repeated, leaving a viscous tar (D) (25.3 g.). Concentration of the combined petroleum ether solutions (Y', Y'', Y''') (water-bath 50–60°), followed by removal of the last traces of solvent under reduced pressure (50°), left a residue of light-colored petroleum ether-soluble ethanolysis oils (43.3 g.) (E).

Solvent Group Fractionation of the Petroleum Ether-soluble Ethanolysis Oils.—The petroleum ether-soluble oils (43.3 g.) were dissolved in benzene (300 cc.) and the solution extracted successively with (a) eight 30-cc. portions of aqueous sodium bisulfite (20%), and the bisulfite extract (F) back-extracted with two 30-cc. portions of benzene which were then combined with the main benzene solution; (b) three 30-cc. portions of 8% sodium bicarbonate (back-extraction as in (a)); and (c) eight 35-cc. portions of 5% sodium hydroxide (back-extraction as in (a)). (Each of the sodium hydroxide extracts was neutralized *immediately* after extraction.) The oil remaining in the benzene solution was the "neutral fraction."

Each of the extracted fractions (a), (b) and (c) was then acidified (Congo red) with dilute sulfuric acid. In the case of the bisulfite extract the sulfur dioxide was removed after acidification by use of a carbon dioxide bubbler under reduced pressure. The various acidified solutions were extracted with benzene, the benzene solutions dried with sodium sulfate and the solvent removed under reduced pressure yielding a bisulfite-soluble fraction (10.3 g.); bicarbonate-soluble fraction (0.4 g.); alkali-soluble ("phenol") fraction (24.7 g.) and "neutral" fraction (5.4 g.).

Acknowledgments.—The authors wish to thank Mr. M. Kulka, Mr. H. E. Fisher and Mr. S. B. Baker for their assistance in carrying out part of the procedure and to express their appreciation of the financial assistance accorded them by the Canadian Pulp and Paper Association and Canadian Industries Limited.

Summary

An improved method for the extraction and isolation of the water-soluble ethanolysis products from maple wood is given. These are free from resinous materials and represent completely distillable (monomeric) oils, amounting to a total of 29% of the original Klason lignin.

MONTREAL, CANADA RECEIVED FEBRUARY 23, 1943

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

Studies on Lignin and Related Compounds. LXVII. Isolation and Identification of 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone and 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone from Maple Wood Ethanolysis Products. Metabolic Changes in Lower and Higher Plants

BY MARSHALL KULKA AND HAROLD HIBBERT

In a previous communication[1] the isolation of 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (I) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,2-propanedione (II) from the carbonyl components of the water-soluble ethanolysis products of maple wood was reported. It was indicated that about 30% of the bisulfite-soluble fraction of the water-soluble maple ethanolysis oils corresponding to 1.3% of the Klason lignin was still unidentified, and that vanillin and syringaldehyde could not be detected, although their presence had been reported earlier.[2] In a later communication[3] it was shown that the amounts of vanillin and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione varied in different spruce ethanolysis experiments, the former actually being absent in certain runs.

The purpose of this investigation was to identify the unknown carbonyl components present in the bisulfite fraction of the maple ethanolysis oils, and to settle the question of the presence or absence of vanillin and syringaldehyde. The presence of the two latter compounds has been established definitely and in addition two hitherto unknown carbonyl components, namely, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV), were isolated and their structures established by direct synthesis.

The ethanolysis procedure used was that described in the preceding communication[4] in which various modifications have been introduced resulting in more complete "group classification" with consequent increase in purity in products. The bisulfite-soluble fraction isolated by this technique was used in this investigation.

Separation and Identification of the Bisulfite-soluble Carbonyl Components.—The dicarbonyl compounds present in the bisulfite fraction were separated quantitatively by precipitation as their

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[1] Kulka, Hawkins and Hibbert, THIS JOURNAL, **63**, 2371 (1941).

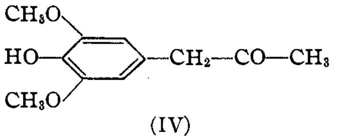
[2] Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

[3] Brickman, Hawkins and Hibbert, *ibid.*, **62**, 2149 (1940).

