Smolyaninova⁷ 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 method¹¹ was due to some side reaction between the trichloroethylene (or some persistent impurity in it), and the *m*-nitrobenzoic hydrazide. Extrac-

(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 fulfillment 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) Shorugin 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

TABLE I
SUMMARY OF PREVIOUS WORK ON FORMATION OF VANILLIN FROM WASTE SULFITE LIQUORS

Author and Year	% Solids in liquor	Vanillin, g. per liter,	Method of formation	Method of determination
Kürschner, ² 1928	64	53	Boil 10 cc. liquor 1.5 hr. with 10 g. NaOH	Colorimetric
Kürschner and Schramek, ³ 1931	Not stated	3.2	Boil 50 cc. liquor 20 hr. with 12 g. NaOH	Acidify, extract with C ₂ HCl ₃ and ppt. directly with <i>m</i> -nitrobenzoic hydrazide
Kürschner and Schramek, ⁴ 1932	Not stated	2.5	Digest 50 cc. liquor 4 hr. at 6 atm. with 3 g. NaOH	As above
Kürschner, ⁵ 1933	Not stated	1.8	Digest 50 cc. liquor 4 hr. at 6 atm. with 3.1 g. CaO and 6 g. Na ₂ CO ₃	As above
Hönig and Ruziczka, ⁶ 1931	Not stated	2.4	Digest 100 cc. liquor 3 hr. at 160° with 100 g. KOH	Acidify, extract with C ₂ HCl ₃ , then with aqueous NaHSO ₃ . Acidify, extract with ether, evap., and ppt. from aqueous soln. with <i>m</i> -nitrobenzoic hydrazide
Shoruigin and Smolyaninova, ⁷ 1934	9	0.63	Boil 300 cc. liquor 7 hr. with 36 g. NaOH	Steam distil the alk. soln. Acidify, extract with ether, evap. to dryness. Dissolve residue in alcohol and ppt. with aqueous <i>m</i> -nitrobenzoic hydrazide

tion of the trichloroethylene solution with sodium bisulfite followed by precipitation of the vanillin from aqueous solution was found to obviate this difficulty. By a modification of this method pure vanillin *m*-nitrobenzoylhydrazide may be obtained directly, and in a control experiment using a known quantity of vanillin 96.6% was recovered.

The influence of time, nature of the alkali used and alkali concentration on the yield of vanillin was studied. In each experiment 50 cc. of commercial sulfite liquor (lignin content estimated at 2.2 ± 0.1 g. per 50 cc.) was boiled under reflux with a specified amount of alkali for a specified period of time (Tables II, III and IV).

Using 12 g. of sodium hydroxide (per 50 cc. liquor) the reaction proceeds rapidly at first, reaching a maximum in six to ten hours. On prolonged heating (forty hours) a slightly lower yield is obtained, apparently due to decomposition of the vanillin. This effect is more pronounced at higher alkali concentration (18 g. of sodium hydroxide per 50 cc.) when after only six hours an appreciable quantity of the vanillin is found to have undergone decomposition. An equivalent of barium hydroxide gives a considerably lower yield than sodium hydroxide, while potassium hydroxide gives a slightly higher. The highest vanillin yield obtained in this series was equivalent to 2.6 g. per liter or 5.9 ± 0.25% based on the estimated lignin content of the liquor.

The character of the lignin sulfonic acids present in waste sulfite liquor is changed markedly by alteration in the sulfite cooking schedule¹² and

YIELD OF VANILLIN FROM 50 CC. SULFITE LIQUOR
(5.6°Bé., 10% total solids, lignin content 2.2 ± 0.1 g. per 50 cc.)

TABLE II
EFFECT OF VARIATION IN TIME

Run	Time, hours	Reagent	Cond. product, g.	Vanillin, ^a g.
1	2	12 g. NaOH	0.1368	0.061
2	6	12 g. NaOH	.2546	.123
3	6	12 g. NaOH	.2501	.121
4	10	12 g. NaOH	.2576	.124
5	20	12 g. NaOH	.2526	.122
6	20	12 g. NaOH	.2321	.112
7	40	12 g. NaOH	.2288	.108

^a Grams vanillin = weight of condensation product × 0.4829.

TABLE III
EFFECT OF INCREASE IN ALKALI CONCENTRATION

2	6	12 g. NaOH	0.2546	0.123
3	6	18 g. NaOH	.1914	.093
5	20	12 g. NaOH	.2526	.122
9	20	18 g. NaOH	.1006	.050

TABLE IV
EFFECT OF VARIATION IN THE NATURE OF THE ALKALI

10	6	47.3 g. Ba(OH) ₂ ·8H ₂ O ^a	0.1509	0.073
2	6	12 g. NaOH	.2546	.123
11	6	16.8 g. KOH ^a	.2698	.130

^a Equivalent to 12 g. of sodium hydroxide.

a number of different liquors were prepared in order to study the effect which might be brought about by such changes. Samples of spruce wood meal (10 g.) were treated with a sulfite cooking liquor of the desired composition under definite conditions of time and temperature. The liquor so obtained was boiled with alkali under standard

TABLE V

THE EFFECT OF VARIATIONS IN THE SULFONATING REACTION ON THE YIELD OF VANILLIN FROM THE SULFITE LIQUOR

9.2 g. of water-free spruce wood meal (containing 2.48 g. lignin) digested with 100 cc. of sulfite liquor of specified composition. Temperature raised to 100° in thirty minutes, held at 100–110° for sixty minutes, then raised to max. temp. in thirty minutes. The waste liquor was boiled with alkali under standard conditions, and the resultant vanillin determined.

