native lignin, have been hydrogenated under similar conditions to those used in the hydrogenation of spruce wood.

2. The ether-linked dimers cleaved at the ether linkage, yielding products similar to those found in the reaction mixture after hydrogenation of spruce wood.

3. The carbon-to-carbon linked dimer did not yield fission products although nuclear reduction occurred. This apparently substantiates the opinions of Hibbert that dimeric, trimeric, etc., substances obtained by the hydrogenation of wood do not arise through the carbon-to-carbon cleavage of similar but more complex polymers. It would therefore appear that these complex substances exist as such in the wood prior to the hydrogenation reaction.

MONTREAL, CANADA RECEIVED APRIL 10, 1947

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

Studies on Lignin and Related Compounds. LXXXVII. High Pressure Hydrogenation of Maple Wood[1]

BY JAMES M. PEPPER[2] AND HAROLD HIBBERT[3]

Although abundant evidence is available[4] which points to the now well-recognized essentially aromatic character of native lignin, the actual yield, to date, of identified products, is in no case very large. By means of the ethanolysis procedure[5] all of the identified lignin products obtained from maple wood are *propylphenol* derivatives but amount to only 9.75% of the original lignin (Klason basis).[6] From nitrobenzene oxidation studies[7] much larger amounts of aromatic compounds are obtained, the total mixed aldehydes (vanillin and syringaldehyde) have been isolated in yields of 43% of the lignin, but in this case it must be remembered that these derivatives have only a C_6–C skeleton and as such cannot be used as positive evidence for the presence of a C_6–C–C–C lignin monomer. Much higher yields of C_6–C–C–C compounds have been obtained by means of the high pressure hydrogenation technique[4] but in every such case these have been *propylcyclohexyl* derivatives, and, although it is improbable that these could arise from any source except a propylphenyl unit, it still remained necessary to isolate the *aromatic* C_6–C–C–C units in high yields to justify the several formulas for native lignin that have been proposed.[4,8]

In a previous communication[9] a new technique has been described by which, under greatly milder conditions of hydrogenation and hydrogenolysis, propylphenol lignin derivatives have been isolated and identified. The apparent advantages of such a method include, apart from the value of the results obtained, the use of a starting material containing *all* of the lignin *in situ* and the stabilization, by reduction, of any reactive groups formed during the pressure cook thereby preventing any subsequent polymerization which might otherwise occur. It was thought that if it were possible to remove the entire lignin fraction from the wood by this means greatly increased yields of aromatic lignin products could be obtained. To effect this a detailed study of the conditions of isolation was undertaken and subsequently when it was found possible to isolate all the lignin as a chloroform-soluble product, characterization of this material was commenced in an attempt to increase the yield of aromatic derivatives.

Preliminary Experiments.—A concurrent investigation[9] had shown that for the hydrogenation of maple wood in a neutral medium (ethanol-water (1:1)), the optimum conditions for lignin removal were 165–170° for four hours at an initial pressure of 3000 lb./sq. in. Such a medium, after the cooking procedure, had a *p*H of 5.5, and this slight acidity may have been sufficient to bring about an effective hydrolysis of any existent lignin–carbohydrate complex. This fact initiated a series of experiments[10] to study the effect of *p*H on the lignin removal by this newly developed technique. Complete solution of the lignin was obtained in both acidic and basic media. The extensive use of an acid medium (hydrochloric acid) was not favored for the following reasons: (a) poisoning of the catalyst (Raney nickel) which does not take place in alkali; (b) the tendency toward increased polymerization which is minimized in alkali due to the blocking of the phenolic hydroxyl groups, and (c) the increased tendency toward formation of hydroaromatic derivatives at a lower temperature.[11]

Dioxane was chosen to replace ethanol in the final large-scale hydrogenation experiments in

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[1] This paper represents part of a thesis submitted to the Graduate Faculty of McGill University by James M. Pepper in partial fulfilment of the requirements for the degree of Doctor of Philosophy, October 1943.

