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

Studies on Lignin and Related Compounds. LIX. Aromatic Aldehydes from Plant Materials

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Recent developments in lignin chemistry have revolved largely around the question of its carbohydrate or aromatic nature.

The formation of vanillin from isoeugenol in high yields by oxidation with aqueous alkali and nitrobenzene sulfonic acid has been known for some time.[1]

Tomlinson[2] treated lignin sulfonic acid by this method, at reflux temperature, and obtained vanillin in an amount of about 3.6%, based on the Klason lignin. More recently, Freudenberg and co-workers,[3] using a larger amount of the oxidizing mixture of nitrobenzene and aqueous alkali and a higher temperature (160°), obtained vanillin from spruce wood and from spruce "Cuproxam" lignin in yields of 25 and 22%, respectively.

In view of these high yields, and their importance relative to problems of lignin structure, the same method has now been applied by the authors to other types of wood.[4]

The experimental results of Freudenberg, *et al.*, on spruce wood were first confirmed, and the method then applied to the following angiosperms: rye straw, corn cobs, bamboo, (monocotyledons); maple, aspen, sassafras, jute (dicotyledons). In the case of the latter type, a mixture of vanillin and syringaldehyde was obtained in yields ranging between 39 and 48%, or approximately twice that obtained from the gymnosperm spruce. The values for the monocotyledons (rye, corn and bamboo) were somewhat lower, amounting to only 21–30% (Table I).

TABLE I

OXIDATIVE ALKALINE CLEAVAGE OF VARIOUS WOODS

Sample	Species	Wt., g.	Klason lignin, %	Wood residue, g.	Amorphous residue, P. I. K. L.[a]	NaHSO$_3$ sol. oils P. I. K. L.[a]	*m*-Nitrobenzoylhydrazone deriv. of bisulfite sol. oils Wt., g.	OCH$_3$, %	Calcd. aldehyde,[b] P. I. K. L.[a]	NaOH sol. oils, P. I. K. L.[a]	NaHCO$_3$ sol. oils, P. I. K. L.[a]
				Gymnosperms							
1	Spruce	35.0	28.6	11.8	40.6	27.1	4.73	9.74	22.8	6.9	...
2	Spruce	35.0	28.6	11.2	37.6	31.0	5.12	9.80	24.7	7.4	...
				Angiosperms, Dicotyledons							
3	Maple	38.5	22.0	13.7	48.5[c]	43.0	7.00	15.3	43.0	4.57	1.3
4	Maple	38.5	22.0	12.8	41.5	44.4	6.75	15.3	41.5	9.65	1.1
5	Sassafras	19.0	22.1	5.50	71.4	52.0	3.70	15.1	45.6	7.9	1.3
6	Sassafras	19.0	22.1	5.67	69.1	47.0	3.52	15.2	43.4	4.4	1.1
7	Aspen	22.0	17.0	8.35	70.9[d]	46.9	3.43	15.0	47.6	7.0	1.7
8	Aspen	22.0	17.0	6.25	65.5	44.4	3.12	15.0	43.3	5.8	1.3
9	Jute	33.5	12.7	13.8	31.1	39.2	3.04	15.0	37.3	5.5	1.0
10	Jute	33.5	12.7	13.6	33.3	39.8	3.02	14.9	36.8	4.7	1.8
				Angiosperms, Monocotyledons							
11	Rye (straw)	19.2	20.2	6.80	63.6	35.5	2.30	12.2	30.6	5.3	1.3
12	Rye (straw)	19.2	20.2	6.20	65.0	34.8	2.29	12.2	30.5	6.1	1.5
13	Corn (cobs)	20.5	13.8	4.45	72.8	29.0	1.18	7.3	21.6	4.1	0.8
14	Corn (cobs)	20.5	13.8	5.00	69.0	28.2	1.16	7.5	21.2	3.8	1.0
15	Bamboo	9.6	22.5	3.20	58.5	41.5	1.20	10.5	29.1	3.5	0.5
16	Bamboo	9.6	22.5	3.20	60.7	40.0	1.18	10.7	28.0	3.8	0.9

[a] P. I. K. L. is abbreviation for "Percentage Initial Klason Lignin." [b] Calculated on a basis of 3 moles syringaldehyde to one mole vanillin. [c] OCH$_3$ = 10.5%. [d] OCH$_3$ = 9.5%.

