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

Studies on Lignin and Related Compounds. LXXIX. Synthesis and Properties of 3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone[1]

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In a previous communication[2] the allylic and dismutation rearrangements attendant upon the conversion of the two halides, 1-bromo-1-(3,4-dimethoxyphenyl)-2-propanone and 3-chloro-1-(3,4-dimethoxyphenyl)-2-propanone, to the corresponding alcohols, acetates and ethyl ethers were reported, and the bearing of these transformations on the relative validity of the Freudenberg and Hibbert theories of lignin structure was discussed.

During the course of that investigation, the synthesis of seventeen of the eighteen possible compounds formed by substitution of bromine, acetyl, hydroxyl and ethoxyl groups in the side chains of 1-(3,4-dimethoxyphenyl)-2-propanone (I) and 1-(3,4-dimethoxyphenyl)-1-propanone (II) was completed and the properties of these derivatives summarized. This communication deals with the synthesis and properties of the eighteenth member of this series (A(iii), Table I), namely, 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone, the veratryl analog of the keto form of β-oxyconiferyl alcohol. Its properties provide further support for the mechanism[2,3,4] suggested to account for the presence of the ethyl ethers of the benzoins, 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone[5] and 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone[6] in the ethanolysis products of spruce wood.

TABLE I

REFERENCE COMPOUNDS OF THE VERATRYL PROPANONE SERIES

	$R—CH_2—CO—CH_3$, I		$R—CO—CH_2—CH_3$, II	
	A	B	C	D
(i)	$R—CH_2—CO—CH_2Br$	$R—CHBr—CO—CH_3$	$R—CO—CHBr—CH_3$	$R—CO—CH_2—CH_2Br$
(ii)	$R—CH_2—CO—CH_2OAc$	$R—CHOAc—CO—CH_3$	$R—CO—CHOAc—CH_3$	$R—CO—CH_2—CH_2OAc$
(iii)	$R—CH_2—CO—CH_2OH$	$R—CHOH—CO—CH_3$	$R—CO—CHOH—CH_3$	$R—CO—CH_2—CH_2OH$
(iv)	$R—CH_2—CO—CH_2OEt$	$R—CHOEt—CO—CH_3$	$R—CO—CHOEt—CH_3$	$R—CO—CH_2—CH_2OEt$

(R = 3,4-dimethoxyphenyl)

The synthesis of the new ketol, 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (A(iii), Table I), was carried out by the series of reactions

$$\underset{\text{III}}{R—CHO} \xrightarrow{KMnO_4} \underset{\text{IV}}{R—COOH} \xrightarrow{SOCl_2} \underset{\text{V}}{R—CO—Cl} \xrightarrow{CH_2N_2}$$

$$\underset{\text{VI}}{R—CO—CHN_2} \xrightarrow[MeOH]{Ag_2O} \underset{\text{VII}}{R—CH_2—CO—OCH_3} \xrightarrow{NaOH}$$

$$\underset{\text{VIII}}{R—CH_2—COOH} \xrightarrow{SOCl_2} \underset{\text{IX}}{R—CH_2—COCl} \xrightarrow{CH_2N_2}$$

$$\underset{\text{X}}{R—CH_2—CO—CHN_2} \xrightarrow{H_2O} \underset{\text{XI}}{R—CH_2—CO—CH_2OH}$$

(R = 3,4-dimethoxyphenyl)

Synthesis of the homoveratric acid (VIII) involved considerable investigation. Among methods investigated were those of Hahn, Stiehl and Schultz,[7] Julian and Sturgis[8] and Arndt and Eistert.[9] A modification of the last-named procedure was finally adopted. This involved rearrangement of the diazoketone (VI) to the methyl ester (VII) followed by saponification of the latter to homoveratric acid (VIII), rather than conversion of (VI) to homoveratric amide and subsequent hydrolysis as employed in the original procedure. This rapid modified Arndt–Eistert synthesis yielded easily purifiable intermediate products in a higher yield (60% based on veratric aldehyde (III)) than by other methods. Conversion of the homoacid (VIII) to homoveratroyl chloride (IX) with thionyl chloride, thence to homoveratroyl diazomethane (X) using diazomethane in ether was effected by the procedure used by Haworth and Atkinson[10] for the synthesis of 3-chloro-1-(3,4-dimethoxyphenyl)-2-propanone. Hydrolysis of the diazoketone was carried out by Wolff's method[11] using water at 100°, as in his conversion of diazoacetophenone to benzoyl carbinol. The ketol (A(iii), Table I) obtained (56% yield based on homoveratric acid) analyzed correctly, and differed in physical properties from the three other isomers (B(iii), C(iii) and D(iii), Table I). Its refractive index, n^{25}_D 1.5485, differed considerably from that of 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone (C(iii), Table I) n^{25}_D 1.5590 while 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (B(iii), Table I) and 3-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone (D(iii), Table I) are

