**Pyrolysis of Acetylsalicylaldehyde.**—Freshly distilled acetylsalicylaldehyde (91.7 g.) was refluxed for ten hours. The refluxing temperature at first was 255° but, as the pyrolysis proceeded, the refluxing became more vigorous, and the temperature had to be reduced. At the end of the run it was 225°. The products, separated by distillation at reduced pressure, were 6 g. of acetic acid and acetic anhydride, 53 g. of recovered acetylsalicylaldehyde, and 7.6 g. of coumarin.

Refluxing 50.7 g. of acetylsalicylaldehyde and one drop of sulfuric acid for ten hours produced 7.0 g. of coumarin, yields of other products being comparable to those in the above run.

Refluxing 53.0 g. of acetylsalicylaldehyde with 5.0 g. of fused sodium acetate for five hours produced about 6 g. of a mixture of acetic acid and acetic anhydride, 11.6 g. of salicylaldehyde, 10.6 g. of acetylsalicylaldehyde, and 7.5 g. of coumarin.

***p*-Acetoxybenzaldehyde.**—Ketene was passed for five hours (2.5 moles) into a solution of 55 g. (0.45 mole) of *p*-hydroxybenzaldehyde in 300 ml. of acetone. On distillation the reaction mixture yielded a 67 g. fraction (0.408 mole, 91% yield) of *p*-acetoxybenzaldehyde, b. p. 119–120° (6 mm.). This substance formed a 2,4-dinitrophenylhydrazone, m. p. 241°. The acetylated aldehyde was very sensitive to the action of aqueous alkali, the acetyl group being removed on short exposure to cold 10% aqueous sodium hydroxide solution. The acetylated aldehyde was also found to be oxidized easily by the action of air, forming *p*-acetoxybenzoic acid, m. p. 118°, a compound which is easily hydrolyzed by the action of cold 10% aqueous sodium hydroxide solution to *p*-hydroxybenzoic acid.

***p*-Acetoxycinnamic Acid.**—Ketene was passed for ten hours (4.5 moles) into a mixture of 61 g. (0.5 mole) of *p*-hydroxybenzaldehyde, 10.6 g. of fused sodium acetate and 300 ml. of benzene. Extraction of the reaction mixture with a 10% aqueous sodium bicarbonate solution, followed by acidification of the extract with phosphoric acid, yielded 18 g. of a crude product from which, after several recrystallizations from water and several treatments with Norit, 6 g. (5% yield) of pure *p*-acetoxycinnamic acid, m. p. 207°, was obtained.

A comparable run in which *p*-acetoxybenzaldehyde was the starting material gave a 6% yield of *p*-acetoxycinnamic acid.

## Summary

The reaction of ketene with salicylaldehyde yielded acetylsalicylaldehyde, coumarin (especially in the presence of sulfuric acid), and, only in the presence of sodium acetate, *o*-acetoxycinnamic acid. The mechanism of the formation of these compounds is discussed.

Pyrolysis of acetylsalicylaldehyde at its boiling point yielded salicylaldehyde, acetic acid, acetic anhydride and coumarin. The presence of sulfuric acid catalyzed the formation of coumarin.

Ketene reacted with *p*-hydroxybenzaldehyde to give a good yield of *p*-acetoxybenzaldehyde. When the reaction was carried out in the presence of sodium acetate, it was possible to isolate some *p*-acetoxycinnamic acid from the reaction mixture.

RECEIVED JULY 26, 1940

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

# Studies on Lignin and Related Compounds. XLIX. Occurrence of the Guaiacyl and Syringyl Groupings in the Ethanolysis Products from Various Plants

BY A. S. MACINNES, EINAR WEST, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

It has been shown that ethanolysis[1] (*i. e.*, treatment with boiling anhydrous ethanol containing hydrogen chloride) of spruce wood,[2] maple wood,[3] and of oak lignin,[4] results in a conversion of a part of the lignin constituents into water-soluble oils. The remainder either remains in the residual plant tissue, or is isolated as the water-insoluble, amorphous, non-distillable "ethanol lignin."

In the present investigation[5] these findings have been extended by subjecting various types of plant materials to ethanolysis[1] and then determining the degree of lignin removal, as well as the amounts of "crude oils" and ethanol lignin formed. The products investigated were California redwood, Douglas fir, red oak, jute, corn stalks, rye straw and bamboo. The water-soluble "crude oils" were separated by the previous method[1] into a bisulfite, bicarbonate, and alkali soluble, as well as a "neutral" fraction. The yields obtained are based on the Klason lignin originally present and are compared with previously published results[1] obtained with spruce and maple (Table I).