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[4] Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

[5] Hibbert, *et al.*, THIS JOURNAL, **65**, 1176 (1943).

[6] Kulka, Fisher, Baker and Hibbert, *ibid.*,, **66**, 39 (1944).

[7] Creighton, McCarthy and Hibbert, *ibid.*, **63**, 312 (1941).

[8] Freudenberg, *Ann. Rev. Biochem.*, **8**, 88–112 (1939).

[9] Brewer, Cooke and Hibbert, THIS JOURNAL, **70**, 57 (1948).

[10] Pepper and Hibbert, unpublished results.

[11] Foresti, *Boll. soc. Eustachiana*, **38**, 19 (1940).

order to prevent any ethoxylation occurring at the elevated temperatures. Duplicate hydrogenation experiments using, on the one hand, a dioxane–water (1:1) solvent and on the other, an ethanol–water (1:1) solvent, showed that in the latter case and not in the former ethoxyl groups (as determined by the method of Cooke and Hibbert)[12] were present to the extent of 5.6%.

Large-scale Hydrogenation Experiments.—In order to obtain the reaction products in amounts sufficient to permit of a detailed study, two 500-g. portions (Series A and B) of extracted wood meal were suspended in dioxane–water (1:1) containing sodium hydroxide (3%) and hydrogenated over Raney nickel catalyst[13] at 173° (initial pressure of hydrogen of 3000 lb./sq. in.) for six hours and the combined products, in each case, treated in the following manner.

After separation of the catalyst and residual wood meal, the filtrate was acidified (congo red) in the presence of chloroform and then thoroughly extracted with chloroform. The residual meal was similarly extracted in a Soxhlet extractor and the two chloroform extracts combined. This process effected an almost complete separation of the extracted lignin from carbohydrate contaminants. From Series A the total chloroform-soluble fraction was distilled from a Claisen flask thus separating it into the fractions: A1, distilling below 150° (bath temperature) (1 mm.); A2, distilling below 250° (1 mm.), and A3, a non-distillable resin. The low-boiling fraction, A1, was divided into water-insoluble (A1x) and water-soluble (A1y) portions and the former (A1x) fractionally distilled through the recently developed spiral screen packed laboratory column[14] (twenty-one theoretical plates) to yield (4-hydroxy-3-methoxyphenyl)-ethane and (4-hydroxy-3,5-dimethoxy-phenyl)-ethane, identified by the preparation of their *p*-nitrobenzoates and comparison with the *p*-nitrobenzoates of authentic samples.

The preparation of Series B was necessary in order to replace the fraction A2 from Series A which was not studied completely. By a treatment similar to that given for Series A, the total chloroform-soluble fraction from Series B, after distillation through a Claisen flask, was divided into four portions according to their boiling ranges: B1, distilling below 180° (bath temperature) (1.2 mm.); B2, at 180–215° (1 mm.); B3, at 215–280° (0.1 mm.) and B4, a non-distillable resin. Distillates B2 and B3 were combined, divided into a water-soluble portion (Bx) and a water-insoluble portion (By) and each of these fractions then fractionally distilled through the spiral screen packed column. From the former portion (Bx) was isolated the crystalline material 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol, identified by formation of the phenyl urethan of its 4-methoxy derivative. The fractionation of the latter portion (By) yielded (4-hydroxy-3,5-dimethoxyphenyl)-ethane, and a fraction which crystallized in the condenser, subsequently identified as 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol by a mixed melting point determination with the previously identified material.

In order to obtain the maximum amount of the isolated lignin as identified products, all the non-distillable (resin) fractions as well as the distilled fractions which were not identified from the various fractionation procedures were combined and rehydrogenated under the conditions (at 280° for twelve hours, initial pressure 3000 lb./sq. in.) used previously.[15] The object was to convert them, if possible, into the known cyclohexyl derivatives: 4-*n*-propylcyclohexanol, 3-cyclohexyl-1-propanol, 3-(4-hydroxycyclohexyl)-propanol-1 and 4-*n*-propylcyclohexane-diol-1,2. Rehydrogenation of the resins followed by fractional distillation of the product yielded three "flats"[15a] whose empirical analyses and molecular weights showed them to be derivatives of the "dimeric" type. Further study on these fractions was not carried out. Similar retreatment of the unidentified fractions and fractionation of the product yielded a distillation curve showing three "flats" which were identified, by means of their phenylurethans, as 4-ethylcyclohexanol, 4-*n*-propylcyclohexanol and 3-cyclohexyl-1-propanol.