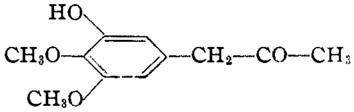
[4] West, MacGregor, Levi, Evans and Hibbert, *ibid.*, **65**, 1176 (1943).

nickel glyoxime salts.[1] Under the conditions employed, it was found that vanillin and syringaldehyde did not form oximes with hydroxylamine, while the unknown carbonyl derivatives reacted readily, so that, after removal of the insoluble nickel salts and extraction of the filtrate with benzene, a mixture of the two aldehydes and the oximes of the new carbonyl derivatives was obtained. The aldehydes were separated from the oximes by extraction with sodium bisulfite solution and from each other by fractional distillation. Hydrolysis of the oximes was accomplished with 7 *N* sulfuric acid, and the resulting free carbonyl compounds separated by fractional distillation in the Cooke–Bower type of micro-fractionating column developed in these laboratories.[5] This column is vacuum-jacketed, 14 cm. long and has an efficiency of seven plates. The details of the separation and isolation are summarized in Chart I and the results of several ethanolysis runs shown in Table I.

The analysis and molecular weight determination of 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV) and the preparation and analysis of its semicarbazone established its empirical formula as $C_{11}H_{14}O_4$, and showed the presence of one carbonyl group. Oxidation of the methylated product with potassium permanganate yielded 3,4,5-trimethoxybenzoic acid, indicating the aromatic nucleus to be either 4-hydroxy-3,5-dimethoxyphenyl-(IV) or 3-hydroxy-4,5-dimethoxyphenyl-(VII). Treatment with alkaline iodine yielded iodoform, thus indicating the presence of a methyl ketone in the side chain. Two formulas (IV) and (VII) thus called for consideration but its identity with the synthetic product (IV) definitely established its structure.



(IV)



(VII)

The identity of 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III) was established in a similar manner.

CHART I

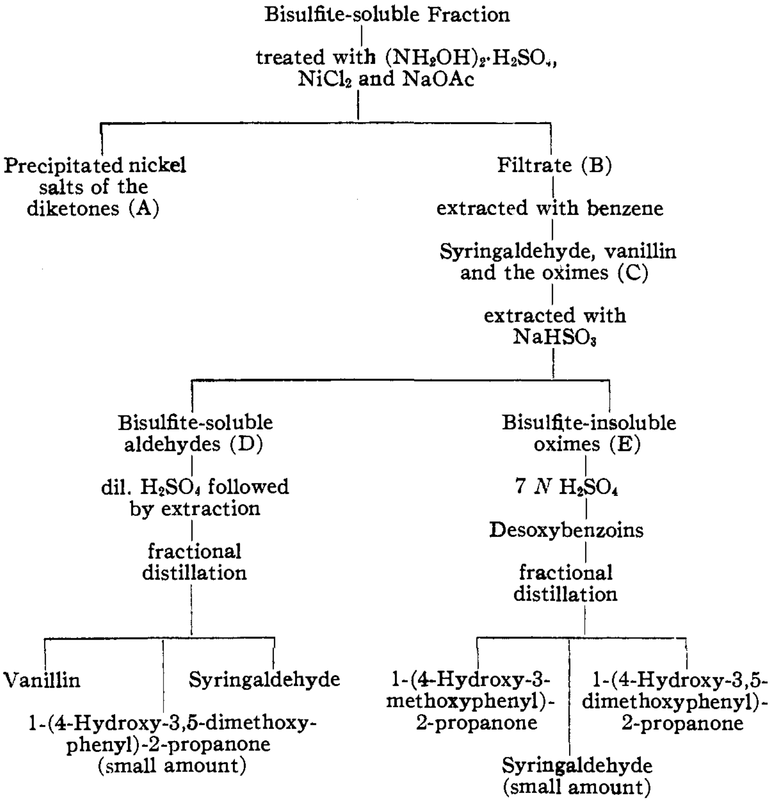


TABLE I

ANALYSIS OF THE BISULFITE-SOLUBLE FRACTION

Amount of dry maple wood meal taken for each experiment was 1000 g. containing 203 g. of Klason lignin