It is apparent that each of these lignin-con-

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[1] Brickman, Pyle, McCarthy and Hibbert, THIS JOURNAL, **61**, 868 (1939).

[2] Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939).

[3] Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

[4] Peniston, McCarthy and Hibbert, *ibid.*, **61**, 530 (1939).

[5] Preliminary results dealing with the present investigation have been reported previously, see ref. 1 and West, MacInnes, McCarthy and Hibbert, *ibid.*, **61**, 2556 (1939).

Table I

Yields of Crude Products from Ethanolysis of Various Plant Materials

| | Initial sample | | Ethanolysis Products | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Plant residue | | | Ethanol lignin | | Bz. sol. oils extd. from ethanol lignin | | Water soluble oils fractionation products | | | | | | | | | |
| | | | | | | | | | | Total crude | | Bisulfite soluble | | Bicarbonate soluble | | Alkali soluble | | "Neutral" | |
| Plant material | Dry wt., g. | Klason lignin, % | Wt., g. | Klason lignin, % | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % | Wt., g. | PIKL.,[a] % |
| Gymnosperms | | | | | | | | | | | | | | | | | | | |
| Spruce[b] | 100 | 28.6 | 68.6 | 26.6 | 64 | 2.96 | 10 | 1.72 | 6 | 3.28 | 12 | 0.51 | 1.8 | 0.10 | 0.4 | 1.15 | 4.0 | 0.21 | 0.8 |
| Redwood | 100 | 38.2 | 70.8 | 36.4 | 67 | 5.18 | 14 | 2.37 | 6 | 2.95 | 8 | .56 | 1.5 | .18 | .5 | 0.67[c] | 1.8[c] | .14 | 0.4 |
| Douglas Fir | 100 | 29.7 | 73.5 | 29.0 | 72 | 2.40 | 8 | 1.65 | 6 | 2.66 | 9 | .63 | 2.1 | .10 | .3 | 1.26 | 4.2 | .30 | 1.0 |
| Angiosperms: Dicotyledons | | | | | | | | | | | | | | | | | | | |
| Maple[b] | 100 | 21.4 | 55.6 | 12.0 | 31 | 8.22 | 38 | 3.80 | 18 | 7.55 | 35 | 1.57 | 7.3 | 0.08 | 0.4 | 2.97 | 14 | 0.79 | 3.7 |
| Red Oak | 100 | 21.0 | 51.0 | 12.8 | 31 | 7.91 | 38 | 4.07 | 19 | 6.63 | 32 | 1.42 | 6.8 | .11 | .5 | 2.18 | 10 | 1.04 | 4.9 |
| Jute | 100 | 12.3 | 62.5 | 6.5 | 33 | 2.68 | 22 | 3.82 | 31 | 5.27 | 43 | 0.68 | 5.5 | .17 | 1.4 | 2.49 | 20 | 0.67 | 5.4 |
| Monocotyledons | | | | | | | | | | | | | | | | | | | |
| Bamboo | 100 | 22.5 | 52.9 | 13.7 | 32 | 6.78 | 30 | 4.60 | 20 | 6.70 | 30 | 0.14 | 0.6 | 0.82 | 3.6 | 1.57 | 7.0 | 0.25 | 1.1 |
| Corn | 100 | 17.9 | 56.0 | 9.0 | 28 | 5.98 | 33 | 6.65 | 37 | 4.03 | 23 | .29 | 1.6 | .07 | 0.4 | 1.94 | 11 | .70 | 3.9 |
| Rye | 100 | 20.2 | 55.1 | 13.4 | 37 | 7.58 | 38 | 5.19 | 26 | 3.01 | 15 | .52 | 2.6 | .12 | .6 | 1.40 | 7.0 | .28 | 1.4 |

[a] "PIKL." abbreviates "percentage of initial Klason lignin" present in the initial plant material; the number of significant figures indicates the estimated accuracy. [b] Data taken from ref. 1. [c] Uncertain.

taining plant materials shows a similar behavior on ethanolysis to that found previously with spruce[2] and maple[3] woods. Furthermore, the yields of the various fractions provide chemical evidence in support of the customary botanical classification. Thus the gymnosperms show a lower degree of delignification on ethanolysis than the angiosperms, while in many respects the monocotyledons appear to occupy a position midway between the dicotyledons and the gymnosperms.