Discussion

Although the entire native lignin has been obtained as a chloroform-soluble material, only a minor part (27.4% on a Klason lignin basis) has been characterized as combined alkylphenolic and alkylcyclohexyl derivatives. However during the various fractionation treatments, a total of 66% (by weight) of the isolated lignin products were distilled through the twenty-one or twenty-eight plate columns[14]: a convincing indication of their relatively simple (low molecular weight) nature and thermal stability. Of the distillable products from 500 g. of maple wood, 45.4 g. of lignin products (42.7% of the Klason lignin) existed either as identifiable "flats" or as crystalline material. A summary of the identified products, from 500 g. of maple wood, their yields, refractive indices and melting points of their characterizing derivatives is given in Table I.

The previously observed more readily extractable syringyl components of the native lignin from maple wood, as compared with those of the guaiacyl type, finds confirmation in these results: the guaiacyl and syringyl components being isolated in a ratio of 1 to 10. Significant, too, is the fact that after removal of the more easily distillable portion of the hydrogenation products,

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[12] Cooke and Hibbert, *Ind. Eng. Chem., Anal. Ed.*, **15**, 24 (1943).

[13] Mozingo, "Organic Syntheses," **21**, 15 (1941).

[14] Bower and Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

[15] Bower, Cooke and Hibbert, THIS JOURNAL, **65**, 1192 (1943).

[15a] Several fractionation samples taken in succession and having similar refractive indices.

TABLE I

IDENTIFIED LIGNIN COMPOUNDS OBTAINED FROM MAPLE WOOD (500 G.)

Identified compound	$n^{25}D$	Weight, g.	%age of Klason lignin	M. p. of derivatives, °C.
				p-Nitrobenzoates
(4-Hydroxy-3-methoxyphenyl)-ethane	1.5240	2.3	2.16	98-99[16]
(4-Hydroxy-3,5-dimethoxyphenyl)-ethane	1.5335	16.4	15.38	153.5–154.5
				α-Naphthyl urethan of methylated product
2-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanol	Cryst.	6.6	6.2	132–133
				Phenyl urethan
4-Ethylcyclohexanol	1.4484	1.99	1.87	113.5–114.5
4-*n*-Propylcyclohexanol	1.4620	0.92	0.86	123.5–124.5
3-Cyclohexyl-1-propanol	1.4656	.87	.82	83–84
Recovery		29.13	27.35	

rehydrogenation of the resins at elevated temperatures (280° instead of 173°) yielded products polymeric in type and having the same general characteristics (empirical analyses, refractive indices, boiling points and molecular weights) as those obtained from the analogous spruce resins which are in all probability polymers having the guaiacyl-type nucleus. Also it may be noted that since rehydrogenation of the resins under the conditions used for direct hydrogenation of wood did *not* give any propylcyclohexyl derivatives, the source of these compounds was the more easily isolated aromatic units obtained by the initial milder treatment.

Comparison of these results with those of Brewer, Cooke and Hibbert[9] shows the pronounced and somewhat drastic effect of the alkali (other conditions being similar) in the isolation of C_6–C–C units and not C_6–C–C–C units as was the case with the neutral medium. The isolation of these C_6–C–C units and most especially the 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol, would seem to indicate their derivation from a polymeric form in which the side chains of the building units are united through an oxygen linkage in the beta position. The presence of this type of linkage in all plant resins (lignans) has been repeatedly emphasized by Erdtman[17] and Haworth.[18]

Experimental

Preparation of Maple Wood Meal.—Maple wood meal (40-mesh) was extracted continuously with a mixture of ethanol and benzene (4:1) for forty-eight hours, then with ethanol for twenty-four hours, washed overnight with hot water, air-dried for three days and finally dried in a vacuum oven at 50–55° (15 mm.) for thirty-six hours.