	Ethanolysis experiment 1	2	3
Total bisulfite-soluble oils, g.	10.30	11.47	10.79
Nickel glyoxime salts found, g.	6.23	6.58	6.20
Mixt. of the diketones (calcd.), g.	4.90	5.16	4.89
Klason lignin, %	2.42	2.54	2.41
Syringaldehyde (pure), found, g.	0.73	1.30	0.67
Klason lignin, %	.36	0.64	.33
Vanillin (pure), found, g.	.08	.23	.14
Klason lignin, %	.04	.11	.07
1-(4-Hydroxy-3,5-dimethoxy-phenyl)-2-propanone (IV) (pure), found, g.	.47	.26	.39
Klason lignin, %	.23	.13	.19
1-(4-Hydroxy-3-methoxy-phenyl)-2-propanone (III) (pure), found, g.	.12	.08	.11
Klason lignin, %	.06	.04	.05

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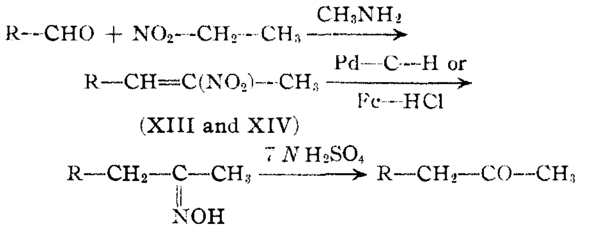
[5] Bower and Cooke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 290 (1943).

The synthesis of the two desoxybenzoins was carried out by the following series of reactions



$$R\text{—}CHO + NO_2\text{—}CH_2\text{—}CH_3 \xrightarrow{CH_3NH_2} R\text{—}CH{=}C(NO_2)\text{—}CH_3 \xrightarrow[Fe\text{—}HCl]{Pd\text{—}C\text{—}H\ \text{or}}$$

(XIII and XIV)

$$R\text{—}CH_2\text{—}\underset{\underset{NOH}{\|}}{C}\text{—}CH_3 \xrightarrow{7\,N\ H_2SO_4} R\text{—}CH_2\text{—}CO\text{—}CH_3$$

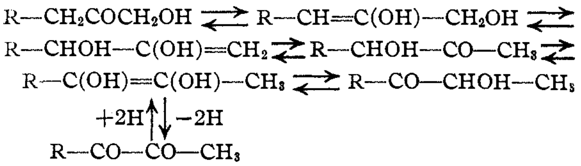
where R is the 1-(4-hydroxy-3,5-dimethoxyphenyl)- or 1-(4-hydroxy-3-methoxyphenyl)- radical. The condensation of aldehydes with nitroalkanes has been carried out previously with various aldehydes.[6] Nitroalkenes have been reduced catalytically to the corresponding oximes using palladiumized charcoal[7] as well as iron powder and hydrochloric acid in dilute ethanol.[8]

Parallelism between Lignin Ethanolysis and Mold Metabolic Products.—The two 1,2-diketones (I) and (II),[1] the two benzoins (VIII) and (IX)[9] (in the form of their ethyl ethers) and the two new desoxybenzoins (III) and (IV) (Chart II), all of which are present in the ethanolysis products from angiosperms (I, III, VIII only from gymnosperms), show a remarkable similarity, especially in the structure of their side chains, to certain metabolic products isolated by Raistrick and Oxford[10] from an aqueous reaction mixture in which various mold strains of the *Penicillium brevi-compactum* family had been grown in a culture medium containing glucose as the sole organic substrate (Chart II).

The products isolated by these workers consisted of a mixture of phenolic acids, namely, 1-(2-carboxy-3,5-dihydroxy-phenyl)-1,2-propandione (X), 2-hydroxy-1-(2-carboxy-3,5-dihydroxy-phenyl)-1-propanone (XII) and 1-(2-carboxy-3,5-dihydroxy-phenyl)-2-propanone (XI), and the similarity of their side-chain structures to those of the wood ethanolysis products (I, II, III, IV, VIII and IX, Chart II) is very striking. The presence of the carboxyl group need occasion no surprise in view of the remarkable ease with which carboxylation of phenols (especially those *meta*-substituted) takes place. Thus resorcinol[11] and phloroglucinol[12] are readily converted into their monocarboxylic acids when warmed with potassium bicarbonate at 50–70°. Phloroglucinol and phloroglucinol carboxylic acid form an equilibrium mixture when carbon dioxide is bubbled into an aqueous solution of either in presence of potassium bicarbonate.[13] Carboxylation of phloroglucinol, to a considerable extent, actually takes place at *room temperature* when carbon dioxide is passed into a glycerol mixture of phloroglucinol and potassium bicarbonate.[14]