Analysis of the various ethanolysis products shows that they possess marked similarity to those obtained in the alkaline cleavage of lignin sulfonic acids[6] in that the guaiacyl residue is again found to be characteristic of the lignin in softwoods, while both guaiacyl and syringyl groups are present in hardwoods. Previous investigations have shown that both guaiacyl and syringyl derivatives can be isolated from the ethanolysis "crude oils" of maple wood[3] but only guaiacyl derivatives from spruce wood.[2]

An attempt was therefore made in the present research to isolate an didentify crystalline derivatives of α-ethoxypropiovanillone[2] and of α-ethoxypropiosyringone[3] from the alkali soluble fractions, using, in general, the methods previously described.[2,3] Likewise, the bisulfite soluble fractions[7] were examined for the presence of derivatives of syringaldehyde,[7a] syringoyl methyl ketone,[7a] vanillin,[7b] and vanilloyl methyl ketone.[7b] The separation of the 2,4-dinitrophenylhydrazone derivatives of vanillin and vanilloyl methyl ketone was carried out according to the recently developed solubility method of Brickman, Hawkins and Hibbert.[7c] Only melting points and mixed melting points of the isolated compounds were determined as the scale upon which the experiments were carried out did not permit accurate determination of yields.

From the results given in Table II it is clear that the ethanolysis reaction is a fairly general one for lignin-containing plant materials, not only with reference to the crude fractions described above but also, in general, to the chemical structure of the crystalline derivatives isolated. Moreover, the lignin in gymnosperms contains the guaiacyl grouping, while that in angiosperms, mono- or dicotyledons as so far investigated contains both guaiacyl and syringyl groupings with, apparently, the single exception of bamboo.

α-Ethoxypropiovanillone was found in each of the alkaline soluble fractions investigated, while α-ethoxypropiosyringone was isolated in all the alkali soluble fractions from angiosperms except that from bamboo, in which latter it is possible that a different series of compounds may be present. No evidence for the presence of either vanillin or syringaldehyde could be found in the bisulfite soluble fraction from red oak, a finding

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[6] Hawkins, Wright and Hibbert, This Journal, 59, 2447 (1937).

[7] (a) Pyle, Brickman and Hibbert, *ibid.*, 61, 2198 (1939); (b) Brickman, Pyle, Hawkins and Hibbert, *ibid.*, 62, 986 (1940); (c) Brickman, Hawkins and Hibbert, *ibid.*, 62, 2149 (1940).

TABLE II: PRODUCTS IDENTIFIED IN THE ETHANOLYSIS EXTRACT OF VARIOUS PLANT MATERIALS

| | | | Gymnosperms | | | Angiosperms | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Dicotyledons | | | Monocotyledons | | |
| | | | Spruce | Redwood | Douglas fir | Maple | Red Oak | Jute | Bamboo | Corn | Rye |
| Alkali soluble fraction | α-Ethoxypropiovanillone methyl ether[a] | M. p., °C. | 81–82 | [b] | 79–80.5 | 81–82 | 78–80 | 78–80 | 79–80 | 79–80 | 78–80 |
| | | M. m. p. °C. | 81–82 | [b] | 78.5–80.0 | 81–82 | 79.5–81 | 79–80.5 | 79–80 | 79–80 | 79–80.5 |
| | α-Ethoxypropiosyringone *p*-nitrobenzoate[a] | M. p., °C. | Absent | Absent | Absent | 141–142 | 140–141 | 139.5–142 | Absent | 139.5–142 | 140–142 |
| | | M. m. p., °C. | Absent | Absent | Absent | 141–142 | 140–142 | 138–140 | Absent | 139–142.5 | 140–142.5 |
| Bisulfite soluble fraction | Vanillin 2,4-dinitrophenylhydrazone[a] | M. p., °C. | 262–263 | 262–263 | 262–263 | [c] | Absent | [b] | 260–261 | 258–259 | 262–263 |
| | | M. m. p., °C. | 262–263 | 262–263 | 263–264 | [c] | Absent | [b] | 262–263 | 259–260 | 262–263 |
| | Vanilloyl methyl ketone 2,4-dinitrophenylhydrazone[a] | M. p., °C. | 226–227 | 221–222 | 225–226 | [d] | [d] | 225–226 | [e] | [d] | 226–227 |
| | | M. m. p., °C. | 226–227 | 223–224 | 225–226 | [d] | [d] | 225–226 | [e] | [d] | 226–227 |
| | Syringaldehyde 2,4-dinitrophenylhydrazone[a] | M. p., °C. | Absent | Absent | Absent | 232–235.5 | Absent | 235–235.5 | Absent | 235–235.5 | 235–235.5 |
| | | M. m. p., °C. | Absent | Absent | Absent | 235–235.5 | Absent | 235–235.5 | Absent | 234–235.5 | 235–235.5 |
| | Syringoyl methyl ketone semicarbazone[a] | M. p., °C. | Absent | Absent | Absent | 209.5–210 | 209–209.5 | 207.5–208 | Absent | 208–208.5 | 207.5–208.5 |
| | | M. m. p., °C. | Absent | Absent | Absent | 209.5–210 | 209–209.5 | 207.5–208.5 | Absent | 208–208.5 | 207–208.5 |

