The very marked parallelism between the red color obtained on testing with the Mäule reagent and the definitely proven presence of the syringyl radical indicates the possibility of using the oxidation technique as a chemical means for checking taxonomic classification.[26]

Acknowledgment.—The authors wish to thank the numerous friends who so kindly provided much of the plant material used in this investigation and to express their appreciation of the valuable assistance rendered by Miss Jean Rosten in the preparation and analysis of the wood samples. One of us (R. H. J. C.) also desires to thank the Canadian Pulp and Paper Association for their financial assistance.

Summary

1. Alkaline nitrobenzene oxidation of forty-seven widely varying accepted forms of gymnosperms and angiosperms has shown that in practically all cases the former yield only vanillin, while the latter give both vanillin and syringaldehyde. This confirms the earlier findings of Hibbert and co-workers.

2. The yields of vanillin, in the case of the gymnosperms, vary between 15 and 24%, based on the Klason lignin. With the angiosperms the combined yield of vanillin and syringaldehyde amounts to 35–51%, the ratio of the former to the latter being approximately 1:3.

3. Considering the highest combined aldehyde yield (silver maple 51%) obtained, this amounts to 61% of the Klason lignin based on the assumption that the native maple lignin is derived essentially from a mixture of anhydro polymeric forms of coniferyl and syringyl alcohols.

4. Exceptions to the above ratio (1:3) of mixed aldehydes were found in the case of certain primitive angiosperms characterized by the absence of vessels, the ratio in this case being 1:1.

5. All genera of the *Gnetales* (a group of uncertain position) gave both vanillin and syringaldehyde on oxidation, a result in harmony with their high lignin and methoxyl values and behavior with the Mäule reagent. Their relationship to the angiosperms rather than to the gymnosperms is thus indicated.

6. Only a very few members of the *Coniferales* were found to yield, on oxidation, an aldehyde mixture containing *both* vanillin and syringaldehyde and to give a definite Mäule reaction.

7. The behavior on oxidation of all the plants investigated is in complete agreement with their color reaction (or its absence) when tested with the Mäule reagent, and thus offers a new chemical procedure for taxonomic classification.

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[26] It is the authors' intention to isolate the red coloring matter obtained by treatment of angiosperms with the Mäule reagent with the object of establishing therein the presence of the syringyl nucleus.

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

Studies on Lignin and Related Compounds. LXXVI. Alkaline Nitrobenzene Oxidation of Corn Stalks. Isolation of *p*-Hydroxybenzaldehyde

BY R. H. J. CREIGHTON[1] AND HAROLD HIBBERT

Alkaline nitrobenzene oxidation of a wide variety of woods[2] has been shown to give high yields of vanillin from gymnosperms and of a mixture of vanillin and syringaldehyde from dicotyledons.

Certain monocotyledons, notably corn (cobs and stalks), bamboo and rye straw, yielded, in addition to vanillin and syringaldehyde, a non-methoxylated carbonyl derivative which could not be separated from vanillin by sublimation. The absence of methoxyl was indicated in the much lower values found for the crude *m*-nitrobenzoylhydrazones derived from the bisulfite fraction[2] isolated from the oxidation products.

The bisulfite fraction from the nitrobenzene oxidation of corn stalks has been reinvestigated and a separation of the unknown product from vanillin effected, based on solubility differences

TABLE I

METHOXYL ANALYSES OF CRUDE *m*-NITROBENZOYL HYDRAZONES FROM THE BISULFITE FRACTION ISOLATED FROM THE ALKALINE NITROBENZENE OXIDATION PRODUCTS OF MONOCOTYLEDONS

Material	OCH$_3$ %
Dracaena sp. (stem)	14.5
Aloe abyssinica (stem)	14.3
Bamboo (unidentified) (stem)	10.8
Zea mays L. (Corn cobs)	5.5
Zea mays L. (Corn stalks)	7.5
Secale cereale L. (Rye straw)	12.1
Saccarhum officinarum L. (Sugar cane stem)	14.0
Dicotyledons (average 6 woods)	14.8
Quercus (Oak)	15.3
Populus (Aspen)	14.7
Juglans (Walnut)	15.0
Tilia (Basswood)	13.8
Robinia (pseudacacia) (Black Locust)	14.6
Liriodendron tulipifera (Yellow poplar)	15.6
Vanillin	9.8

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[1] This paper represents part of a thesis presented by R. H. J. Creighton to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1943.

[2] Creighton, Gibbs and Hibbert, THIS JOURNAL, **66**, 32 (1944).

in cold benzene. The non-methoxyl-containing constituent has been identified as *p*-hydroxybenzaldehyde. The yields of the three aldehydes obtained in the oxidation of corn stalks are summarized in Table II.