It seems highly probable, as indicated previously,[15] that phloroglucinol (presumably derived from inositol, originating in turn from glycolic aldehyde[15]) is the primary product formed by the mold. This phenol could undergo carboxylation and simultaneous or subsequent condensation (through its mono-keto form) with methyl glyoxal, followed by loss of water and reduction to give R—CH_2COCH_2OH (R = phloroglucinol-carboxylic acid nucleus) the enol form of which is the analog of oxyconiferyl alcohol. The latter represents the first member of Hibbert's system of lignin respiratory hydrogen transportation catalysts assumed to function in the higher plants.[15]

Recent investigations in these Laboratories[16] have proved that products containing the side chain —CH_2COCH_2OH attached to an aromatic ring are extraordinarily reactive substances which readily undergo, in presence of mild reagents, a primary allyl shift followed by equilibrium dismutation changes and oxidation-reduction reactions as outlined below[15]



$$\begin{aligned}&R\text{—}CH_2COCH_2OH \rightleftarrows R\text{—}CH{=}C(OH)\text{—}CH_2OH \rightleftarrows\\&R\text{—}CHOH\text{—}C(OH){=}CH_2 \rightleftarrows R\text{—}CHOH\text{—}CO\text{—}CH_3 \rightleftarrows\\&R\text{—}C(OH){=}C(OH)\text{—}CH_3 \rightleftarrows R\text{—}CO\text{—}CHOH\text{—}CH_3\\&\qquad +2H \uparrow\downarrow -2H\\&R\text{—}CO\text{—}CO\text{—}CH_3\end{aligned}$$

(R = phenolic nucleus)

It is thus highly probable that Raistrick's phenol carboxylic acids may actually function similarly as respiratory catalysts and presumably represent, at least in part, stabilized end-products originating from more reactive forms. By operating exactly at the neutral point throughout, instead

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(6) (a) Knoevenagel and Walther, *Ber.*, **37**, 4502 (1904); (b) Kauffmann, *ibid.*, **52**, 1431 (1919); (c) Worrall, THIS JOURNAL, **56**, 1556 (1934); (d) Alles, *ibid.*, **54**, 271 (1932).

(7) (a) Reichert and Hoffman, *Arch. Pharm.*, **274**, 153 (1936); (b) Reichert and Koch, *ibid.*, **273**, 265 (1935).

(8) Purdue Research Institute, U. S. Patent 2,233,823 (March 4, 1941).

(9) (a) Cramer, Hunter and Hibbert, THIS JOURNAL, **61**, 509 (1939); (b) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939).

(10) Oxford and Raistrick, *Biochem. J.*, **27**, 634 (1933).

(11) Bistrzycki and Kostanecki, *Ber.*, **18**, 1985 (1885).

(12) Will and Albrecht, *ibid.*, **18**, 1323 (1885).

(13) Af Hällström, *ibid.*, **38**, 2288 (1905).

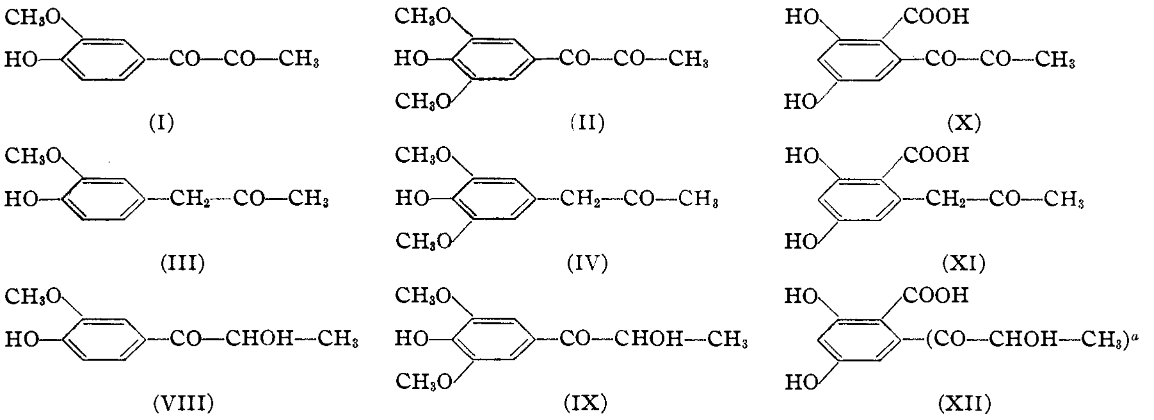
(14) Brunner, *Ann.*, **351**, 313 (1907).

