Studies on Lignin and Related Products. XVI.[1] Synthesis of Lignin Model Compounds of the Phenylglycerol β-Ether and Related Series

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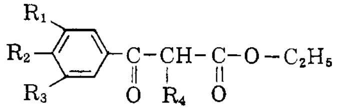
Received December 21, 1961

Substituted ethyl benzoylacetates have been employed for the preparation of lignin model compounds in the phenylpropane-1,3-diol and phenylpropane-1,2,3-triol series. Direct reduction of these esters with lithium aluminum hydride yields the corresponding phenylpropane-1,3-diol. Bromination followed by condensation with a phenol and reduction with lithium aluminum hydride of the resulting ether yields the phenylglycerol-β-aryl ether. Bromination followed by acetylation and reduction yields the phenylpropane-1,2,3-triol. Models in the veratryl, 3,4,5-trimethoxyphenyl, 4-hydroxy-3,5-dimethoxyphenyl, 4-benzyloxy-3,5-dimethoxyphenyl, and 4-acetoxy-3,5-dimethoxyphenyl series were prepared.

In connection with continued studies on the oxidation[3] of and on the hydrolysis[4] of lignin model compounds it was necessary to prepare a number of such model compounds which comprised β-aryl ethers of phenylglycerols of the guaiacyl and syringyl series and their derived ethers and esters. Earlier procedures,[5, 6] which included as one of the steps the hydroxymethylation with formaldehyde of a previously formed ω-phenoxyacetophenone were tried, but the hydroxymethylation step proved difficult in some instances and impossible in others. Accordingly, procedures which obviated the hydroxymethylation step were investigated. The present paper reports our experience with ethyl esters of substituted benzoylacetic acids as intermediates for the synthesis of these lignin model compounds.

Ethyl veratroylacetate (I) was brominated to give ethyl α-bromo-α-veratroylacetate (II), which in turn was condensed with guaiacol to yield ethyl α-(2-methoxyphenoxy)-α-veratroylacetate (III). Reduction of III with lithium aluminum hydride in tetrahydrofuran resulted in reduction of both the ester and the carbonyl groups to yield the desired veratrylglycerol β-guaiacyl ether (IV). Similarly, II was condensed with dihydroeugenol to yield ethyl α-(2-methoxy-4-propylphenoxy)-α-veratroylacetate (V), which in turn was reduced with lithium aluminum hydride to veratrylglycerol β-(2-methoxy-4-propylphenyl) ether (VI).

Having demonstrated the feasibility of ethyl benzoylacetates as intermediates for the preparation of β-aryl ethers of substituted phenylglycerols, we were encouraged to investigate their use for the preparation of other possible types of lignin model compounds as suggested by Fig. 1. Several of these routes have been investigated with a few guaiacyl and syringyl derivatives.



I. $R_1 = R_2 = CH_3O$; $R_3 = R_4 = H$

II. $R_1 = R_2 = CH_3O$; $R_3 = H$; $R_4 = Br$

III. $R_1 = R_2 = CH_3O$; $R_3 = H$; $R_4 =$ 2-$CH_3OC_6H_4O$

V. $R_1 = R_2 = CH_3O$; $R_3 = H$; $R_4 =$ 2,4-$(CH_3O)(CH_3CH_2CH_2)C_6H_3O$

VIII. $R_1 = R_2 = R_3 = CH_3O$; $R_4 = H$

X. $R_1 = R_3 = CH_3O$; $R_2 = C_6H_5CH_2O$; $R_4 = H$

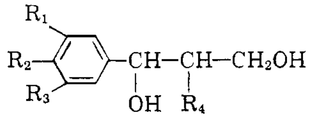
XII. $R_1 = R_3 = CH_3O$; $R_2 = CH_3COO$; $R_4 = H$