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(1) From a thesis submitted to the Graduate Faculty of McGill University by Herbert E. Fisher in partial fulfillment of the requirements for the degree of Doctor of Philosophy, October, 1943.

(2) Eastham, Fisher, Kulka and Hibbert, THIS JOURNAL, **66**, 26 (1944).

(3) Hibbert, *Paper Trade J.*, **113**, No. 4, 35 (1941).

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

(5) West, MacInnes and Hibbert, THIS JOURNAL, **65**, 1187 (1943).

(6) Cramer, Hunter and Hibbert, *ibid.*, **61**, 509 (1939).

(7) Hahn, Stiehl and Schultz, *Ber.*, **72**, 1291 (1939).

(8) Julian and Sturgis, THIS JOURNAL, **57**, 1126 (1935).

(9) Arndt and Eistert, *Ber.*, **68**, 200 (1935).

(10) Haworth and Atkinson, *J. Chem. Soc.*, 797 (1938).

(11) Wolff, *Ann.*, **394**, 25 (1912).

known solids, m. p. 77–78° and 83–84°, respectively. Moreover the semicarbazone of the new ketol, m. p. 123–124°, differed from those of the known ketols. Final conclusive evidence for its structure was obtained by acetylation with acetyl chloride and pyridine.[12] The reaction product was identified as 3-acetoxy-1-(3,4-dimethoxyphenyl)-2-propanone (A(ii), Table I) by melting point and mixed melting point determinations with an authentic sample.[2]

The behavior of 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (XI) toward acidic and basic reagents was studied. On heating with dilute (5%) sulfuric acid at 100° it yielded a relatively small amount (20%) of amorphous polymer, but more concentrated acid (72%), under the conditions of the Klason lignin procedure, brought about polymerization to the extent of over 60%. Strong bases, even in high dilution, caused marked polymerization particularly in aqueous media. Thus treatment with aqueous 1% sodium hydroxide at 100° for twenty-four hours gave more than 50% of a polymer, while 3% aqueous sodium hydroxide, even at room temperature, polymerized it to the extent of 80% in three days. With 3% aqueous-ethanolic (1:1) sodium hydroxide, under the former conditions, only 17% of polymer was formed.

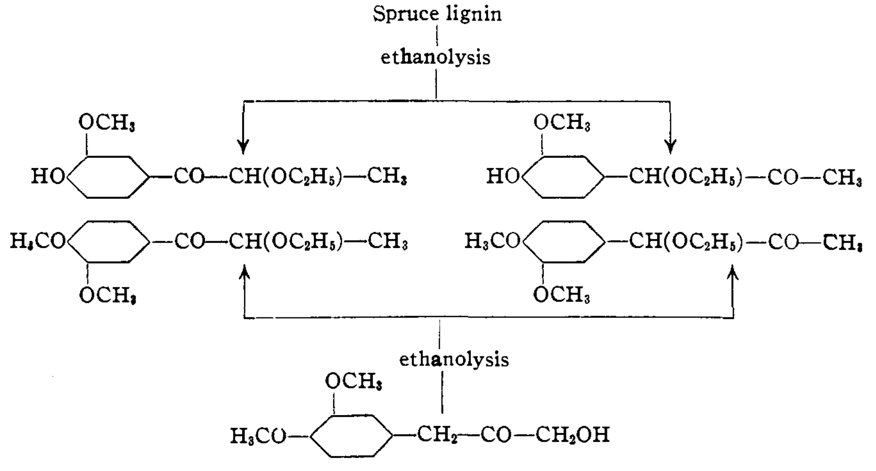
On treatment of (XI) with 5% aqueous potassium acetate under the same conditions which brought about rearrangement[2] of (B(iii)) to (C(iii)), no change was apparent, the ketol (XI) (75%), identified as its semicarbazone, being recovered unchanged.