Freudenberg's method of aldehyde isolation was varied in that the crude reaction mixture left after the steam distillation was acidified to a

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(1) Hoffman-LaRoche and Co., A. G., British Patent, 392,399, May 18, 1933.

(2) G. H. Tomlinson, Ph.D. Thesis, Division of Industrial and Cellulose Chemistry, McGill University, April, 1935.

(3) (a) Freudenberg, Lautsch and Engler, *Ber.*, **73**, 167 (1940); (b) Lautsch, Plankenhorn and Klink, *Angew. Chem.*, **53**, 450 (1940); (c) Lautsch and Piazolo, *Ber.*, **73**, 317 (1940).

(4) Creighton, McCarthy and Hibbert, THIS JOURNAL, **63**, 312 (1941).

TABLE II

YIELDS OF VANILLIN AND SYRINGALDEHYDE IN BISULFITE FRACTION FROM ANGIOSPERMS[b]

Species	Vanillin sublimate[c]		Intermediate sublimate		Syringaldehyde sublimate		Ratio of aldehydes
	Calcd. wt., g.	P. I. K. L.[a]	Wt., g.	P. I. K. L.[a]	Wt., g.	P. I. K. L.[a]	
			Dicotyledons				
Maple	0.67	7.9	0.08	1.0	2.42	28.6	1:3.6
Maple	.72	8.5	.07	0.9	2.48	29.4	1:3.5
Sassafras	.41	9.8	.05	1.2	1.27	30.2	1:3.1
Sassafras	.42	10.0	.08	2.0	1.21	28.8	1:2.9
Aspen	.40	10.7	.05	1.4	1.25	33.4	1:3.1
Aspen	.30	8.1	.11	2.7	1.15	30.8	1:3.8
Jute	.35	8.3	.03	0.8	1.02	23.9	1:2.9
Jute	.33	7.7	.07	1.6	1.09	25.5	1:3.3
			Monocotyledons				
Rye (straw)	.55	14.3	.10	2.5	0.60	15.5	1:1.1
Rye (straw)	.54	13.9	.07	1.8	.59	15.2	1:1.1
Corn (cobs)	.51[d]	17.9	.02	0.7	.16	5.8	1:0.3
Corn (cobs)	.46[d]	16.3	.03	1.0	.18	6.2	1:0.3
Bamboo	.31[d]	14.7	.03	1.4	.26	12.2	1:0.8
Bamboo	.33[d]	15.5	.04	1.9	.23	10.8	1:0.7

[a] P. I. K. L. abbreviates "percentage of initial Klason lignin" present in the plant materials. [b] Percentage of initial Klason lignin for crude aldehyde fractions taken are shown in Table I, Column 7. [c] Values calculated from weight of *m*-nitrobenzoylhydrazones. [d] Consists of mixture of vanillin and an unidentified carbonyl-containing constituent subliming with the vanillin.

TABLE III

METHOXYL VALUES OF *m*-NITROBENZOYLHYDRAZONES OF VANILLIN SUBLIMATES

Species............	Maple	Sassafras	Aspen	Jute	Rye Straw	Corn Cobs	Bamboo
M. p., °C.	202–205	203–206	201–205	200–205	202–206	210–245	210–243
Methoxyl,[a] %	$\left.\begin{matrix}10.1\\9.8\end{matrix}\right\}9.95$	$\left.\begin{matrix}9.9\\10.2\end{matrix}\right\}10.05$	$\left.\begin{matrix}9.8\\10.0\end{matrix}\right\}9.9$	$\left.\begin{matrix}9.8\\10.1\end{matrix}\right\}9.95$	$\left.\begin{matrix}9.8\\10.0\end{matrix}\right\}9.9$	$\left.\begin{matrix}7.1\\7.4\end{matrix}\right\}7.25$	$\left.\begin{matrix}7.3\\7.5\end{matrix}\right\}7.4$

[a] Theoretical value (OCH_3) = 9.84%.

