

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

Studies on Lignin and Related Compounds. XXXIV. Acetovanillone and Acetosyringone as Degradation Products of Lignin Sulfonic Acids

BY FRANK LÉGER AND HAROLD HIBBERT

In previous communications¹ it was shown that treatment of a commercial waste sulfite pulp liquor prepared from a mixture of soft woods (principally spruce and balsam) gave a mixture of various phenolic substances, from which vanillin and acetovanillone were isolated in yields of 7 and 0.30–0.35%, respectively, of the lignin present.

Inasmuch as the guaiacyl and syringyl radicals recently have been shown to form part of the lignin structure² it was of interest to find whether this was also true of the acetoguaiacyl and acetosyringyl groupings.

It was found that the action of hot aqueous alkali on spruce lignin sulfonic acid gave a mixture containing both vanillin and acetovanillone, together with other phenols, while birch lignin sulfonic acid gave vanillin, syringic aldehyde, acetosyringone and other lower boiling phenols but no acetovanillone.

That all these substances are true degradation products of lignin was proved by subjecting the original finely ground woodmeals to a thorough preliminary extraction with alcohol and benzene (1:1), followed by alcohol, and water, successively, in order to remove all resins, waxes, etc., which might function as a possible source of the aceto derivatives. As a further precaution, the "sulfite liquor," obtained by heating these extracted woods with aqueous sodium bisulfite and free sulfurous acid under pressure, was thoroughly extracted with benzene prior to treatment with alkali.

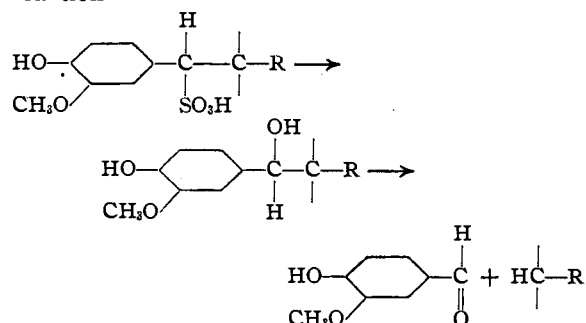
Additional confirmatory evidence was obtained in the case of spruce lignin sulfonic acid by subjecting the carefully purified potassium salt to the same treatment. Acetovanillone and vanillin also were obtained in this case, in yields of 0.2 and 4.6%, respectively.

It is of interest that the combined yield of lower boiling phenols, aceto derivative and tar resin left after removal of the vanillin in the case of spruce (or vanillin–syringic aldehyde mixture in the case of birch) amounts to about 1%. If the tarry resinous material is also aromatic in type,

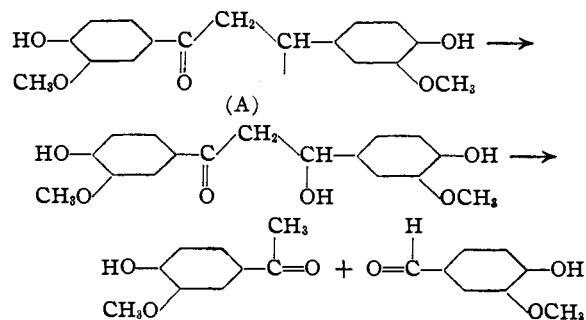
this would indicate a combined yield of around 8% aromatic derivatives present in the lignin building unit.

Structure of Lignin.—While both vanillin and acetovanillone are now shown to be true degradation products of spruce lignin sulfonic acid, nothing is yet known definitely of the mechanism by which they are formed under the influence of alkali.

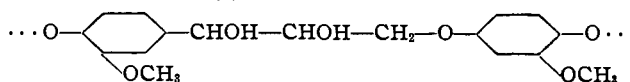
In an earlier paper³ it was suggested that the vanillin is formed as the result of a reversed aldol reaction



It is of interest that a similar reaction would account for the formation of *both* degradation products



The earlier theory put forward by Freudenberg⁴ assumed that lignin is formed in the plant as the result of a series of condensation reactions between mono- or dihydroxypropylguaiacols, to give polymers of the type



lignin sulfonic acids being formed as the result of sulfitation of an aromatic nucleus.

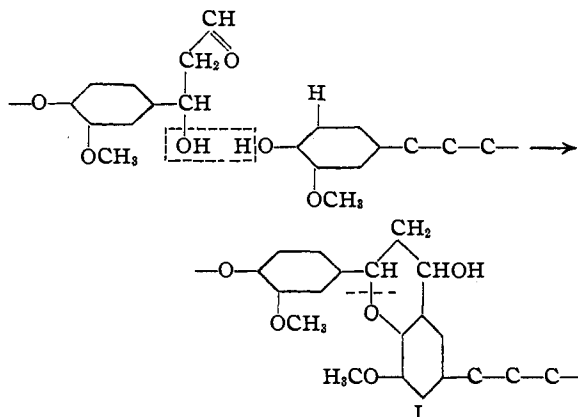
(1) Buckland, Tomlinson and Hibbert, *THIS JOURNAL*, **59**, 597 (1937); *Can. J. Research*, **B16**, 54 (1938).