Treatment of (XI) with ethanolic hydrogen chloride (2%) under the same conditions used for the ethanolysis of wood[5] yielded a bisulfite insoluble fraction containing a mixture of 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone (C(iv), Table I) and the corresponding isomer, 1-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone (B(iv), Table I) in a ratio of 3 to 7, the combined yield being 80%. The very small bisulfite soluble fraction apparently contained no 1,2-diketone.

These results, taken in conjunction with those obtained previously[2] on the hydrolysis of the corresponding halides and acetates ($R{-}CH_2{-}CO{-}CH_2X$; X = Br, Cl, $OCOCH_3$) supply strong experimental support for the theory that formation of the two isomeric ethyl ethers takes place by the following series of reactions[2]

$$\begin{array}{l}
R{-}CH_2{-}CO{-}CH_2OH \rightleftarrows R{-}CH{=}C(OH){-}CH_2OH \rightleftarrows R{-}CHOH{-}C(OH){=}CH_2 \rightleftarrows \\
R{-}CHOH{-}CO{-}CH_3 \rightleftarrows R{-}C(OH){=}C(OH){-}CH_3 \rightleftarrows R{-}CO{-}CHOH{-}CH_3 \\
\quad \text{EtOH}\downarrow\text{HCl} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{EtOH}\downarrow\text{HCl} \\
R{-}CH(OC_2H_5){-}CO{-}CH_3 \qquad\qquad\qquad\qquad\qquad\qquad R{-}CO{-}CH(OC_2H_5){-}CH_3
\end{array}$$

The connection of these products with the postulated lignin progenitor, β-oxyconiferyl alcohol (keto-form), is shown below.



The occurrence of the guaiacyl analogs among the ethanolysis products of spruce and maple wood thus finds a satisfactory explanation in the assumption of their presence as stabilized end-products arising from a more reactive native lignin building unit, namely, β-oxyconiferyl alcohol or its keto-isomer[2,4] and provides further support in favor of the validity of Hibbert's and the non-validity of Freudenberg's theory of lignin structure.[2,4,13]

Experimental

Synthesis of Homoveratric Acid: Modified Arndt–Eistert Method

Veratric Acid.—Veratric aldehyde (25 g.) was oxidized to the corresponding acid with aqueous potassium permanganate according to the directions of Shriner and Kleiderer[14]; yield, 24.7 g. (90%). Recrystallized from absolute ethanol, m. p. 180–181°, the product gave no depression in melting point when mixed with an authentic sample of veratric acid.

Veratroyl Chloride.—Veratric acid (15.0 g.) was converted to the chloride with freshly purified[15] thionyl chloride, according to the procedure of Arndt and Eistert[9]; yield of crude product, 16.7 g. (100%). A small amount, purified by distillation, melted at 70–71°. The melting point of veratroyl chloride is 70° according to Mayer.[16]

Veratroyl Diazomethane.—Crude veratroyl chloride (16.7 g.) was treated with a solution of diazomethane in ether by the procedure of Arndt and Eistert,[9] yielding a yellow solid (17.0 g. (100%)) which, after recrystallization from benzene-petroleum ether (b. p. 30–50°), gave fine

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(12) Smith and Bryant, This Journal, **57**, 61 (1935).

(13) MacGregor, Evans and Hibbert, *ibid.*, **66**, 41 (1944).

(14) Shriner and Kleiderer, *Org. Syntheses*, **10**, 82 (1930).

(15) Fieser, "Experiments in Organic Chemistry," D. C. Heat and Co., N. Y., 2nd ed., 1941, p. 381

(16) Mayer, *Monatsh.*, **22**, 428 (1879).

yellow needles, m. p. 76–77° (Arndt and Eistert, m. p. 75°).

Methyl Homoveratrate.—Recrystallized veratroyl diazomethane (12.4 g., m. p. 76–77°) was dissolved in absolute methanol (200 cc.) and warmed to 55–60° in a three-necked flask equipped with reflux condenser, stirrer and thermometer. At ten-minute intervals four portions of a slurry of freshly prepared silver oxide (from 2.5 g. of silver nitrate in 35 cc. methanol) were added to the rapidly stirred solution, which was maintained under an atmosphere of carbon dioxide throughout the reaction period, and the solution then refluxed for four hours.