*p*H 3 (instead of *p*H 8) prior to extraction with benzene. The benzene solution was shaken successively with aqueous sodium bisulfite, sodium bicarbonate and sodium hydroxide and the total aldehyde present in the bisulfite fraction then estimated by precipitation with *m*-nitrobenzoylhydrazine.

Considerable difficulty was experienced in separating the two aldehydes quantitatively. Using the method of Hunter and Hibbert,[5] namely, precipitation of the syringyl ammonium salt with anhydrous ethanol–ammonia, brought about a separation of 90–95% of the total syringaldehyde as the ammonium salt but only 50–60% of the vanillin could then be recovered from the filtrate, due presumably to secondary reactions occurring between the vanillin and ammonia.

A satisfactory separation of the aldehydes was achieved by use of the sublimation technique developed by Hawkins, Wright and Hibbert.[6]

By careful control, the intermediate mixed fraction could be reduced to 5%, or less, of the original material.

While the syringaldehyde sublimate could be purified readily by recrystallization, due to the presence of small amounts of phenolic impurities it was found desirable to determine the vanillin present in the initial sublimate, by means of its *m*-nitrobenzoylhydrazone.

The dicotyledons on oxidation gave a constant ratio of syringaldehyde to vanillin of about 1:3, whereas with the monocotyledons the value obtained was about 1:1. However, with two of the latter, namely, corn cobs and bamboo, considerable difficulty was encountered in obtaining pure sublimed vanillin due to the accompaniment of an appreciable quantity (5–10%) of an as yet unidentified carbonyl-containing constituent, its presence being indicated by the much lower methoxyl values found for the *m*-nitrobenzoylhydrazones obtained from the vanillin sublimates (Tables II and III). The matter is being investigated further.

In addition to the vanillin and syringaldehyde isolated from the bisulfite extract there were found present in each case, in the sodium bicar-

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(5) Hunter and Hibbert, THIS JOURNAL, **61**, 2190 (1939).

(6) Hawkins, Wright and Hibbert, *ibid.*, **59**, 2447 (1937).

bonate and alkali extracts, small amounts of acidic and phenolic constituents, respectively, the nature of which is also under investigation. There was obtained also, on filtration of the benzene-extracted, acidified aqueous reaction liquors, a nitrogen-containing, brown, amorphous powder with a methoxyl content of around 10%.

In blank experiments carried out by Mr. W. B. Hewson in this Laboratory with both vanillin and syringaldehyde under identical conditions, a recovery of 90–95% of each of the aldehydes was obtained.

In the light of Hibbert's recent theory of lignin structure[7] as consisting of polymerized products derived from a C_6–C_3 unit, the total lignin accounted for as mixed aldehydes in the case of maple wood (calculated on a basis of the experimental ratio of syringaldehyde to vanillin of 1:3 and the building unit R—CO—CHOH—CH_3 (R = syringyl or guaiacyl)) amounts to 51%. This calculation is based on the assumption that one mole of α-hydroxypropiovanillone and three of α-hydroxypropiosyringone (Hibbert building units) condense together with loss of three moles of water.

The isolation of aromatic constituents in such high yields definitely disproves the various theories advanced by different workers as to the carbohydrate structure of lignin[8] and in addition offers the possibility of serving as a new tool for taxonomic classification. Such an application is at present being investigated.

Experimental

Preparation of Plant Materials.—The plant materials, after grinding in a Wiley mill to a particle size below 40 mesh, were extracted continuously for forty-eight hours with ethanol–benzene (1:1), then for twenty-four hours with ethanol and finally with water. The aspen was extracted for one week with ethanol only and finally with water. The materials were used in the air-dried condition (*ca.* 4% H_2O).

