

solution of ethanol (25 cc.) and water (60 cc.), and to the solution iron powder (5.0 g.), ferric chloride (0.2 g.) and concentrated hydrochloric acid (2.5 cc.) then added. The reaction mixture was refluxed for five hours, concentrated to about 50 cc. at atmospheric pressure, filtered, the iron oxide washed with water and ether, and the combined filtrate and washings extracted with ether. The ether solution was extracted eight times with 8-cc. portions of sodium bisulfite solution (20%), the bisulfite solution acidified, sulfur dioxide removed by bubbling in carbon dioxide under reduced pressure and the resulting solution extracted with ether. The ether extract was dried and the solvent removed, yielding 1.4 g. of a yellow oil. The ether solution, containing a small amount of the bisulfite-insoluble oxime was evaporated to dryness, the residue hydrolyzed by treatment with 7 *N* sulfuric acid (25 cc.) for twenty-four hours at room temperature, and the acid solution extracted with ether yielding an additional 0.1 g. of the ketone (IV); total yield, 1.5 g. (68%). The yellow oil was distilled at 0.15 mm. pressure and 165–180° bath temperature;  $n_D^{25}$  1.5330. *Anal.* Calcd. for  $C_{12}H_{16}O_4$ : C, 64.3; H, 7.1; alkoxy, 27.7. Found: C, 64.1; H, 7.4; alkoxy, 27.4.

**Semicarbazone of 3-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (IV).**—White crystals from water or ethanol-petroleum ether, m. p. 144–144.5°. *Anal.* Calcd. for  $C_{13}H_{18}O_4N_2$ : C, 55.5; H, 6.8; alkoxy, 22.1. Found: C, 55.3; H, 6.8; alkoxy, 22.2.

**3-Ethoxy-2-nitro-1-(3,4-dimethoxyphenyl)-1-propene (VII').**—Veratric aldehyde was condensed with 1-nitro-2-ethoxyethane in the same manner as was vanillin; yield of the yellow needle-like crystals, 25%; recrystallized from dilute ethanol and then from ethyl acetate-petroleum ether; m. p. 90–91°. *Anal.* Calcd. for  $C_{13}H_{17}O_5N$ : C, 58.4; H, 6.4; alkoxy, 34.9. Found: C, 58.3; H, 6.5; alkoxy, 34.7.

**3-Ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone (IV').**—3-Ethoxy-2-nitro-1-(3,4-dimethoxyphenyl)-1-propene

(VII') was reduced with iron powder, ferric chloride and hydrochloric acid in the same manner as was 3-ethoxy-2-nitro-1-(4-hydroxy-3-methoxyphenyl)-1-propene; yield of the ketone (IV'), 67%. Fractional distillation at 0.1 mm. pressure gave a pure homogeneous reduction product,  $n_D^{25}$  1.5215. *Anal.* Calcd. for  $C_{13}H_{18}O_4$ : C, 65.5; H, 7.6; alkoxy, 39.1. Found: C, 65.4; H, 8.0; alkoxy, 39.0.

**2,4-Dinitrophenylhydrazone of 3-Ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone.**—Orange needle-like crystals from ethanol and from ethanol-petroleum ether; m. p. 114–116°. *Anal.* Calcd. for  $C_{19}H_{22}O_6N_4$ : C, 54.5; H, 5.3; alkoxy, 22.3. Found: C, 54.7; H, 5.4; alkoxy, 22.4.

**Acknowledgment.**—The writers wish to acknowledge their indebtedness to Dr. L. M. Cooke for his assistance in preliminary work on this investigation. They also express their appreciation to the Canadian Industries Limited for the award of a Fellowship to one of them (M. K.).

### Summary

The four products, 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, 1-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 3-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone required as reference products in connection with studies on lignin structure have been synthesized and their properties compared with those of their known isomers previously isolated from wood ethanolysis products.