(15) (a) Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941); (b) Hibbert, *Ann. Rev. Biochem.*, **11**, 183 (1942).

(16) Eastham, Fisher, Kulka and Hibbert, in process of publication.

CHART II

Water-soluble Ethanolysis Products from Maple Wood — *Water-soluble Mold Metabolism Products from Glucose (Raistrick)*



[a] The structure of the side chain was not determined with certainty but indicated by Oxford and Raistrick[10] as either (a) $—CO—CHOH—CH_3$, (b) $—CHOH—CO—CH_3$, (c) $—C(OH){=}C(OH)—CH_3$, (d) $—CH—C(OH)—CH_3$ (with —O— bridging CH and C(OH)) or (e) $—C(OH—CH)—CH_3$ (with —O— bridging C and CH).

of under the slightly acidic conditions used by Raistrick, it might be possible to isolate, in addition to the products found by him, the more reactive analogs of the Hibbert respiratory system.

Of particular interest is the observation of Oxford and Raistrick[17] that, when the mold was deprived of substrate, the amount of diketone (X) increased, such increase, however, being accompanied by a marked simultaneous decrease in the quantity of (XII). Such changes are presumably due to an increased amount of oxidation of the enediol, resulting in increased water formation, which, in turn, provides the additional energy required. These changes thus furnish indirect evidence in support of Hibbert's views.

Experimental

Investigation of the Bisulfite-Soluble Fraction

The separation was carried out according to the scheme shown in Chart I.

(a) **Removal of the Diketones.**—The bisulfite-soluble fraction (10.79 g.) was dissolved in water, and the solution treated with hydroxylamine sulfate, nickel chloride and sodium acetate as described previously.[1] The filtrate (B) was extracted with benzene, the benzene extract dried over sodium sulfate, and the solvent removed, leaving a mixture of the aldehydes and the oximes (C).

(b) **Isolation of Vanillin and Syringaldehyde.**—The residue (C) (4.72 g.) was dissolved in benzene (70 cc.) and extracted with seven 17-cc. portions of 20% sodium bisulfite solution. (During the extraction, a non-distillable tar (0.55 g.) separated at the interface of the benzene-bisulfite solution and was later removed.) The bisulfite solution was back-extracted with benzene (20 cc.) and this extract was combined with the main benzene solution containing the bisulfite-insoluble oximes. The bisulfite solution (D) containing the aldehydes was neutralized with dilute sulfuric acid, the sulfur dioxide removed by bubbling in carbon dioxide under reduced pressure, and the resulting solution extracted with benzene. The benzene solution was dried and the solvent removed, leaving a mixture of the two aldehydes (1.68 g.) which were separated by fractional distillation in the Cooke–Bower column.

TABLE II

FRACTIONAL DISTILLATION OF THE MIXTURE OF VANILLIN AND SYRINGALDEHYDE (PRESSURE, 0.25 MM.)

Fraction no.	Bath temp., °C.	Column temp., °C.	Weight crude, g.	Weight[a] purified, g.	Identified as
1	168	94	0.19	0.14	Vanillin
2	179	102	.06	.03	Syringaldehyde
3	189	106	.54	.54	Syringaldehyde
4	195	110	.10	.05	Syringaldehyde
5	200	117	.13	.05	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV)
6	>200	>117	.06	..	......

[a] Fraction 1 was recrystallized from water; m. p. 80–81°; no m. p. depression when mixed with vanillin. Fractions 2, 3 and 4 were each recrystallized from water; m. p. 111–112°; no m. p. depression when mixed with syringaldehyde.