Oxidative Alkaline Cleavage.[9]—The plant material (20 g.), nitrobenzene (12 cc.) and aqueous sodium hydroxide solution (400 cc. of 8%) were heated at 160° for three hours, with violent agitation, in a sealed, stainless steel bomb (500-cc. capacity). After cooling, the alkaline reaction mixture was steam distilled to remove nitrogenous products, filtered and the wood residue washed with alkali and water, and dried. The filtrate and washings were acidified to *p*H 3, and the resulting mixture continuously extracted for forty-eight hours with benzene. The benzene extract was shaken successively with sodium bisulfite (20%), sodium bicarbonate (8%) and sodium hydroxide (5%) and these fractions treated as below. The residual liquor was filtered, the amorphous residue washed with water, dried, weighed and analyzed for methoxyl content.

Examination of the Bisulfite Fraction.—The aqueous bisulfite solution was acidified, the sulfur dioxide removed under reduced pressure at room temperature, filtered and diluted to 500 cc.

The total aldehydes in a definite volume (50 cc.) were determined by precipitation as the *m*-nitrobenzoylhydrazone[10] after buffering with sodium acetate (15 g.).

Total bisulfite-soluble oils were isolated by extraction of the remaining solution with benzene and removal of the solvent.

The syringaldehyde and vanillin were isolated from these oils by sublimation of about 0.400 g. from a small subliming tube ($5^1/_2'' \times {}^3/_4''$), fitted with a cold finger, for eight to ten hours at 61° (1.5 mm.).

The vanillin sublimate was dissolved in dry ether and the solvent removed (reduced pressure), leaving in general 0.080 to 0.090 g. of vanillin, m. p. 65–75°. The cold finger was replaced, the temperature of the bath raised to 100° and the sublimation continued (1.5 mm.) for a further fifteen to twenty minutes, whereby 0.010 to 0.020 g. of an intermediate fraction consisting of a mixture of vanillin and syringaldehyde was obtained. This small mixed fraction was likewise removed from the cold finger by solution in dry ether, and the sublimation continued for twelve to eighteen hours at 100° (1.5 mm.). Weight of the syringaldehyde fraction was in most cases 0.20–0.25 g., m. p. 105–110°. It could be recrystallized from water, with less than 3% loss, m. p. 110–112°; a mixed m. p. gave no depression.

The crude vanillin sublimate was dissolved in hot water (10 cc.), acidified slightly with acetic acid and then mixed, at 60°, with a hot solution of *m*-nitrobenzoylhydrazine, 0.15 g. in 10 cc. of water. After standing for thirty minutes at 60°, and then overnight at room temperature, the hydrazone was filtered, dried and weighed, m. p. 202–205°. Methoxyl: found, 9.8–10.0%; calcd. 9.85% (Table III).

Examination of the Sodium Hydroxide and Bicarbonate Extracts.—These were acidified, extracted exhaustively with benzene, the solvent removed under nitrogen and the residual oil weighed. The results are shown in Table I.

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Summary

1. The recovery of vanillin in yield of 25% from spruce wood by the action of a hot aqueous mixture of alkali and nitrobenzene (Freudenberg and co-workers) has been confirmed.

2. Application of the procedure to various

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[7] Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941).

[8] Hilpert and Hellwäge, *Ber.*, **68**, 380 (1935); Hilpert, *Cellulosechem.*, **17**, 25 (1936).

[9] Use of alkali–nitrobenzene mixtures as oxidizing agents for organic substances is attended with marked danger in certain cases due to the sudden exothermal reaction taking place at a relatively low temperature. While in the present investigation the gaskets of the bombs were blown in several cases, no untoward accident was experienced under the conditions outlined.

[10] Tomlinson and Hibbert, THIS JOURNAL, **58**, 345 (1936).

angiosperms gives yields of a mixture of vanillin and syringaldehyde amounting to 25–45% (Klason lignin basis).

3. In the case of the dicotyledons (maple, aspen, sassafras, jute) the yield is 40–45%, and the ratio of vanillin to syringaldehyde about 1:3. With the monocotyledons (rye straw, corn cobs, bamboo) the yield is lower (25–31%) and the ratio of the two aldehydes about 1:1.