MONTREAL, CANADA

RECEIVED FEBRUARY 23, 1943

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

## Studies on Lignin and Related Compounds. LXIX. Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone and 1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone from the Ethanolysis Products of Spruce Wood<sup>1</sup>

BY EINAR WEST, A. S. MACINNES AND HAROLD HIBBERT

In a previous communication<sup>2</sup> an account was given of the isolation of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone from the ethanolysis products of maple wood. Since other ethanolysis<sup>3</sup> and oxidation<sup>4</sup> studies on a variety of woods had established the presence of 4-hydroxy-3-

methoxyphenyl derivatives in gymnosperms and both the 4-hydroxy-3-methoxyphenyl and 4-hydroxy-3,5-dimethoxyphenyl types in angiosperms, it seemed probable that the application of a modification of the procedure already outlined for maple wood<sup>2</sup> should also lead to the isolation of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone among the ethanolysis products from spruce wood.

This substance has now been isolated (0.02% of the initial Klason lignin) from the water-soluble ethanolysis products and identified as its thio-

(1) From a thesis submitted to the Graduate Faculty of McGill University by Einar West in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1942.

(2) Kulka and Hibbert, *THIS JOURNAL*, **65**, 1180 (1943).

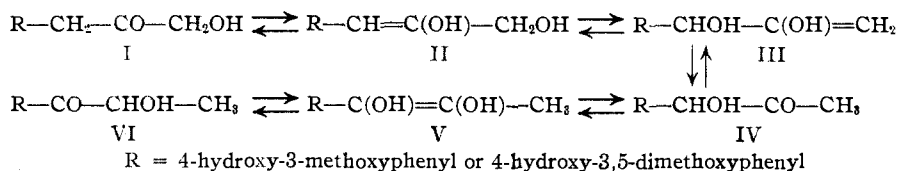
(3) MacInnes, West, McCarthy and Hibbert, *ibid.*, **62**, 2803 (1940).

(4) Creighton, McCarthy and Hibbert, *ibid.*, **63**, 3049 (1941).

semicarbazone by analysis and mixed melting point with the synthetic product.

Hibbert<sup>5</sup> has suggested that certain of the ethanolysis products may represent the stabilized end-products of the initial lignin precursors which probably function as plant respiratory catalysts in a system analogous to the C<sub>4</sub>-dicarboxylic acid animal cell system of Szent-Györgyi.<sup>6</sup>

In a previous comparison<sup>5</sup> of the two systems it was pointed out that only one of the suggested plant respiratory catalysts, namely, coniferyl alcohol, has been shown to exist in plants. The fact that the others have not been found, as yet, in the ethanolysis products may be due to one or both of two reasons: (i) the assumed hydrogen transportation catalysts may undergo polymerization or rearrangement to more stable end-products at certain stages of plant growth, and (ii) the reagents used in the extraction process probably bring about a rearrangement of the original lignin precursors, or of units resulting from the break-down of the polymers, since it is a necessary postulate that they should be highly reactive substances. Thus, as already pointed out,<sup>5</sup> under the influence of ethanolic hydrogen chloride the initial member of the series (R—CH<sub>2</sub>—CO—CH<sub>2</sub>OH) (I) would probably be found to undergo an allylic rearrangement followed by dismutation changes to yield both IV and VI.



Actually, only the isomer VI in the form of the ethyl ethers 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and 2-ethoxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone has been found hitherto in wood ethanolysis products. However, experimental support for the above theoretical considerations is provided in the behavior of the methylated derivative, 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone<sup>7</sup> which is so extraordinarily reactive that it has not been possible, as yet, to effect its isolation as such due to its remarkable tendency to undergo the above series of transformations. Valuable support for Hibbert's views would be found in the isolation of the hypothetical dismutation isomer IV in the

form of its ethyl ether, 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, from the spruce ethanolysis mixture and the present investigation is concerned with the actual achievement of this desired result.