The sludge of metallic silver and silver oxide was removed by filtration, and fresh silver oxide (from 2 g. of silver nitrate) was added, in four portions, as before, at 55–60°. On completion of the second series of additions, the mixture was again refluxed for three hours, until a drop of the solution, tested with concentrated hydrochloric acid, evolved no nitrogen, indicating complete reaction of the diazoketone. The reaction mixture was then filtered, and the filtrate freed from solvent under reduced pressure (carbon dioxide atmosphere) at 50°, leaving a crude oily product weighing 12.4 g. (98%).

On distillation of the crude product in high vacuum at 135–145° (bath temperature), two fractions were obtained: (I) b. 110–113° (0.03 mm.); 9.10 g. (72%); n^{25}_D 1.5300; straw-colored mobile liquid. (II) b. p. 128–130° (0.03 mm.); 1.48 g. (12%); semi-crystalline.

The first fraction, on analysis, proved to be pure methyl homoveratrate. *Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 63.0; H, 6.74; OCH_3, 29.6. Found: C, 63.1; H, 6.90; OCH_3, 29.4. The second fraction was not investigated.

Homoveratric Acid.—Methyl homoveratrate (9.0 g.) was saponified by the procedure described by Snyder, Buck and Ide.[17] The white crystalline product (7.85 g., 95% yield) was recrystallized from benzene–petroleum ether (60–70°); white plates, m. p. 98–99°. A mixed melting point with homoveratric acid showed no depression.

Synthesis of 3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone

Homoveratroyl Chloride.—Homoveratric acid (10.0 g.) was refluxed gently for forty-five minutes with freshly purified[15] thionyl chloride (20 cc.) in an all-glass apparatus under an atmosphere of carbon dioxide. Four portions (25 cc.) of benzene were successively added and removed by distillation under reduced pressure (carbon dioxide) in order to free the acid chloride from excess thionyl chloride. The dark red oil (10.9 g., 100% yield) was treated, without purification, as follows:

Homoveratroyl Diazomethane.—The homoveratroyl chloride (10.9 g.) was dissolved in benzene (50 cc.) and added slowly, with stirring, at 0° to a solution of diazomethane (from 40 g. nitrosomethyl urea) in ether (400 cc.). The solution was allowed to warm slowly to room temperature and react overnight. On removal of the solvents under reduced pressure (carbon dioxide) at room temperature, a red oily product weighing 11.2 g. (100%) was obtained.

3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone.—The homoveratroyldiazomethane (11.2 g.) was dissolved in absolute ethanol (90 cc.) and added, over a period of thirty minutes, to water (500 cc.) heated to 70°, with stirring. After addition of the diazoketone was complete, the reaction mixture was refluxed for three hours, cooled, and concentrated at room temperature under reduced pressure (carbon dioxide) to remove ethanol. The aqueous solution was then extracted five times with chloroform, the extract concentrated to a small volume (50 cc.) under reduced pressure (carbon dioxide) and precipitated three times successively in a thin stream from this solvent into rapidly stirred petroleum ether (b. p. 30–50°). The latter solvent was then removed and the residual oil distilled at 150–160° (bath temperature) and 0.05 mm., yielding a pale yellow oil, n^{25}_D 1.5485, weighing 6.0 g. (56%). *Anal.* Calcd. for $C_{11}H_{14}O_4$: C, 63.0; H, 6.74; OCH_3, 29.6. Found: C, 62.8; H, 6.78; OCH_3, 29.6.

Semicarbazone of 3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone.—White microscopic needles from water, m. p. 123–124°. *Anal.* Calcd. for $C_{12}H_{17}O_4N_3$: C, 53.9; H, 6.42; OCH_3, 23.2. Found: C, 53.7; H, 6.83; OCH_3, 23.1.

Characterization of 3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone

Acetylation.—Oily 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (0.505 g.) was acetylated with acetyl chloride (4 g.) in toluene (30 cc.) to which pyridine (6 cc.) had been added. The mixture was allowed to react for eleven hours at room temperature, after which the complex was decomposed by the addition of distilled water (500 cc.). The toluene layer was separated, washed three times with water, filtered and dried over anhydrous sodium sulfate. On removal of the solvent under reduced pressure (CO_2) at 35°, a viscous oily product remained weighing 0.450 g. (75%). This was dissolved in ether, filtered, petroleum ether (b. p. 30–50°) added, and the solution chilled to −15°. On scratching, a white crystalline product was obtained which was filtered off, recrystallized from dilute ethanol, and dried *in vacuo;* m. p. 55–56°. A mixed melting point determination with an authentic sample of 3-acetoxy-1-(3,4-dimethoxyphenyl)-2-propanone[2] showed no depression. The mixed melting point with 2-acetoxy-1-(3,4-dimethoxyphenyl)-1-propanone was 45°.