(2) Bell, Hawkins, Wright and Hibbert, *THIS JOURNAL*, **59**, 598 (1937); Hawkins, Wright and Hibbert, *ibid.*, **59**, 2447 (1937).

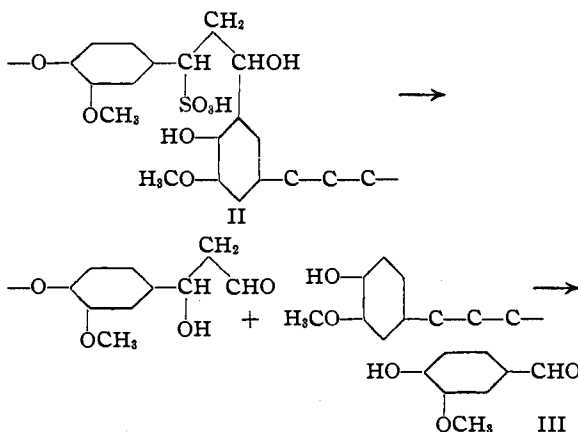
(3) Tomlinson and Hibbert, *ibid.*, **58**, 348 (1936).

(4) Freudenberg, "Tannin, Cellulose, Lignin," Verlag von J. Springer, Berlin, 1933, p. 128.

The well-established synthesis of vanillin from lignin sulfonic acid by Hibbert and co-workers³ made such a theory quite untenable and, in view of this, in a more recent paper⁵ Freudenberg assumes that lignin is formed as the result of condensation reactions between the α -hydroxyl group of an oxypropane side chain of one guaiacyl radical and the hydroxyl group and an ortho-nuclear hydrogen of a second, giving a series of pyran rings (I).



The action of sulfurous acid on this leads to ring fission with sulfitation of the α -carbon atom of the side chain (II). Further treatment of this with alkali would account for vanillin formation (III).

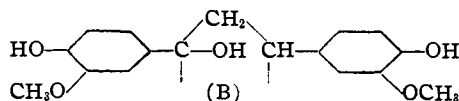


Even admitting the somewhat doubtful possibility of such a series of reactions proceeding during the course of plant synthesis, this modified theory is quite incapable of providing an explanation of the formation of acetovanillone and acetosyringone from lignin sulfonic acids.

It is not to be assumed that such a fragment as (A) shown above *actually exists as such* in the lignin molecule but rather that this is probably a deg-

(5) Freudenberg, Meister and Flickinger, *Ber.*, **70**, 500 (1937).

radation product formed from a central residual carbohydrate group (B) (derived originally from a fructose unit) as indicated below⁶



Experimental

Action of Alkali on Spruce Lignin Sulfonic Acid.—Finely ground spruce woodmeal (1400 g.) was extracted successively with alcohol-benzene (1:1), with alcohol and with water for forty-eight hours in each case, at the end of which period complete extraction of resins, waxes, fats, etc., had been completed. The air-dried woodmeal was then heated with 11.4 liters of a sodium bisulfite cooking liquor containing 1.2% free and 4.7% combined sulfur dioxide (two and one-quarter hours' slow rise to 110°, followed by eight hours at 125°).

The reaction product was filtered and the "sulfite liquor" extracted continuously for several days with benzene. No soluble material was obtained. The liquor was then treated with hot alkali according to the customary vanillin procedure⁷ and the resulting benzene solution (obtained from 3 liters of the treated liquor, representing 111 g. of lignin) shaken twice with 20% aqueous sodium bisulfite to remove all vanillin (7.16 g.). Evaporation of the solvent (benzene) left a viscous oil (1 g.) which was then given a combined distillation-sublimation treatment. For this purpose the product was placed in a small test-tube, inside of which a water-cooled inner tube ("cold finger") was inserted. As the bath temperature was raised from 55 to 100° (8 mm.) about 50 mg. of an oily distillate collected on the "finger" along with a few crystals. The "finger" was changed and no further deposition occurred until the bath temperature had reached 136° (8 mm.) when a crystalline sublimate collected. The temperature of the bath was raised to 200° when no further material sublimed. The residue in the flask weighed 450 mg. The crystalline sublimate was resublimed twice, and then recrystallized from benzene-petroleum ether to yield 300 mg. (or 0.27% based on weight of lignin) of a colorless product, m. p. 113.5–114.5°.

Anal. Calcd. for $C_8H_7O_2(OCH_3)$: OCH_3 , 18.7.⁸ Found: OCH_3 , 18.5.

There was no depression in melting point on mixing with an authentic sample of acetovanillone.

The semicarbazone melted at 165.5–166.5°; mixed melting point with the semicarbazone of authentic acetovanillone showed no depression.

Anal. Calcd. for $C_9H_{10}N_2O_2(OCH_3)$: OCH_3 , 13.9. Found: OCH_3 , 13.9.

Estimation of Vanillin.—A determination of vanillin in the same sulfite liquor, using *m*-nitrobenzoylhydrazide⁹

(6) Evidence has been submitted in a forthcoming communication indicating that this fragment is a 2-keto-5-pentanal condensation product derived from fructose, and that lignin represents a condensation of this with guaiacol. A comprehensive discussion of this new guaiacol lignin structure is in process of publication.