Treatment of an ether solution of the phenol fraction of the water-soluble spruce ethanolysis products with gaseous ammonia yielded the insoluble ammonium salt of 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and a residual ether-ammonia soluble oil. From the latter a semicarbazone was obtained which was purified readily by recrystallization and which could be converted into the free ketone by hydrolysis with dilute acid<sup>8</sup> (Flow Sheet 2).

Analysis and molecular weight determinations established the empirical formula of the free ketone as C<sub>12</sub>H<sub>16</sub>O<sub>4</sub> (an isomer of 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone) and methylation followed by alkaline permanganate oxidation yielded veratric acid as proof of the presence of the 4-hydroxy-3-methoxyphenyl or 3-hydroxy-4-methoxyphenyl nucleus.

The formation of a semicarbazone proved the presence of a carbonyl group and since analysis showed the presence of one methoxyl and one ethoxyl group, the empirical formula was indicated to be R—CO—C<sub>2</sub>H<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>) (where R is 4-hydroxy-3-methoxyphenyl or 3-hydroxy-

4-methoxyphenyl). Four propylphenol-type structures are possible: R—CO—CH(OC<sub>2</sub>H<sub>5</sub>)CH<sub>3</sub> (VII); R—CO—CH<sub>2</sub>—CH<sub>2</sub>O—C<sub>2</sub>H<sub>5</sub> (VIII); R—CH<sub>2</sub>—CO—CH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub> (IX) or R—CH(OC<sub>2</sub>H<sub>5</sub>)CO—CH<sub>3</sub> (X).

VII and VIII were improbable on the basis of refractive indices and ultraviolet absorption data. Acetic acid formation by chromic acid oxidation,<sup>9</sup> a specific, almost quantitative, reaction for methyl groups not attached directly to the benzene nucleus, yielded *two* equivalents of acetic acid rather than *one*, indicating the structure to be X (1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone) rather than IX and this was proved by direct synthesis as outlined in the preceding communication.<sup>10</sup>