Properties of 3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone

Action of 5% Sulfuric Acid.—The ketol (0.529 g.) was mixed with 5% sulfuric acid (50 cc.) and refluxed for twenty-four hours. The amorphous black residue was filtered off, the portion adhering to the flask dissolved in chloroform, the main product added, and the solution evaporated to dryness; yield, 0.103 g. (19.5%).

Action of 72% Sulfuric Acid.—The ketol (0.505 g.) was treated with 72% sulfuric acid (4 cc.) at room temperature for two hours. The dark solution was then diluted to 150 cc. with distilled water, refluxed for four hours, cooled, and the amorphous dark brown lignin-like product filtered, washed with water, and dried in an Abderhalden drier at 61°; product, 0.101 g. The filtrate from the amorphous precipitate was extracted three times with chloroform, the extract concentrated, under reduced pressure, to a small volume (7 cc.) and precipitated into rapidly-stirred low-boiling petroleum ether (75 cc.). An additional quantity of amorphous product, dry weight 0.215 g., was thus obtained; total yield 0.316 g. (62.5%).

Action of 1% Sodium Hydroxide at 100°.—The ketol (0.514 g.) was refluxed with dilute (1%) aqueous sodium hydroxide (50 cc.) for twenty-four hours. After neutralization (congo red) of the mixture with dilute sulfuric acid, the product was filtered, the amorphous residue dissolved in chloroform, evaporated to dryness, and the residue dried similarly and weighed; yield of amorphous product, 0.276 g. (54%).

Action of 3% Aqueous Sodium Hydroxide at Room Temperature.—The ketol (0.250 g.) was allowed to stand at room temperature for seventy-two hours with 3% aqueous sodium hydroxide. After neutralization of the mixture with 10% hydrochloric acid (4 cc.) the polymer was filtered off, washed with water, and dried; yield of amorphous brown product, 0.200 g. (80%).

Action of 3% Ethanolic Sodium Hydroxide at Room Temperature.—The ketol (0.120 g.) was dissolved in ethanol (5 cc.) and 6% aqueous sodium hydroxide (5 cc.) added. After standing at room temperature for three days, chloroform (5 cc.) was added, and carbon dioxide allowed to bubble through the solution for three days. After extraction of the reaction mixture with six portions of chloroform, the extract was washed with water, dried over anhydrous sodium sulfate, concentrated to a small volume (3 cc.) and precipitated, in a fine stream, into rapidly-stirred petroleum ether (b. p. 30–50°). The flaky white polymer was filtered and dried; wt., 0.020 g. (17%).

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[17] Snyder, Buck and Ide, "Organic Syntheses," **15**, 31 (1935).

Action of 5% Aqueous Potassium Acetate.—The ketol (1.02 g., $n^{25}\text{D}$ 1.5490) was refluxed with 5% aqueous potassium acetate (100 cc.) for twelve hours in an atmosphere of carbon dioxide. The resulting solution was extracted four times with chloroform, the extract dried as above and the solvent removed at room temperature under reduced pressure (CO_2). Distillation of the residual oil at 150–160° bath temperature and 0.015 mm. pressure yielded a pale yellow oil weighing 0.75 g. (75%); $n^{25}\text{D}$ 1.5485.

Seeding a small portion of the product with the isomeric ketol, 1-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone produced no effect, and its relatively low refractive index (1.5485) indicated absence of the isomeric 2-hydroxy-1-(3,4-dimethoxyphenyl)-1-propanone ($n^{25}\text{D}$ 1.5610). The semicarbazone of the product was prepared and recrystallized from water; m. p. 122–123°. A mixed melting point determination with an authentic sample of the semicarbazone of 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone showed no depression. Thus so far as could be ascertained, treatment of 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone with 5% aqueous potassium acetate did not induce rearrangement of the ketol.