(c) **Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III) and 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV).**—The benzene solution containing the oximes (E) was filtered to remove the tar, then dried and the solvent removed. The residue (2.30 g.) was treated with 7 *N* sulfuric acid (150 cc.) at room temperature for twenty-four hours followed by four hours at 40°. The acid solution was extracted with benzene, the benzene extract dried over sodium sulfate and sodium bicarbonate, and the solvent removed by distillation. The residue (1.56 g.) was distilled from a Späth bulb and the distillate (1.23 g.) fractionally distilled in the Cooke–Bower column.

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(17) Oxford and Raistrick, *Biochem. J.*, **27**, 1473 (1933).

TABLE III

FRACTIONAL DISTILLATION OF THE MIXTURE OF 1-(4-HYDROXY-3-METHOXYPHENYL)-2-PROPANONE (III) AND 1-(4-HYDROXY-3,5-DIMETHOXYPHENYL-2-PROPANONE) (IV) (PRESSURE, 0.25 MM.)

Fraction no.	Bath temp., °C.	Column temp., °C.	Weight crude, g.	Weight purified g.	Identified as
1	165	89	0.08	0.03	1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III)
2	175	99	.09	.06	
3	185	107	.05	.02	
4	192	114	.08	.05	Syringaldehyde
5	198	124	.13	.06	1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV)
6	200	130	.27	.27	
7	202	130	.05	.01	
8	202	130	.06	..	......

1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV) (Fractions 5, 6 and 7) was recrystallized from a mixture of petroleum ether (b. p. 30–70°) and ether; m. p. 68–69°; no melting point depression when mixed with the synthetic product. *Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 62.8; H, 6.7; OCH_3, 29.5; mol. wt., 210.1. Found: C, 62.9; H, 6.7; OCH_3, 29.5; mol. wt. (Rast), 218.

Alkaline Cleavage of 1-(3,4,5-Trimethoxyphenyl)-2-propanone.—1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV) (0.15 g.) was methylated with diazomethane and the methylated product oxidized by boiling for three hours with a 3% solution of potassium permanganate (25 cc.). The reaction mixture was extracted with ether, then acidified and again extracted. The second extract contained 3,4,5-trimethoxybenzoic acid (0.053 g.); recrystallized from water; m. p. 165–167°; no melting point depression when mixed with an authentic sample of 3,4,5-trimethoxybenzoic acid.

Semicarbazone of 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV).—Fine, white, needle-like crystals from ethanol; m. p. 155–156°; no melting point depression when mixed with the synthetic product. *Anal.* Calcd. for $C_{12}H_{17}O_4N_3$: C, 53.9; H, 6.4; OCH_3, 23.2; N, 15.7. Found: C, 53.8; H, 6.6; OCH_3, 23.1; N, 15.8.

Semicarbazone of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III).—Fine, white, needle-like crystals from ethanol; m. p. 157–158°; no melting point depression when mixed with the synthetic product. *Anal.* Calcd. for $C_{11}H_{15}O_3N_3$: C, 55.7; H, 6.3; OCH_3, 13.1; N, 17.7. Found: C, 55.7; H, 6.5; OCH_3, 13.1; N, 17.7.

Thiosemicarbazone of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III).—Microscopic, white, needle-like crystals from ethanol; m. p. 187–188°; no melting point depression when mixed with the synthetic product. *Anal.* Calcd. for $C_{11}H_{15}O_2SN_3$: C, 52.2; H, 6.0; OCH_3, 12.3; N, 16.6. Found: C, 52.2; H, 6.4; OCH_3, 12.4; N, 16.6.

Synthesis of 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV) and 1-(4-Hydroxy-3-methoxyphenyl-2-propanone (III)

2-Nitro-1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propene (XIII).—Syringaldehyde (3.0 g.) was dissolved in ethanol (12 cc.) and, to the solution, nitroethane (1.5 cc.), methylamine hydrochloride (0.1 g.) and sodium carbonate (0.08 g.) were added. After standing for fourteen days at room temperature in the dark, the reaction mixture was cooled to 0°, the orange needle-like crystals filtered off, washed with dilute sulfuric acid and with water, then dried; yield, 3.4 g. (85%); m. p. 101–102°; recrystallized from ethanol and from ether; m. p. 103–104°. *Anal.* Calcd. for $C_{11}H_{13}O_5N$: C, 55.2; H, 5.4; OCH_3, 26.0; N, 5.9. Found: C, 55.1; H, 5.6; OCH_3, 26.1; N, 5.8.