(5) Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

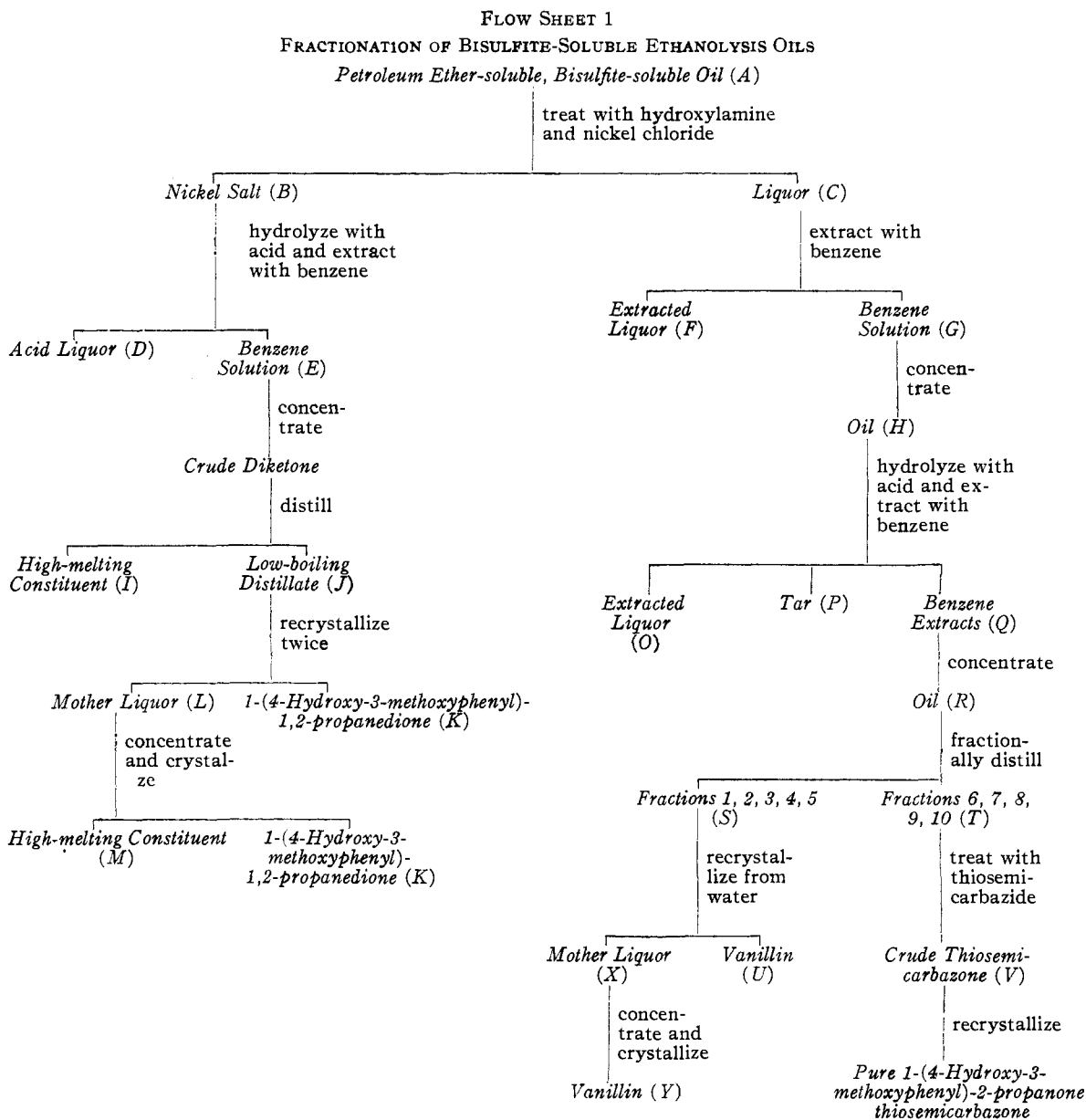
(6) Szent-Györgyi, *Ber.*, **72A**, 53 (1939).

(7) Eastham, Kulka, Fisher and Hibbert, unpublished results.

(8) Kon, *J. Chem. Soc.*, 1616 (1930).

(9) MacGregor and Hibbert, unpublished results.

(10) Kulka and Hibbert, *This Journal*, **65**, 1185 (1943).



Investigation of the Bisulfite-Soluble Fraction (Flow Sheet 1)

### Experimental

**Ethanolysis and Fractionation.**—The procedure used in the present work for the ethanolysis of spruce sapwood meal and the method of fractionation of the ethanol lignin were those outlined in a previous paper<sup>11</sup> except that the aqueous precipitation liquors were concentrated prior to the extraction with benzene. The yields are given in Tables I and II.

Precipitation of the crude bisulfite soluble oil (3.88 g.) into petroleum ether<sup>11</sup> yielded 3.38 g. of petroleum ether-soluble, bisulfite-soluble oil (A,<sup>11a</sup> Flow Sheet 1) and 0.43 g. of tar.

(11) MacGregor, West, Levi, Evans and Hibbert, *THIS JOURNAL*, **65**, 1176 (1943).

(11a) The capitalized letters (A), etc., refer to Flow Sheet 1 while those designated (A'), etc., refer to Flow Sheet (2).

**Separation of 1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione.**—The oil (A) (3.38 g.), nickel chloride (44.3 cc. of 5% solution), hydroxylamine sulfate (4.3 g.) and sodium acetate (33.8 g.) were dissolved in water (1500 cc.) and treated in the manner described for maple bisulfite-soluble oil<sup>12</sup> to yield the nickel glyoxime salt (B) (1.732 g.).