TABLE II

SUMMARY OF YIELDS FROM THE ALKALINE NITROBENZENE OXIDATION OF CORN STALKS

Fraction	Crude product	Recrystallized product
	% Klason lignin	
Total aldehydes determined as *m*-nitrobenzoylhydrazones	18.7	
Crude bisulfite soluble oils	16.7	
Total distillable oils	10.3	
Vanillin	5.3	4.5
p-Hydroxybenzaldehyde	1.8	1.4
Syringaldehyde	3.2	2.6

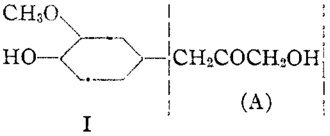
The presence of the *p*-oxyphenylmethane ($—O—C_6H_4—C—$) grouping in corn cob lignin has been shown previously by Phillips and Goss[3] who isolated anisic acid from the oxidation products of a methylated alkali corn-cob lignin, but obtained only oxalic acid from the unmethylated lignin. Phillips[4] also claims to have obtained anisic acid by permanganate oxidation of a fraction isolated from the dry distillation of an alkali corn cob lignin, presumably unmethylated. It seems likely that one of the products obtained in this same investigation, and characterized by them as a dimethoxycarboxylic acid, $C_8H_6O_2(OCH_3)_2$, was in reality acetosyringone, this having the same empirical composition and melting point, 120.5–121.5°.[5]

The experimental results may provide a means of distinguishing between mono- and dicotyledons. Substantial experimental evidence has been obtained by Hibbert and co-workers to show that the lignin complex in gymnosperms is derived from I; that in angiosperms from I and II.

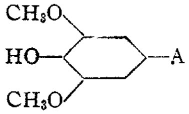
It is possible that all monocotyledons may contain, in addition to lignins derived from I and II, a new type derived from III, oxidation of which would give *p*-hydroxybenzaldehyde.

On the other hand Raistrick's metabolic products obtained by the action of molds (*Penicillium brevi-compactum*) on glucose as sole substrate[6] contain the aromatic nucleus IV and presumably are also stabilized end products arising from V, the —COOH group being introduced as a secondary type reaction.

A common feature of all plants would seem to consist in their ability to synthesize metabolic products containing a similarly-functioning propyl side-chain (A) attached to a varying type of aromatic phenol unit. The products I, II, III, V, etc., may exist as such or in the form of condensation polymers.



I



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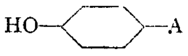

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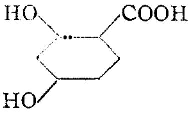

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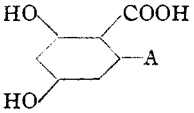

V

Experimental

Corn-stalk meal (previously extracted successively with ethanol–benzene, ethanol and hot water) (50.0 g. containing 10.0 g. of Klason lignin), nitrobenzene (30 cc.) and aqueous sodium hydroxide (600 cc. of 2 *N*) were heated for three hours at 160° with vigorous agitation as outlined in the previous paper[2]; yield of crude bisulfite soluble oils, 1.503 g.

Separation of Syringaldehyde.—The crude oil (1.503 g.) on distillation yielded two crystalline fractions; (1) b. p. 130–160° (0.2 mm.); 0.825 g.; OCH_3 (of different portions) 12–17%; (2) b. p. 210–230° (0.25 mm.); 0.284 g. The second fraction was recrystallized from water and gave syringaldehyde; m. p. 110–112°; no mixed melting point depression.

Isolation of Vanillin and *p*-Hydroxybenzaldehyde.—Fraction (1) (0.825 g.) was mixed with 10 cc. of dry benzene and stirred for one hour at 20°, the mixture then centrifuged, the benzene-soluble portion evaporated to dryness and re-treated similarly with a further 5 cc. of benzene. The final benzene-soluble fraction left after the second treatment was recrystallized from water, and gave 0.451 g. of pure vanillin; m. p. 81–82°.

The benzene-insoluble fractions from the two treatments were combined, and recrystallized from water; yield, 0.126 g.; white crystalline product, m. p. 116–117°. A mixed melting point with *p*-hydroxybenzaldehyde showed no depression, as was also the case with the phenylhydrazones.

Summary

Oxidation of corn stalks by nitrobenzene and alkali gives, as actual pure products, vanillin, syringaldehyde and *p*-hydroxybenzaldehyde in yields of 4.5, 2.6 and 1.4%, respectively, based on the Klason lignin content of the corn stalks, the crude yields being 5.3, 3.2 and 1.8%, respectively.

This represents the first isolation of *free p*-hydroxybenzaldehyde from lignin. Its presence may serve as a distinguishing characteristic between the mono- and dicotyledons.

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[3] Phillips and Goss, THIS JOURNAL, **55**, 3466 (1933).

[4] Phillips and Goss, *Ind. Eng. Chem.*, **24**, 1436 (1932).

[5] Leger and Hibbert, THIS JOURNAL, **60**, 565 (1938).

[6] Oxford and Raistrick, *Biochem. J.*, **27**, 634, 1473 (1933).