Anal. Moisture, 3.5; OCH_3, 5.95; Klason lignin, 20.6.

Hydrogenation of Maple Wood (Series A and B).—Seven portions of solvent extracted maple wood meal together totaling 500 g. (Series A) were hydrogenated in an Aminco hydrogenator (2500 cc. capacity). A typical run is described as follows: wood meal (75.5 g.) was suspended in dioxane–water (1:1) (900 cc.) containing sodium hydroxide (27 g.) and hydrogenated over Raney nickel catalyst (55 g.) (wet with ethanol) at 173° (initial hydrogen pressure, cold, 3000 lb./sq. in.) for six hours. At the end of this time hydrogen absorption had ceased, the total hydrogen used being 0.38 mole per 100 g. of wood. A further seven portions of similar wood meal together weighing 500 g. (Series B) were hydrogenated under the same conditions. For each series the bomb contents were examined initially by the procedure outlined previously. For Series A, from the 500 g. wood meal there was obtained 364 g. of dried pulp and catalyst (equivalent approximately to 130 g. of residual pulp), and a chloroform soluble fraction containing 107.3 g. of hydrogenation products.

Examination of the Hydrogenation Products (Series A).—The total chloroform soluble fraction (107.3 g.) was distilled from a Claisen flask, thus dividing it into three portions; fraction A1 (36.7 g.) distilling below 150° (bath temperature) (1 mm.), fraction A2 (26.5 g.) distilling 150 to 250° (1 mm.) and a non-distillable resin A3 (26.0 g.). Distillate A1 (36.7 g.) was dissolved in chloroform (300 cc.) and extracted successively with five portions of saturated sodium bicarbonate solution giving a bicarbonate- and water-insoluble fraction A1x (25.9 g.) and a bicarbonate-soluble fraction A1y.

Fractional Distillation of Bicarbonate- and Water-Insoluble Fraction A1x.—Fraction A1x (24.6 g.) was fractionated through the Cooke–Bower spiral screen type fractionating column (14) (twenty-one plates). Two distinct "flats" were obtained, one in the $n^{25}D$ 1.5230–1.5251 range and the second in the $n^{25}D$ 1.5323–1.5344 range. Conversion of test samples from the first "flat" into their *p*-nitrobenzoates showed the former to be 4-hydroxy-3-methoxyphenylethane (m. p. of the *p*-nitrobenzoate 98–99°, mixed m. p. with an authentic sample showed no depression).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; H, 7.9; OCH_3, 20.4. Found: C, 70.4; H, 7.8; OCH_3, 20.5.

The second "flat" upon similar treatment proved to be 4-hydroxy-3,5-dimethoxyphenylethane (m. p. of the *p*-nitrobenzoate 153.5–154.5°, mixed m. p. with an authentic sample gave no depression).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.8; OCH_3, 34.1. Found: C, 65.2; H, 7.; OCH_3, 33.6.

Examination of the Hydrogenation Products (Series B).—The total chloroform-soluble fraction (123.1 g.) was distilled from a Claisen flask thus dividing it into four portions; fraction B1 (33.8 g.) distilling below 180° (bath temperature) (1.2 mm.), fraction B2 (23.4 g.) distilling 180 to 215° (1 mm.), fraction B3 (15.2 g.) distilling 215 to 280° (0.1 mm.) and a non-distillable resin B4 (48.6 g.). Distillates B2 and B3 were combined (38.7 g.), dissolved in chloroform (150 cc.) and extracted with water (4 × 30 cc.) and the aqueous extract back-extracted once with chloroform (20 cc.). This yielded a water-soluble fraction Bx (5.0 g.) and a water-insoluble fraction By (33.3 g.).