Distillation of the crude diketone obtained from the hydrolysis of the nickel glyoxime salt<sup>12</sup> yielded a distillate (J) (0.820 g.) which solidified upon standing. Two recrystallizations from water gave a yellow product (K) (0.456 g.) which melted at 68–69° and showed no depression in a mixed melting point with an authentic sample of 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione. Small

(12) Kulka, Hawkins and Hibbert, *THIS JOURNAL*, **63**, 2371 (1941).

TABLE I  
YIELDS FROM THE ETHANOLYSIS OF SPRUCE SAPWOOD

Product	Weight, g.	Klason lignin, %	g.	% of initial Klason lignin
Starting material, spruce				
sapwood meal	828	29.2	242	100
Wood residue	510	27.3	139	57.5
Ethanol lignin	70.8			29.2
Tar from water concentration	18.9			7.83
Oil from aqueous distillate	1.45			0.60
Crude water-soluble oil	33.8			14.0
Total recovery of initial Klason lignin <sup>a</sup>				109.13

<sup>a</sup> No correction has been made for added ethoxyl groups.

TABLE II  
FRACTIONATION OF THE SPRUCE SAPWOOD PETROLEUM ETHER SOLUBLE ETHANOLYSIS OILS

Fraction	Weight, g.	% of starting material	% of initial Klason lignin
Starting material	23.82	100	10.1
Bisulfite-soluble	3.88	16.3	1.65
Bicarbonate-soluble	0.35	1.5	0.15
Alkali-soluble	12.92	54.2	5.48
Neutral	1.80	7.5	0.76
Recovery		79.5	8.04

amounts of high melting material were obtained in the distillation (I) and recrystallizations (M) but they were not investigated.

**Separation of Vanillin and 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone.**—The oil (H) (1.51 g.) remaining after the separation of the nickel salt was treated with 7 *N* sulfuric acid at 0° for one hour, at room temperature for twenty-four hours and at 40° for four hours. After separation from the tar (P) (0.234 g.), the acid solution was extracted exhaustively with benzene. Evaporation of the combined benzene extraction solutions (Q) and distillation (120–150°/0.06 mm.) of the residual oil gave 0.790 g. of distillate (R). This distillate was fractionated into eleven fractions (b. p. 135–180° (0.6 mm.)) in a 6" Cooke-Bower column.<sup>13</sup> Fractions 1–5 (0.29 g. or 36.7%) were recrystallized from water and yielded 0.245 g. of vanillin, m. p. 81–82°, not depressed by admixture with an authentic specimen. Fractions 6 to 9 were oils with refractive indices between 1.5434 and 1.5525, and together amounted to 0.251 g. or 31.7%. These fractions were converted to thiosemicarbazones in a combined yield of 0.139 g. after recrystallization from ethanol. Their melting point of 183–184° was raised to the correct value of 186–187° on admixture with the thiosemicarbazone of authentic 1-(4-hydroxy-3-methoxyphenyl)-2-propanone. Another 0.01 g. of the recrystallized semicarbazone, m. p. 179–181°, was obtained from the 0.067 g. of distillate constituting fraction 10. *Anal.* Calcd. for C<sub>11</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub>S: C, 52.2; H, 6.0; OCH<sub>3</sub>, 12.2. Found: C, 52.1; H, 6.4; OCH<sub>3</sub>, 12.0. Applying corrections for the material lost in determination

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

of the refractive index, the yield of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone is 0.040 g.

#### Investigation of the Alkali Soluble ("Phenol") Fraction, Flow Sheet (2)

**Petroleum Ether Precipitation.**—Precipitation of the crude phenol fraction (A', Flow Sheet 2) (12.92 g.)<sup>10</sup> into petroleum ether (30–50°) yielded 0.89 g. of tar (B') and 12.02 g. of petroleum ether-soluble phenol oil (D').