1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV).—The nitroalkene (XIII) (1.1 g.) was dissolved in hot ethanol (10 cc.) and hot water (25 cc.) added, followed by iron powder (2.0 g.), ferric chloride (0.08 g.) and concentrated hydrochloric acid (1 cc.). The reaction mixture was refluxed for five hours, concentrated to about half the original volume, then filtered, and the black iron oxide washed with hot water. The combined filtrate and washings were extracted with benzene, the benzene solution extracted with 20% sodium bisulfite, the bisulfite solution acidified, the sulfur dioxide removed, and the resulting solution extracted with ether. The ether extract was dried and the solvent removed, leaving a residual oil (0.50 g.) which crystallized rapidly. The benzene solution, containing the oxime, was evaporated to dryness and the residue treated with 7 *N* sulfuric acid (20 cc.) for twenty-four hours at room temperature, followed by four hours at 40°. Extraction of the acid solution with benzene yielded an additional amount (0.12 g.) of the ketone; total yield, 0.62 g. (87% distillable (0.05 mm.)); fine, white, needle-like crystals from a mixture of petroleum ether and ether; m. p. 68–69°. *Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 62.8; H, 6.7; OCH_3, 29.5. Found: C, 62.8; H, 6.7; OCH_3, 29.4.

Semicarbazone of 1-(4-Hydroxy-3,5-dimethoxyphenyl)-2-propanone (IV).—Fine, white, needle-like crystals from ethanol; m. p. 155–156°. *Anal.* Calcd. for $C_{12}H_{17}O_4N_3$: C, 53.9; H, 6.4; OCH_3, 23.2; N, 15.7. Found: C, 54.0; H, 6.5; OCH_3, 23.1; N, 15.5.

2-Nitro-1-(4-hydroxy-3-methoxyphenyl)-1-propene (XIV).—Vanillin was dissolved in a minimum amount of warm ethanol and condensed with nitroethane, the technique being the same as that used for the preparation of (XIII); yield, 75%; m. p. 99–100°; recrystallized from ethanol and from ether; m. p. 101–102°; yellow plates. *Anal.* Calcd. for $C_{10}H_{11}O_4N$: C, 57.4; H, 5.3; OCH_3, 14.8; N, 6.7. Found: C, 57.5; H, 5.4; OCH_3, 14.7; N, 6.6.

1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III).—The nitroalkene (XIV) was reduced with iron and hydrochloric acid as described in the preparation of (IV); total yield, 70%. The yellow oil was 94% distillable; b. p. 115° (0.15 mm.), $n^{25}D$ 1.5444. *Anal.* Calcd. for $C_{10}H_{12}O_3$: C, 66.6; H, 6.7; OCH_3, 17.2. Found: C, 66.5; H, 6.7; OCH_3, 17.1.

Semicarbazone of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III).—Fine, white, needle-like crystals from ethanol; m. p. 157–158°. *Anal.* Calcd. for $C_{11}H_{15}O_3N_3$: C, 55.7; H, 6.3; OCH_3, 13.1; N, 17.7. Found: C, 55.8; H, 6.5; OCH_3, 13.1; N, 17.4.

Thiosemicarbazone of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone (III).—Microscopic, white, needle-like crystals from ethanol; m. p. 187–188° (rate of heating 5–6° per minute). *Anal.* Calcd. for $C_{11}H_{15}O_2SN_3$: C, 52.2; H, 6.0; OCH_3, 12.3; N, 16.6. Found: C, 52.1; H, 6.2; OCH_3, 12.4; N, 16.7.