Fractional Distillation of Water-soluble Fraction Bx.—The water-soluble fraction Bx (5.0 g.) was fractionated through the twenty-one plate column. Distillation was discontinued when a white crystalline material accumulated in the take-off condenser. The combined distillates (2.71 g.) contained no identifiable "flats" but the crude crystalline material (1.15 g.) was partially identified as 2-(4-hydroxy-3,5-dimethoxyphenylethanol (0.82 g.) (see below). The non-distillable resin (0.76 g.) was rehydrogenated (see below).

Fractional Distillation of Water-insoluble Fraction By.—The water-insoluble fraction By (33.3 g.) was fractionated as before (28-plate column). The distillation was discontinued when, as before, a crystalline material accumulated in the condenser. This effected a separation into a distilled portion (17.12 g.), an undistilled portion (14,3 g.) and the residue (crystalline) remaining in the condenser and column (0.94 g.). The fractionation curve of the distilled portion showed one pronounced "flat" in the $n^{25}D$

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(16) Reported by Reichstein (*Helv. Chim. Acta*, **15**, 1450 (1932)) to be 100°.

(17) Erdtman, *Svensk Papperstidn.*, **44**, 243–253 (1941).

(18) Haworth, *J. Chem. Soc.*, 448 (1942).

1.5320–1.5339 range. Conversion of test samples of this "flat" into their p-nitrobenzoates showed this product to be 4-hydroxy-3,5-dimethoxyphenylethane (m. p. of the p-nitrobenzoate 153.5–154.5°, mixed m. p. with an authentic sample showed no depression).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.9; H, 7.8; OCH_3, 34.1. Found: C, 65.3; H, 7.8; OCH_3, 33.8.

Isolation and Identification of 2-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanol. Isolation.—The undistilled portion (14.3 g.) of the water-insoluble fraction By was distilled through a "goose-neck,"[19] thus separating it into a distillate (13.0 g.) and a non-distillable resin (1.2 g.). Washing of the distillate, which had become partially crystalline on standing, with ether removed the occluded non-crystalline fraction (8.2 g.) and left a non-ether-soluble crystalline portion (4.8 g.). Added to this was the material obtained from the column holdups in the fractionation of the water-insoluble fraction By (0.94 g.) and in the fractionation of the water-soluble portion Bx (0.82 g.) to give a total recovery of the pure material of 6.6 g. A sample of this crystalline product was recrystallized from ether–petroleum ether and from ethanol–petroleum ether and melted 116–117°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.6; H, 7.1; OCH_3, 31.1. Found: C, 60.7; H, 6.9; OCH_3, 31.3.

Identification.—2-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanol (0.6 g.) was methylated with diazomethane (three times), the methylated product dissolved in acetone–water (1:1) (20 cc.) and oxidized by boiling for one hour with a 3% solution of potassium permanganate (40 cc.). The reaction mixture was extracted with ether, then acidified and again extracted with ether. The second extract contained 3,4,5-trimethoxy-benzoic acid (0.12 g.); recrystallized from ether–petroleum ether, m. p. 167–168°; no m. p. depression when mixed with an authentic sample of 3,4,5-trimethoxybenzoic acid. This gave strong evidence that the compound had a syringyl type nucleus. 2-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanol (1.0 g.) was methylated (four times) with diazomethane (400% excess). The methylated product was distilled at 220–235° (bath temperature) (0.02 mm.); yield 0.44 g.

Anal. Calcd. for $C_{11}H_{16}O_4$: OCH_3, 43.8. Found: OCH_3, 43.6.

The 2-(3,4,5-trimethoxyphenyl)-ethanol was identified by preparation of the α-naphthyl urethan derivative, m. p. 132–133°; mixed m. p. with an authentic sample showing no depression.