**Isolation of 2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone as its Ammonium Salt.**—The petroleum ether-soluble phenol oil (D') (12.02 g.) was dissolved in anhydrous diethyl ether (300 cc.), cooled in an ice-bath and treated with gaseous ammonia for thirty minutes. The yellow precipitate (E') which formed was filtered off and washed, then dried in a vacuum desiccator (5.07 g.). The ether filtrate was combined with the washings (F') and the solvent removed under reduced pressure. The residual oil was dissolved in ether (150 cc.) and treated with ammonia as above to yield an additional precipitate (G') (3.31 g.). The combined filtrate and washings from the second treatment yielded a brown oil (I') (4.00 g.) which was dissolved in ether (100 cc.) and again treated with gaseous ammonia. No additional precipitate was formed and the oil (I') was recovered by evaporation of the solvent.

Two precipitations of this oil (I') into petroleum ether (30–50°) yielded 3.59 g. of petroleum ether-soluble, ether-ammonia-soluble oil (L') and 0.37 g. of tar (J').

**Methylation of the Ammonium Salt (E').**—The first ammonium salt precipitate (E') (5.07 g.) was dissolved in 5% sodium hydroxide solution (30 cc.) in a three-necked flask immersed in a cooling bath and fitted with a stirrer and two burets. Dimethyl sulfate (15 cc.) and sodium hydroxide (15 cc. of a solution of 30 g. of sodium hydroxide in 100 cc. of solution) were added simultaneously in 1-cc. portions at two-minute intervals. After standing at room temperature for three hours, the crystalline precipitate was filtered off, washed, dried and recrystallized from ethanol-water (1:1) yielding impure 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone (3.16 g.) melting at 79–80°. Further recrystallization of a portion (0.19 g.) of this material raised the melting point to 81–81.5°, and a mixed melting point with an authentic sample of 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone showed no depression.

**Isolation and Purification of 1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone.**—Fractional distillation was first used to separate the constituents of the oil (I') remaining after the removal of 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone as its ammonium salt (E' and G'), but it was found that better yields could be obtained by semicarbazone formation.

Semicarbazide hydrochloride (1.7 g.) and potassium acetate (1.7 g.) were added to a solution of a portion of the oil (L') (3.39 g.) in ethanol (34 cc.) and water (100 cc.). After standing overnight a copious precipitate had formed (N') (1.82 g.) (m. p. 169–170°). Recrystallization of a portion (1.07 g.) of this material from ethyl acetate-petroleum ether (1:3) gave 0.977 g. of a semicarbazone (O') melting at 172–173°. Further successive recrystallizations from water, ethyl acetate and ethanol-petroleum ether (1:1) failed to raise the melting point. *Anal.*



portion of which (0.332 g.) was taken up in diethyl ether (4 cc.) and extracted with 5% sodium hydroxide solution. Evaporation of the ether yielded an oil from which a light colored distillate (0.269 g.) was obtained upon distillation (135–160° (0.1 mm.)). *Anal.* Calcd. for  $C_{13}H_{18}O_4$ : OR as  $OCH_3$ , 39.1. Found: OR as  $OCH_3$ , 38.8.

A portion (0.237 g.) of the methylated product was dispersed in 2% sodium hydroxide solution (50 cc.) and the mixture warmed on a steam-bath. A solution of 4% potassium permanganate was added dropwise with stirring until the permanganate color persisted for several minutes. After heating for an additional two hours, a few cc. of methanol was added to decompose the excess permanganate. The solution was filtered and the alkaline filtrate extracted four times with diethyl ether, acidified and then extracted five times with diethyl ether. The latter five extracts were combined and on evaporation gave a brown semicrystalline material (0.118 g.) which upon recrystallization from water and then from ethanol gave veratric acid (0.032 g.), identified by its melting point and mixed melting point.