Action of 2% Ethanolic Hydrogen Chloride.—3-Hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone (2.85 g.) was refluxed for forty-eight hours under an atmosphere of carbon dioxide in an all-glass apparatus with 2% ethanolic hydrogen chloride (300 cc.).[5] At the conclusion of the reaction period the solution was cooled, water (5 cc.) added, and the solution neutralized (congo red) by the addition of small portions of solid sodium bicarbonate. After filtration, the solution was evaporated to dryness under reduced pressure (carbon dioxide) at room temperature. The residue was dissolved in benzene, the solution filtered, then extracted three times with 10% sodium bisulfite solution. After the bisulfite extract had been back-extracted twice with benzene, the combined benzene solutions were washed once with water, treated with decolorizing charcoal, and dried over anhydrous sodium sulfate (Extract I).

The bisulfite extract, after neutralization (congo red) with dilute sulfuric acid, was freed from sulfur dioxide under reduced pressure (carbon dioxide) and extracted three times with benzene. The benzene extract was washed with water, 1% aqueous sodium bicarbonate, again with water, and dried over anhydrous sodium sulfate (Extract II).

Extract I.—After removal of the solvent under reduced pressure (carbon dioxide) the residual oil was distilled at 125–135° (bath temperature) and 0.01 mm. pressure, yielding a pale yellow distillate, weighing 2.304 g., which slowly crystallized to a semi-solid yellow mass on cooling. The undistilled residue (polymerized by heat) weighed 0.276 g. The total bisulfite-insoluble fraction weighed 2.580 g. (80% of the theoretical ethylated product). The semi-solid product was washed with warm petroleum ether (10 cc.), then filtered on a glass nail and dried *in vacuo;* weight of crystalline product, 0.640 g. (28%). Recrystallization from dilute ethanol yielded a white crystalline material, m. p. 82–83°. A mixed melting point determination with an authentic sample of 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone showed no depression.

The 2,4-dinitrophenylhydrazone of the non-crystalline material ($n^{25}\text{D}$ 1.5220) recovered from the petroleum ether washings, after recrystallization from absolute ethanol, melted at 139–141°. A mixed melting point determination with an authentic sample of 1-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone 2,4-dinitrophenylhydrazone gave no depression.

Extract II.—Removal of the solvent under reduced pressure (carbon dioxide) left a crystalline residue weighing 0.350 g. The residue was washed with diethyl ether, this removing a portion of the material, and then with absolute ethanol, which dissolved the remainder. Addition of petroleum ether to this ethanol solution and chilling to 0° for several days resulted in the formation of a very small amount of long, light red, rod-like crystals; m. p. 138–139°. (A possible product of the reaction, 1-(3,4-dimethoxyphenyl)-1,2-propanedione, m. p. 68–69°, was thus eliminated.) The product was not identified.

No result was observed on addition of petroleum ether to the ether washings, and chilling to 0°. The combined ethanol and ether washings were evaporated to dryness, and tested for the presence of the diketone (1-(3,4-dimethoxyphenyl)-1,2-propanedione) by dissolving the residue in ethanol (10 cc.), adding water (50 cc.), hydroxylamine sulfate (0.2 g.), sodium acetate (1.0 g.) and 5% aqueous nickel chloride (1.5 cc.) and refluxing the solution gently under an atmosphere of carbon dioxide for twenty-four hours. Only a small amount (0.02 g.) of amorphous brown precipitate was formed; the characteristic red crystalline nickel glyoxime of the diketone was not obtained.

The action of 2% ethanolic hydrogen chloride on 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone thus produced the allylic rearrangement product, 1-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone, and its dismutation isomer 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone, in yields of 56 and 24%, respectively, together with a small amount of unidentified bisulfite soluble material.

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Summary

1. The synthesis of 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone has been carried out, the process involving a modification of the Arndt–Eistert synthesis for the preparation of the intermediary homoveratric acid.

2. Acids, and to a greater degree alkalies, readily convert the ketol into a lignin-like product in high yield.

3. When subjected to the ethanolysis procedure, as used for the extraction of lignin from wood, 3-hydroxy-1-(3,4-dimethoxyphenyl)-2-propanone gives a mixture of 1-ethoxy-1-(3,4-dimethoxyphenyl)-2-propanone and 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone in a combined yield of 80%.

4. The formation of these products undoubtedly takes place through the medium of an allyl shift followed by dismutation changes. Such transformations are regarded as providing valuable support for Hibbert's postulation of their presence (as guaiacyl derivatives) in the ethanolysis mixture from spruce wood as the result of similar reactions involving a β-oxyconiferyl type of lignin building unit present in spruce native lignin.

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