Rehydrogenation of Resins from Claisen and Fractional Distillations of the Hydrogenation Products from Series B.—Part (42.0 g.) of the non-distillable resins (50.5 g.) obtained during the fractionation of the hydrogenation products of Series B were dissolved in dioxane (645 cc.) and hydrogenated over copper chromium oxide (18 g.) at 255° (initial hydrogen pressure, cold, 3000 lb./sq. in.) for six hours. Total hydrogen absorption was 3.4 moles per 100 g. of resin. Half of the product from this hydrogenation (14.9 g.) (4.2% methoxyl) was dissolved in dioxane (200 cc.) and rehydrogenated over copper chromium oxide (6.0 g.) at 280° (initial hydrogen pressure, 3000 lb./sq. in.) for six hours. Total absorption was 1.81 moles per 100 g. starting material.

The colorless, methoxyl-free product (12.5 g.) was fractionated through the previously described column (28-plates) to yield a distillable fraction (9.39 g.) and a non-distillable fraction (2.81 g.). The fractionation curve showed three "flats" in the $n^{25}D$ 1.4882–1.4900 (I), 1.4909–4910 (II) and 1.4992–1.5007 (III) ranges.

Anal. Found for "flat" I: C, 79.9; H, 11.9; mol. wt. (Rast), 235. II: C, 81.3; H, 12.7; mol. wt. (Rast), 215. III: C, 82.5; H, 12.6; mol. wt. (Rast), 288.

Rehydrogenation of Non-identified Portions from Fractional Distillations of Hydrogenated Products, Series A and B.—All the non-identified portions, representing 7.57 g. from Series A and 16.43 g. from Series B, were combined (24.0 g.), dissolved in dioxane (200 cc.) and rehydrogenated over copper chromium oxide (9.29 g.) at 280–290° (initial hydrogen pressure, 3000 lb./sq. in.) for eighteen hours. The product (10.1 g.) was fractionated through the 28-plate column, yielding a distillable portion (7.63 g.) and a non-distillable resin (2.37 g.). The distillation curve showed three "flats," in the $n^{25}D$ 1.4582–1.4611, 1.4616–1.4629 and 1.4650–1.4664 ranges. Conversion of test samples from these "flats" into their phenyl urethans showed these products to be 4-ethylcyclohexanol, m. p. of phenyl urethan 113.5–114.5°; 4-n-propylcyclohexanol, m. p. of phenyl urethan 124–125°; and 3-cyclohexyl-1-propanol, m. p. of phenyl urethan 83–84°, respectively; mixed melting points with authentic samples of their phenylurethanes showing no depression.

Syntheses of Reference Compounds

(1) **Synthesis of 4-Hydroxy-3-methoxyphenylethane.**—4-Hydroxy-3-methoxyphenyl methyl ketone (10.0 g.) was dissolved in ethanol (100 cc.) and hydrogenated (initial hydrogen pressure, cold, 2950 lb./sq. in.) over Raney nickel (4.0 g.) at 180–190° for thirty-five minutes. The product (7.8 g.) on distillation gave a fraction b. p. 90–100° (15 mm.), $n^{25}D$ 1.5281, whose p-nitrobenzoate derivative, recrystallized from ethanol–water, melted at 98–99°. Reported m. p. of this compound is 100°.[16]

(2) **Synthesis of 4-Hydroxy-3,5-dimethoxyphenylethane.**[20] **A. Preparation of 1-Acetyl-2,6-dimethylpyrogallol.**—2,6-Dimethylpyrogallol (5.0 g.) was dissolved in anhydrous benzene (5.0 cc.) containing anhydrous pyridine (3.3 g.) and acetyl chloride (3.0 g.) added dropwise to the vigorously stirred solution. The mixture was then heated at 60° for two hours, cooled and filtered. Removal of the solvent from the filtrate and distillation of the residual oil at 120–130° (bath temperature) (0.01 mm.) gave the required product: yield, 5.7 g.

Anal. Calcd. for $C_{10}H_{12}O_3$: OCH_3, 31.6. Found: OCH_3, 31.0.