Run	Reagent	% SO ₂		Time at maximum temp.,		Lignin in liquor, g.	Vanillin formed, g.	% Vanillin based on lignin in liquor	
		"total"	"combined"	hrs.	°C.			wt. of wood	wt. of wood
1	Ca(HSO ₃) ₂	6	1.2	4	125	2.36	0.156	6.60	1.70
18	Ca(HSO ₃) ₂	6	1.2	12	125	2.47	.169	6.83	1.84
7	KHSO ₃	6	1.2	12	125	2.48	.167	6.72	1.82
23	KHSO ₃	9	1.2	12	125	2.48	.180	7.26	1.96
26	KHSO ₃	4.2	1.2	12	125	2.30	.146	6.35	1.58
21	KHSO ₃	3	1.2	12	125	1.81	.081	4.50	0.88
24	KHSO ₃	6	2.7	12	125	1.96	.067	3.44	.73
16	Ca(HSO ₃) ₂	5	1.2	20	110	2.30	.167	7.27	1.82
4	Ca(HSO ₃) ₂	6	1.2	12	140	2.48	.040	1.61	0.44

conditions, and the resulting vanillin determined. As the amount of lignin in the sulfite liquor could be estimated with relative accuracy it was possible to calculate the percentage yield of vanillin on this basis as well as on the weight of the original wood.

In some twenty-five experiments which covered a wide range of experimental conditions, the vanillin yield was never higher than 7.3% calculated on the weight of the lignin, or 2.0% calculated on the weight of the spruce meal. The results obtained in several of these experiments are recorded in Table V.

Prolonged heating of the lignin sulfonate solution at moderate temperature did not bring about any appreciable change in the vanillin yield on subsequent alkaline treatment (Runs 1 and 18), although at high temperature there resulted a very dark liquor which gave only a small quantity of vanillin (Run 4). By using a potassium bisulfite liquor it is possible to cover a considerably wider range of liquor concentrations than is possible when a calcium base is used. Liquors prepared with low "free" sulfur dioxide contents were found to give low vanillin yields (Runs 21 and 24) as compared with those prepared with high "free" sulfur dioxide contents (Runs 7 and 23). Using conditions analogous to commercial sulfite pulping the vanillin yield was found to be 6.5–7% based on the lignin content of the liquor.

Experimental

The waste sulfite liquor (prepared from a mixture of spruce wood and balsam (approx. 75:25)) was obtained from the Cornwall Division of the Howard Smith Paper Mills, and had a gravity of 5.6°Bé. The lignin content was estimated from the methoxyl content of the dry solids obtained on evaporation by assuming that the lignin in the

liquor had a methoxyl content of 15.5%.¹² Ten cc. of liquor contained 0.998 g. total solids. *Anal.* OCH₃, 6.95, 6.84%. Thus 10 cc. of liquor contained 0.44 ± 0.02 g. of lignin.

Kürschner's Method of Vanillin Determination.—Fifty cc. of the above liquor was boiled with 12 g. of sodium hydroxide for twenty hours, and the vanillin extracted and determined as described by Kürschner.^{3,4} The weight of precipitate obtained was 0.3598 g.

Anal. Calcd. for vanillin *m*-nitrobenzoylhydrazone: OCH₃, 9.84. Found: OCH₃, 3.62, 3.87.

The crude product was extracted with boiling alcohol, and the insoluble residue which comprised about 60%, and contained no methoxyl, was filtered off. The alcoholic solution was heated with charcoal, filtered, concentrated and diluted with an equal volume of water. The pale yellow crystalline precipitate which formed on cooling was then filtered off. *Anal.* OCH₃, 9.76; m. p. 209–211°; m. p. of vanillin *m*-nitrobenzoylhydrazone prepared from pure vanillin, 212°; mixed m. p., 211–212°.

New Method of Vanillin Determination.—Fifty cubic centimeters of waste sulfite liquor was boiled under reflux for twenty hours with 12 g. of sodium hydroxide, and the solution was acidified with sulfuric acid. The following method of extraction and estimation was adopted from a study of the results obtained in a large number of control experiments.