[a] The uncorrected melting points of the pure derivatives are as follows: α-ethoxypropiovanillone methyl ether, 81–82[2]; α-ethoxypropiosyringone *p*-nitrobenzoate, 141–142.5[3]; vanillin-2,4-dinitrophenylhydrazone, 263–264[7c]; vanilloyl methyl ketone 2,4-dinitrophenylhydrazone, 226–227[7c]; syringaldehyde 2,4-dinitrophenylhydrazone, 235–235.5[7a]; syringoyl methyl ketone semicarbazone, 210–210.5[7b]; more recently it has been found that the semicarbazone of synthetically prepared material melted at 213°. [b] Not investigated. [c] Vanillin 2,4-dinitrophenylhydrazone could not be isolated. [d] Vanilloyl methyl ketone 2,4-dinitrophenylhydrazone (m. p. 226–227°) was apparently absent. Instead, a compound of m. p. 194–195° was obtained. [e] Vanilloyl methyl ketone 2,4-dinitrophenylhydrazone apparently was absent.

not necessarily of significance since Brickman, Hawkins and Hibbert[8] have found that certain samples of spruce wood appear to yield no vanillin on ethanolysis. From red oak, corn stalks, and bamboo, no derivative of vanilloyl methyl ketone could be isolated, although, in the case of the first two plant materials, as well as in maple, there was present an unknown substance which is now being investigated (see footnote *d*, Table II).

**Acknowledgment.**—The authors desire to express their best thanks to the Spruce Falls Power and Paper Company and to the Howard Smith Paper Mills Limited for their kindness in awarding Scholarships to the junior authors.

## Experimental Part

Since in general the procedures used were the same as those already published, only a few pertinent remarks are necessary.

**Preparation of Materials.**—The woods used were air-dried and chipped. All materials were ground in the Wiley mill to pass a 40-mesh screen. Corn stalks obtained in the air-dried form were separated from leaves and pith, then ground. Jute fibers were carefully washed with hot water, then cut into short lengths, air-dried and ground. Green bamboo shoots were separated from leaves, air-dried, then ground. Rye straw, from which leaves and nodes had been removed, was air-dried, then ground.

After the usual benzene–alcohol and water extraction, and subsequent air-drying, the materials were finally dried by refluxing twice for several hours with anhydrous ethanol.

**Ethanolysis and Fractionation.**—These processes were carried out on 100-g. portions of the prepared plant materials, using suitably adjusted quantities of reagents.

**Identification of Ethanolysis Products.**—The procedures previously described were used for the isolation and identification of the derivatives of α-ethoxypropiosyringone,[3] syringaldehyde,[7a] syringoyl methyl ketone,[7b] vanillin,[7c] vanilloyl methyl ketone.[7c]

The method of Cramer, Hunter and Hibbert[2] for the isolation of the methyl ether of α-ethoxypropiovanillone was slightly modified. Instead of 150% of the theoretical requirement of diazomethane, 350% of the reagent was used in ether solution (water- and methanol-free) to methylate the distilled guaiacyl alkali-soluble portion of the water-soluble oils. This require-

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(8) Brickman, Hawkins and Hibbert, unpublished results.

ment was based upon the assumption that all of the portion to be methylated was $\alpha$-ethoxypropiovanillone.