B. Preparation of 4-Hydroxy-3,5-dimethoxyphenyl Methyl Ketone.—1-Acetyl-2,6-dimethylpyrogallol (5.7 g.) and powdered anhydrous aluminum chloride (7.7 g.) were added to nitrobenzene (35 cc.) in a three-necked flask fitted with a mercury-sealed stirrer and a reflux condenser. The solution was stirred for two hours at 2–5°, allowed to stand at room temperature for twenty-two hours and then poured into a mixture of ice (250 g.) and concentrated hydrochloric acid (25 cc.). The resultant product, after solvent removal, was distilled at 160–175° (bath temperature) (0.01 mm.) to yield a crystalline product (0.80 g.); recrystallized from ether, m. p. 121–122°. A mixed m. p. with an authentic sample showed no depression.

C. Reduction of 4-Hydroxy-3,5-dimethoxyacetophenone.—4-Hydroxy-3,5-dimethoxyacetophenone (0.4 g.), zinc amalgam (amalgamated prior to use) (20 g.) and 50% hydrochloric acid (100 cc.) were refluxed for six hours. The resultant product was distilled at 160–170° (bath temperature) (0.02 mm.): yield, 0.17 g.

Anal. Calcd. for $C_{10}H_{14}O_3$: OCH_3, 34.1. Found: OCH_3, 33.8. The p-nitrobenzoate derivative of this oil, recrystallized from ethanol–water and ether–petroleum ether, melted at 151–152°.

(3) **Synthesis of 2-(3,4,5-Trimethoxyphenyl)-ethanol.**[21] **A. Preparation of 3,4,5-Trimethoxybenzoyl Chloride.**—Trimethylgallic acid (2.0 g.) and purified thionyl chloride (7 cc.) were heated under reflux in an all-glass apparatus for one hour. The reaction mixture was then transferred to a small Claisen flask and the excess thionyl chloride removed by co-distillation with anhydrous benzene. The resulting product was used directly in the next procedure.

B. Preparation of 3,4,5-Trimethoxyphenyl Diazomethyl Ketone.—The 3,4,5-trimethoxybenzoyl chloride

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(19) A "goose-neck" consists of a piece of 6 mm. (i. d.) tubing, 12.5-cm. in length bent at the middle to an angle of 60° and connected to the distillation pot through a ground joint.

(20) Synthesized by Samuel B. Baker.

(21) Synthesized by Samuel B. Baker and James M. Pepper.

(see above) was dissolved in benzene and the solution added slowly to an ethereal solution of diazomethane prepared from nitrosomethylurea (7.0 g.) and allowed to stand at 0° for sixteen hours. The solvent, together with the excess diazomethane, were removed under reduced pressure. The crude product (2.1 g.) was used directly in the following procedure.

C., Hydrolysis of 3,4,5-Trimethoxyphenyl Diazomethyl Ketone.—The 3,4,5-trimethoxyphenyl diazomethyl ketone (2.1 g.) (see above) was hydrolyzed by heating at 70° for three hours with aqueous 2% sulfuric acid (100 cc.). The solution, after cooling, was extracted with chloroform, the chloroform solution dried and the solvent removed. The resulting product was recrystallized from ether: yield, 1.5 g., m. p. 77–78°.

Anal. Calcd. for $C_{11}H_{14}O_5$: OCH_3, 41.1. Found: OCH_3, 40.85.

D. Reduction of 3,4,5-Trimethoxyphenyl Hydroxymethyl Ketone.—3,4,5-Trimethoxyphenyl hydroxymethyl ketone (1.0 g.) was dissolved in ethanol (100 cc.) and hydrogenated over copper chromium oxide (0.5 g.) at 150–160° for one hour. The bomb contents were filtered, the filtrate concentrated under reduced pressure and the resulting yellow oil distilled at 220–240° (bath temperature) (0.02 mm.): yield, 0.8 g.

Anal. Calcd. for $C_{11}H_{16}O_4$: OCH_3, 43.8. Found: OCH_3, 43.5.

The α-naphthyl urethan derivative of this oil melted at 131–133°.