The acidified solution was extracted five times by refluxing for half an hour in each case with 25-cc. portions of trichloroethylene. The trichloroethylene, because of its higher specific gravity and lower boiling point than water, is in constant agitation with the aqueous solution during the refluxing treatment. Since the emulsion obtained in this way is readily broken, the trichloroethylene may be withdrawn immediately by means of a pipet from the cooled mixture. The combined trichloroethylene solutions were extracted ten times by shaking with 15-cc. portions of 5% aqueous sodium bisulfite solution. Three cc. of concentrated sulfuric acid was added to the combined bisulfite extracts, and the solution heated under reflux on the water-bath (with a slow stream of air bubbling through) until the odor of sulfur dioxide could no longer be detected. Ten grams of sodium acetate was added, the solution filtered and heated to 60°. To this was added

25 cc. of an aqueous solution containing 0.3 g. of *m*-nitrobenzoic hydrazide. A yellow precipitate formed almost immediately. The mixture was allowed to stand on the water-bath for half an hour, and at room temperature overnight. The precipitate was filtered off on to a sintered glass filter, washed with distilled water and dried to constant weight. Yield of condensation product, 0.2321 g.; vanillin yield, 0.112 g. (factor = 0.4829). *Anal.* of original product, without recrystallization. Calcd. for vanillin *m*-nitrobenzoylhydrazone: OCH₃, 9.84. Found: OCH₃, 9.74.

When 0.1000 g. of vanillin dissolved in 50 cc. of water was boiled for twenty hours with 12 g. of sodium hydroxide, acidified and extracted as described, 92% of the original vanillin was recovered.

When 0.1000 g. of vanillin dissolved in 50 cc. of water was treated in identical manner but without boiling the alkaline solution, 96.6% of the original vanillin was recovered.

By the use of this method of extraction and estimation the vanillin is recovered almost quantitatively, and the original condensation product obtained from the alkaline-treated waste liquor is sufficiently pure to allow a direct calculation of yield. The loss of vanillin due to the Cannizzaro reaction is slight. The values obtained in Tables II, III, IV were obtained by this method.

Effect of Alteration in the Waste Sulfite Liquor on Vanillin Yield.—The alcohol-benzene extracted spruce wood meal gave the following analysis: moisture, 8%; on a water-free basis, OCH₃, 4.9; lignin, 27.0.¹³ In each run a 10-g. sample of spruce wood meal (9.2 g. on water-free basis) was sealed in a stainless steel autoclave of 120-cc. capacity with 100 cc. of bisulfite cooking liquor of the desired con-

(13) Method of Ritter, Seborg, and Mitchell *Ind. Eng. Chem., Anal. Ed.*, **4**, 202 (1932).

centration. The same preliminary temperature schedule was used in each case. The bomb was heated to 100° in the course of thirty minutes, maintained at 100–110° for sixty minutes and then heated to the specified temperature (say 125°) in the next thirty minutes. It was maintained at this temperature for the desired length of time, and then withdrawn from the bath and cooled by quenching in cold water. The pulp was filtered off, washed and its yield and lignin content determined. The liquor and wash solution were concentrated under reduced pressure at 40° to 50 cc., and this solution was boiled under reflux with 12 g. of sodium hydroxide for twelve hours in an atmosphere of nitrogen. The solution was acidified, and the vanillin which had formed was extracted and estimated by the new method described above. The lignin content of the liquor was obtained by subtracting the lignin content of the pulp from the 2.48 g. in the original wood meal. The results obtained in a number of these experiments are summarized in Table V.

Summary

1. The formation of vanillin by the action of hot alkalies on waste sulfite liquor has been confirmed and a satisfactory method developed for its estimation and quantitative extraction from the reaction mixture.

2. The effect on vanillin yield of variations in the alkaline cooking treatment has been studied.

3. Using a standard method of vanillin formation, the effect of alteration in the nature of the sulfite liquor from spruce wood has been investigated.

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Studies on Lignin and Related Compounds. XXV. Mechanism of Vanillin Formation from Spruce Lignin Sulfonic Acids in Relation to Lignin Structure¹

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In previous investigations on the formation of vanillin from waste sulfite liquors² no proof has been given that its formation actually results from a decomposition of the lignin sulfonic acids present. Hoffmeister³ has stated that hadromal, which he considers identical with coniferyl aldehyde, exists to the extent of 3% in wood (oak) and the possibility thus exists that this or some

other non-ligneous constituent of the liquor may be the source of the vanillin.

Discussion

All of the spruce lignin sulfonic acid fractions prepared both by the use of calcium and of potassium bisulfites, and described in a previous communication,⁴ were found to yield vanillin on treatment with alkali (Table I). The vanillin from each of these fractions was formed under standard conditions (19.4% sodium hydroxide) and determined analytically as the *m*-nitrobenzoyl-

(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 fulfillment of the requirements for the Ph.D. degree, April, 1935.

(2) For list of references see Part XXIV, *THIS JOURNAL*, **58**, 345 (1936).

(3) Hoffmeister, *Ber.*, **60**, 2062 (1927).

(4) Part XXIII, *THIS JOURNAL*, **58**, 340 (1936).