Catalytic Reduction of 2-Nitro-1-(4-hydroxy-3-methoxyphenyl)-1-propene (XIV).—Animal charcoal was heated on a steam-bath, with a mixture of 20% hydrochloric acid containing a few cc. of concentrated nitric acid, until the supernatant solution no longer contained iron. The charcoal was filtered off, washed with water and dried at 100° under reduced pressure (15 mm.) for eight hours. This purified charcoal was activated by heating (luminous flame of a Bunsen burner) in an evacuated test-tube (20 mm.) for fifteen minutes. The activated charcoal (3.0 g.) was suspended in a mixture of palladium chloride (0.5 g.) in concentrated hydrochloric acid (0.5 cc.) and water (25 cc.), and cooled to 5°. While the suspension was stirred vigorously, 40% formaldehyde (10 cc.) was added, followed by a drop-by-drop addition of a 50% solution of potassium hydroxide (10 cc.), the temperature being kept below 5°. The temperature of the mixture was raised slowly to 60° and maintained there for a few hours. The catalyst was filtered off, washed successively with water, dilute acetic acid, and hot water until the filtrate gave no test for chloride, then dried under reduced pressure.

The palladiumized carbon (0.5 g.) was suspended in a solution of 2-nitro-1-(4-hydroxy-3-methoxyphenyl)-1-propene (XIV) (2.0 g.) in pyridine (25 cc.) and the suspension shaken in an atmosphere of pure hydrogen at 60–65° until 2 moles of hydrogen had been absorbed (eight hours). The catalyst was filtered off and washed with pyridine. The solvent was removed from the combined filtrate and washings under reduced pressure (20 mm.) and the residual oxime hydrolyzed as described above. The ketone (0.94 g.) (56%) was obtained by extraction of the acid solution.

Raney nickel was also employed as a catalyst for the reduction of the nitroalkenes under similar conditions at room temperature, but only low yields (15–25%) of the ketones were obtained.

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Summary

1. Two additional products, 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-propanone and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone have been isolated from the water-soluble lignin ethanolysis fraction of maple wood.

2. The similarity of their side-chains and those of previously-isolated lignin entities with those present in the phenol carboxylic acids obtained by the action of molds on glucose as sole organic substrate (Raistrick and Oxford) is pointed out.

3. The specific variation noted in the nature of the side chain of the latter products when the mold functions with a shortage of metabolite provides indirect evidence in support of Hibbert's views on the biological significance of lignin in plant metabolism.

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

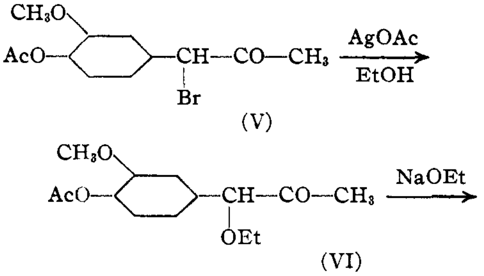
Studies on Lignin and Related Compounds. LXVIII. Synthesis and Properties of 1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, 3-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone and Their Methyl Ethers

BY MARSHALL KULKA AND HAROLD HIBBERT

Two isomeric ethyl ethers have been found in the water-soluble ethanolysis products of spruce wood, namely, 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (I)[1] and 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (II).[2] A third isomer, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (III)[3] has been synthesized but not as yet isolated from the ethanolysis products of spruce or other woods. A fourth isomer of this series, 3-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (IV) representing the ethyl ether of the first member of the Hibbert system[4] of plant respiratory catalysts has been neither synthesized nor isolated from the ethanolysis products.

The purpose of this investigation was to synthesize the isomeric ethyl ethers (R—CH(OC_2H_5)$COCH_3$) (II) and R—$CH_2COCH_2(OC_2H_5)$ (IV) and to compare their properties with those of R—COCH(OC_2H_5)CH_3 (I), and R—$COCH_2$-$CH_2(OC_2H_5)$ (III) (R = 4-hydroxy-3-methoxyphenyl).

The isomer II was synthesized by the following procedure



(V)

(VI)

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[1] (a) Cramer and Hibbert, THIS JOURNAL, **61**, 2204 (1939); (b) Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939).

[2] E. West, MacInnes and Hibbert, *ibid.*, **65**, 1187 (1943).

[3] (a) K. A. West and Hibbert, *ibid.*, **65**, 1170 (1943); (b) K. A. West, Hawkins and Hibbert, *ibid.*, **63**, 3035 (1941).

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