Acknowledgment.—The authors wish to thank the National Research Council of Canada for the award of two studentships to one of them (J. M. P.) and also the Canadian Pulp and Paper Association for their kind financial assistance. The authors also wish to thank Dr. R. F. Patterson who so kindly assisted in the lengthy continuous fractionation procedures.

Summary

1. Maple wood meal has been suspended in dioxane containing 3% sodium hydroxide and hydrogenated over Raney nickel catalyst using an initial pressure of 3000 lb./sq. in. and a temperature of 170° and complete conversion of the lignin portion of the wood into chloroform-soluble products has been effected.

2. From the reaction mixture three new lignin aromatic degradation products were isolated: 4-hydroxy-3-methoxyphenylethane, 4-hydroxy-3,5-dimethoxyphenylethane and 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol in yields of 2.2, 15.4 and 6.2% (based on the Klason lignin content of the wood), respectively.

3. The syntheses of 4-hydroxy-3-methoxyphenylethane, 4-hydroxy-3,5-dimethoxyphenylethane and 2-(3,4,5-trimethoxyphenyl)-ethanol were accomplished.

4. The isolation of these lignin derivatives thus provides further confirmatory evidence for the essentially aromatic (alkylphenolic) nature of lignin; and for the belief that the lignin of hardwoods is composed of units of both the guaiacyl and syringyl types, compounds containing the latter type being the more readily isolated.

5. The isolation of 2-(4-hydroxy-3,5-dimethoxyphenyl)-ethanol as a lignin degradation product provides some evidence for a carbon–oxygen linkage through the β-carbon atom of the alkyl side chain.

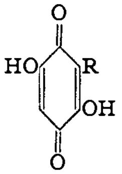
MONTREAL, CANADA RECEIVED APRIL 10, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Synthesis of Embelin, Rapanone and Related Quinones by Peroxide Alkylation[1]

BY LOUIS F. FIESER AND EARL M. CHAMBERLIN

Embelin, an orange pigment isolated from the berries of the Indian shrub *Embelia ribes*, is of interest because of early reports that the substance, like the fruit from which it is derived, possesses valuable properties as an anthelmintic agent, particularly against tapeworm.[2] Degradative studies of the substance led to varying conclusions[3]; then Hasan and Stedman[4] synthesized 2,5-dihydroxy-3-lauryl-1,4-benzoquinone (II) and an isomer and concluded from the results of their comparisons that embelin is identical with synthetic II. More recently Asano and Yamaguti[5] obtained analytical data pointing to a structure with one less methylene group. The latter investigators synthesized both II and the lower homolog I and found that both quinones have very nearly the same melting point as embelin and give no depression when mixed with the natural pigment. However, they observed that although the three hydroquinone tetraacetates likewise had very similar melting points, the derivative of II gave a definite, slight depression when mixed with the embelin derivative (Hasan and Stedman indeed reported a mixed melting point 1–2° below that of either component). We have not found in the Japanese paper any statement of a comparison of the derivatives of I and of embelin.



I, R = $-(CH_2)_{10}CH_3$
II, R = $-(CH_2)_{11}CH_3$
III, R = $-(CH_2)_{12}CH_3$

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[1] Based largely upon the doctoral dissertation of Earl M. Chamberlin, May 6, 1946.

[2] Paranjpe and Gokhale, *Arch. intern. pharmacodyn.*, **42**, 212 (1932) [*C. A.*, **27**, 1400 (1933); E. Merck's *Jahresber.*, **20**, 33 (1906)].

[3] Heffter and Feuerstein, *Arch. Pharm.*, **238**, 15 (1900); Kaul, Ray and Dutt, *J. Indian Chem. Soc.*, **6**, 577 (1929); **8**, 231 (1931); Nargund and Bhide, *ibid.*, **8**, 237 (1931).

[4] Hasan and Stedman, *J. Chem. Soc.*, 2112 (1931).

[5] Asano and Yamaguti, *J: Pharm. Soc. Japan*, **60**, 105 (1940 [*C. A.*, **34**, 5069 (1940)].