**Ultraviolet Absorption Spectrum of the Free Ketone.**<sup>15</sup>—A sample of the free ketone (0.0039 g.) was dissolved in 10 cc. of absolute ethanol and a portion (1.3 cc.) was diluted with absolute ethanol (8.7 cc.) giving a 0.0051% solution. The absorption curves obtained from the solution with a Hilger Spekkerphotometer and a Hilger E2 quartz spectrograph showed a single well-defined maximum at 1060

(15) Carried out by Mr. R. F. Patterson.

fresnel units ( $E_{max.} = 1.66$ ) and a minimum at 1145 fresnel units ( $E_{min.} = 1.06$ ), after which the curve rose sharply to the limit of the photometric range (1224 f at  $E = 2.0$ ).<sup>16</sup>

**Oxidation with Chromic Acid.**—A modification<sup>9</sup> of the Kuhn and L'Orsa method<sup>17</sup> was used. This modification involves an acetyl determination on the distillate which serves as a check on the first titration of the acetic acid. Titration of the acetic acid produced by the oxidation of the semicarbazone (0.1648 g.) of the new phenolic constituent (X) required 10.60 cc. of 0.103 *N* alkali (corrected for blank) which is equivalent to 39.8% acetic acid or 93.2% of the theoretical amount for 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone semicarbazone.

### Summary

1. Two new products, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, have been isolated from the ethanolysis products of spruce wood.

2. Their existence in the ethanolysis mixture is in accordance with previous predictions relating to their derivation from more reactive lignin progenitors, the latter possessing the function of plant respiratory catalysts.

(16) Patterson and Hibbert, unpublished results.

(17) Kuhn and L'Orsa, *Z. angew. Chem.*, **44**, 847 (1931).

MONTREAL, CANADA

RECEIVED MARCH 11, 1943

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

## Studies on Lignin and Related Compounds. LXX. Hydrogenolysis and Hydrogenation of Maple Wood

BY JOHN R. BOWER, JR.,<sup>1</sup> LLOYD M. COOKE AND HAROLD HIBBERT

Earlier work<sup>2</sup> has shown that, using a copper chromite catalyst, high yields (up to 78% of propylcyclohexyl derivatives are obtainable by high-pressure hydrogenation of monomeric propyl phenol derivatives related to the proposed  $C_6$ - $C_3$  lignin structure.<sup>3</sup> It was further shown<sup>2</sup> that hydrogenation of 3-(4-hydroxycyclohexyl)-1-propanol over copper chromite at 250° in dioxane solution resulted in the loss of at least 60% of the primary hydroxyl groups and formation of 4-*n*-propylcyclohexanol, one of the principal products obtained from the hydrogenation of lignin.<sup>4</sup> This result, together with those ob-

(1) This paper represents part of a thesis submitted to the Faculty of Graduate Studies of McGill University by John R. Bower, Jr. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, November, 1942.

(2) Cooke, McCarthy and Hibbert, *THIS JOURNAL*, **63**, 3052 (1941).

(3) Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

(4) (a) Cooke, McCarthy and Hibbert, *THIS JOURNAL*, **63**, 3056 (1941); (b) Godard, McCarthy and Hibbert, *ibid.*, **63**, 3062 (1941); (c) Harris, D'Ianni and Adkins, *ibid.*, **60**, 1467 (1938).

tained in recent investigations<sup>5</sup> on the chromic acid oxidation of wood and extracted lignins, indicates the essentially complete absence of terminal methyl groups in native lignin and has emphasized the importance of determining the extent to which terminal  $-CH_2O-$  units present in native lignin undergo conversion into entities with terminal methyl groups during hydrogenation.

Preliminary work was undertaken with 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, a typical propyl phenolic substance containing both a primary and a phenolic hydroxyl group. Hydrogenation of this pure substance in dioxane solution over copper chromite gave an 81% yield (minimum value) of 4-*n*-propylcyclohexanol (24%) and 3-cyclohexyl-1-propanol (76%). The former, a previously-investigated hydrogenation product of lignin

(5) MacGregor and Hibbert, unpublished results.