(7) Tomlinson and Hibbert, *THIS JOURNAL*, **53**, 345 (1936).

(8) The micromethoxyl analyses were carried out by Mr. Cyril Marks.

(9) Tomlinson and Hibbert, *THIS JOURNAL*, **55**, 340 (1936).

showed 6.4% present on the basis of lignin, or a ratio of acetovanillone to vanillin of approximately 1:24.

Action of Alkali on Purified Potassium Spruce Lignin Sulfonate.—The carefully purified potassium salt⁹ (OCH_3 , 12.3; S, 5.3; wt., 4.5 g.) was heated with 150 cc. of caustic soda (20% by weight) for twelve hours under reflux in a current of nitrogen, and the reaction product then extracted as above. After removal of the vanillin (0.206 g.), the benzene solution yielded 50 mg. of a residual oil which on a distillation-sublimation treatment gave 20 mg. of an oily phenolic distillate, a few mg. of acetovanillone and 20 mg. of a residual tarry resin. A mixed melting point of the purified material with authentic acetovanillone showed no depression.

Action of Alkali on Birch Lignin Sulfonic Acid.—Finely ground birch woodmeal (1200 g.) was solvent-extracted, air-dried and heated with 10 liters of acid sodium bisulfite solution under the same conditions as outlined for the spruce woodmeal.

The "sulfite liquor," after a thorough extraction with benzene (no extractable material being found), was then given the same alkali treatment as in the case of the spruce woodmeal. The benzene solution (obtained from 3 liters of the liquor, representing 59 g. of lignin) remaining after removal of the combined vanillin-syringic aldehyde fraction² yielded on evaporation of the solvent 1.5 g. of a viscous oil which on a combined distillation-sublimation treatment (at 7 mm. pressure) yielded: (1) 100 mg. of an oily product (bath temp. 50–100°); (2) 500 mg. of a cream-colored crystalline sublimate (bath temp. 100–200°); and (3) 800 mg. of a residual resin. The crystalline sublimate was removed from the "cold finger" and submitted to a second sublimation giving a pale yellow crystalline product.

Identification of Acetosyringone.—The material was recrystallized, first from a benzene-petroleum ether mixture and then from water, in the form of white needles, m. p. 120.5–121.5°; m. p. of acetosyringone, 122°.¹⁰ A mixed melting point with an authentic sample showed no depression.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{O}_2(\text{OCH}_3)_2$: OCH_3 , 31.6. Found: OCH_3 , 31.8.

The *p*-nitrophenylhydrazone melted at 194.5–195.5°; no depression when mixed with the *p*-nitrophenylhydrazone from authentic acetosyringone.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_8(\text{OCH}_3)_2$: OCH_3 , 18.7. Found: OCH_3 , 18.7.

Synthesis of Acetosyringone.—Acetosyringone was prepared from 5 g. of pyrogallol 1,3-dimethyl ether according to the method of Mauthner¹⁰ by acetylation of this followed by rearrangement using anhydrous aluminum chloride

in nitrobenzene solution: yield of recrystallized product, 0.7 g.; m. p. 120.5–121.5°.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{O}_2(\text{OCH}_3)_2$: OCH_3 , 31.6. Found: OCH_3 , 31.9.

Melting point of *p*-nitrophenylhydrazone, 194.5–195.5° as compared with 189–190° reported by Mauthner.¹⁰

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_8(\text{OCH}_3)_2$: OCH_3 , 18.7. Found: OCH_3 , 18.6.

Determination of Total Vanillin and Syringic Aldehydes.—These were determined together by precipitation as the *m*-nitrobenzoylhydrazones; 3000 cc. of treated liquor gave 6.8 g. of combined hydrazones, or 5.8% of the mixed aldehydes on the basis of lignin. The yield of acetosyringone from the same volume of liquor was 500 mg., equivalent to 0.84% on weight of lignin present. The ratio of acetosyringone to combined aldehydes was 1:7.

The authors wish to thank the Howard Smith Paper Mills, Limited, for their kindness in placing at their disposal the special equipment for the preparation of the sulfonic acids.

Summary

1. Spruce lignin sulfonic acid on treatment with hot aqueous alkali gives, in addition to vanillin (6–7%), acetovanillone in a yield of approximately 0.2–0.3% of the weight of lignin present.

2. Birch lignin sulfonic acid under the same conditions gives a mixture of vanillin, syringic aldehyde, and acetosyringone in yields of approximately 2.9, 2.9 and 0.8%, respectively, of the weight of lignin present.

3. The experimental data indicate the presence of the guaiacyl and the acetoguaiacyl radicals in the spruce lignin building unit, and of the guaiacyl, syringyl and acetosyringyl radicals in the birch lignin building unit. It is probable that the acetoguaiacyl and acetosyringyl radicals do not exist as such but are present as aldol or enol types.

4. The disagreement of these results with Freudenberg's theory of lignin as a polymerization product derived by condensation reactions of a dioxyphenyl hydroxylated propane building-unit is pointed out.

(10) Mauthner, *J. prakt. Chem.*, [2] 121, 255 (1929).