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Studies on Lignin and Related Compounds. LX. Hydrogenation Studies on Maple Ethanolysis Products (Part 1)

BY LLOYD M. COOKE,[1] JOSEPH L. MCCARTHY AND HAROLD HIBBERT

By treating maple wood with ethanol–hydrogen chloride, Hibbert and co-workers have been able to isolate α-ethoxypropiovanillone,[2] I (Fig. 1), vanilloyl methyl ketone,[3] V (Fig. 1), and their syringyl homologs,[2,3] as well as amorphous lignin fractions which are differentiated by solubility and chemical characteristics.[4] Simultaneously with the isolation of these propylphenol "lignin building units," Harris, D'Ianni and Adkins[5] obtained 4-*n*-propylcyclohexanol, III (Fig. 1), 4-*n*-propylcyclohexanediol-1,2, IV (Fig. 1), and 3-(4-hydroxycyclohexyl)-propanol-1, IX (Fig. 1), by the high-pressure catalytic hydrogenation of a methanol lignin isolated from aspen wood. In view of the close structural relationship apparently existing between the products of lignin ethanolysis and of lignin hydrogenation, a study of the hydrogenation of (a) certain monomolecular constituents of maple lignin ethanolysis products; and of (b) the amorphous maple lignin ethanolysis fractions was undertaken. This paper deals with the hydrogenation of the former and development of a general quantitative technique applicable to small amounts (10–15 g.) of ligneous materials.

The hydrogenation of propylphenol type substances may be expected to occur in a stepwise manner, the individual changes proceeding to a degree determined by the reactivity of the grouping in a particular environment and by catalyst specificity. For example, with vanillin (possibly originating during ethanolysis of wood by cleavage from lignin propylphenol-type substances), high-pressure hydrogenation over copper chromite appeared to bring about a stepwise reduction[6] of the aldehyde to the alcohol, the alcohol to the hydrocarbon, cleavage of the methoxyl grouping, and finally saturation of the ring, to give methylcyclohexanol. Similarly with vanilloyl methyl ketone (V), the work of Adkins and co-workers[7] indicates that with copper chromite catalyst at 250° and 300 atmospheres of hydrogen pressure, its reduction can be expected to proceed rapidly to give 4-*n*-propylcyclohexanol (III) as the major final product, the formation possibly taking place through intermediates VI or IV, or both (Fig. 1).

However, in the case of α-ethoxypropiovanillone (I) there appear to be no good literature examples indicating the probable course of its hydrogenation, although the final formation of 4-*n*-propylcyclohexanol (III), perhaps taking place through 4-*n*-propylcyclohexanediol-1,2 (IV) or else through II or VI (Fig. 1), seems probable.

To determine the actual course followed, α-ethoxypropiovanillone (I) was hydrogenated over copper chromite catalyst at 250° at a hydrogen pressure of 5000 lb./sq. in. and the reaction products (Table I) isolated and identified by use of the new, generally applicable, small-scale technique. The large amount of water and the low yields of methanol and ethanol indicate the probable partial occurrence of reactions of types I $\rightarrow$ II $\rightarrow$ III and I $\rightarrow$ IV $\rightarrow$ III (Fig. 1) to produce methane[8] and ethane followed by the hydrogenolysis of the newly-formed hydroxyl groups to give

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[1] This paper is part of a thesis submitted to the Faculty of Graduate Studies, McGill University, by Lloyd M. Cooke in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1941.

[2] Hunter, Cramer and Hibbert, THIS JOURNAL, **61**, 516 (1939).

[3] Brickman, Pyle, Hawkins and Hibbert, *ibid.*, **62**, 986 (1940).

[4] (a) Brickman, Pyle, McCarthy and Hibbert, *ibid.*, **61**, 868 (1939); (b) Patterson, West, Lovell, Hawkins and Hibbert, *ibid.*, **63**, 2065 (1941); (c) Lovell and Hibbert, *ibid.*, **63**, 2070 (1941).

[5] Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

[6] Godard, Ph.D. thesis, McGill University, 1941.

[7] Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937.

[8] (a) Wojcik and Adkins, THIS JOURNAL, **55**, 1293 (1933); (b) Wojcik, Covert and Adkins, *ibid.*, **55**, 1669 (1933).