## Summary

1. All lignin-containing materials appear to undergo the same type of ethanolysis reaction when refluxed with absolute ethanol containing hydrogen chloride. California redwood, Douglas fir, red oak, bamboo, corn stalks, rye straw, and jute are found to give crude oils and crystalline derivatives similar to those obtained previously from spruce and maple woods.

2. A botanical classification of gymnosperms and angiosperms is indicated from results of the present experiments on ethanolysis; the lignin present in materials of the former class contains guaiacyl units only while that in the latter both guaiacyl and syringyl groupings. This is in agreement with similar results obtained in the alkaline degradation of lignin sulfonic acids. On ethanolysis only about one-third of the Klason lignin is removed from gymnosperms and about two-thirds from angiosperms.

MONTREAL, QUEBEC, CANADA RECEIVED JUNE 4, 1940

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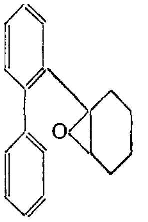
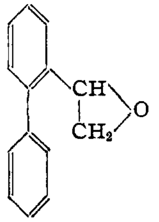
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

# Aromatic Cyclodehydration.[1] VII.[2] Phenanthrene

BY CHARLES K. BRADSHER AND ROBERT W. WERT

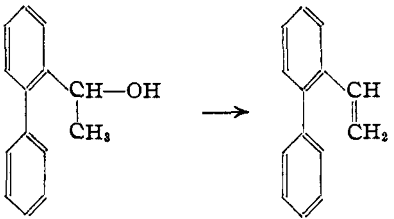
The success met with in the synthesis of tetrahydrotriphenylene from the oxide (I) of 1-(2-biphenyl)-cyclohexene-1 suggested that phenanthrene might be prepared from *o*-phenylstyrene oxide (II).


I



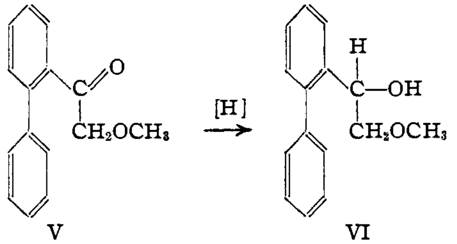
II

A Grignard reagent prepared from 2-iodobiphenyl was treated with acetaldehyde to give 1-(2-biphenyl)-ethanol-1 (III) which upon dehydration gave some *o*-phenylstyrene (IV). The oxide (II) prepared from this by the action of monoperphthalic acid, underwent cyclization in a boiling mixture of hydrobromic acid and acetic acid to give a small amount of phenanthrene.



III IV

In an effort to find a more promising method of synthesis, we decided to attempt the cyclization of 1-(2-biphenyl)-2-methoxyethanol-1 (VI), since it had been shown[2c] that the corresponding propanol gave 9-methylphenanthrene. The crude carbinol (VI) obtained by the aluminum isopropylate reduction of 2-($\omega$-methoxy)-acetobiphenyl (V), was cyclized by hydrobromic and acetic acids to give the desired hydrocarbon in an overall yield of 46%.



V VI

Although our experiments afford no direct evidence as to the course of the reaction, our belief that the intermediate is 2-biphenylacetaldehyde (VII) gains support from the observation of Tiffeneau[3] that 1-phenyl-2-methoxyethanol-1 (VIII) is converted to phenylacetaldehyde under conditions comparable to those used by us in the cyclization. We predict that the biphenylacetaldehyde, as well as any compound converted to

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(1) The term "aromatic cyclodehydration" is used here to designate the type of cyclization in which the elements of water are eliminated from a compound with the establishment of a new aromatic ring. This is in contradistinction to the type which leads to the formation of hydroaromatic rings.

(2) The preceding papers of this series are: (a) Bradsher and Schneider, THIS JOURNAL, **60**, 2960 (1938); (b) Bradsher and Rosher, *ibid.*, **61**, 1524 (1939); (c) Bradsher and Tess, *ibid.*, **61**, 2184 (1939); (d) Bradsher, *ibid.*, **61**, 3131 (1939); (e) Bradsher, *ibid.*, **62**, 486 (1940); (f) Bradsher, *ibid.*, **62**, 1077 (1940).

(3) Tiffeneau, *Compt. rend.*, **145**, 811 (1907).