XIV. $R_1 = R_3 = CH_3O$; $R_2 = CH_3COO$; $R_4 = Br$

XV. $R_1 = R_3 = CH_3O$; $R_2 = R_4 = CH_3COO$

XVII. $R_1 = CH_3O$; $R_2 = HO$; $R_3 = R_4 = H$

XVIII. $R_1 = CH_3O$; $R_2 = CH_3COO$; $R_3 = R_4 = H$



IV. $R_1 = R_2 = CH_3O$; $R_3 = H$; $R_4 =$ 2-$CH_3OC_6H_4O$

VI. $R_1 = R_2 = CH_3O$; $R_3 = H$; $R_4 =$ 2,4-$(CH_3O)(CH_3CH_2CH_2)C_6H_3O$

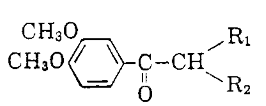
VII. $R_1 = R_2 = CH_3O$; $R_3 = R_4 = H$

IX. $R_1 = R_2 = R_3 = CH_3O$; $R_4 = H$

XI. $R_1 = R_3 = CH_3O$; $R_2 = C_6H_5CH_2O$; $R_4 = H$

XIII. $R_1 = R_3 = CH_3O$; $R_2 = CH_3COO$; $R_4 = H$

XVI. $R_1 = R_3 = CH_3O$; $R_2 = R_4 = HO$



XIX. $R_1 =$ 2,4-$(CH_3O)(CH_3CH{=}CH)C_6H_3O$; $R_2 = H$

XX. $R_1 = Br$; $R_2 = H$

XXI. $R_1 =$ 2,4-$(CH_3O)(CH_3CH{=}CH)C_6H_3O$; $R_2 = HOCH_2$

I was reduced directly with lithium aluminum hydride to yield 1-(3,4-dimethoxyphenyl)-1,3-propanediol (VII). Ethyl 3,4,5-trimethoxybenzoylacetate (VIII) yielded 1-(3,4,5-trimethoxyphenyl)-1,3-propanediol (IX), and ethyl 4-benzyloxy-3,5-dimethoxybenzoylacetate (X) yielded 1-(4-benzyloxy-3,5-dimethoxy)-1,3-propanediol (XI) by the same procedure. By similar reduction with lithium aluminum hydride of the acetyl syringyl compound, ethyl 4-acetoxy-3,5-dimethoxybenzoylacetate (XII), the parent 1-(4-hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol (XIII) was obtained.

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[1] For paper XV of this series, see *Forest Prods. J.*, **11**, 442 (1961).

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[3] I. A. Pearl, *J. Am. Chem. Soc.*, **78**, 5672 (1956).

[4] K. Kratzl and J. Gratzl, *Mitt. Österr. Ges. Holzforsch.*, **12**, 8 (1960).

[5] E. Adler, B. C. Lindgren, and U. Saeden, *Svensk Papperstidn.*, **55**, 245 (1952).

[6] K. Freudenberg and E. Eisenhut, *Chem. Ber.*, **88**, 626 (1955).

Bromination of XII yielded ethyl α-bromo-α-(4 - acetoxy - 3,5 - dimethoxybenzoyl)acetate (XIV), and treatment of XIV with potassium acetate in a mixture of acetic acid and acetic anhydride yielded ethyl α-acetoxy-α-(4-acetoxy-3,5-dimethoxybenzoyl)acetate (XV). Reduction of XV with lithium aluminum hydride yielded α-(3,5-dimethoxy-4-hydroxyphenyl)glycerol (XVI).

Some other intermediates of the types described were synthesized during the course of this investigation by essentially the same procedures. These included ethyl α-vanilloylacetate (XVII) and ethyl α - (4 - acetoxy - 3 - methoxybenzoyl)acetate (XVIII). Studies on the conversion of these and other similar intermediates to lignin models of Fig. 1 will be reported in the future.

During the evaluation of the earlier procedure for preparation of substituted phenylglycerol β-aryl ethers,[5] ω-(2-methoxy-4-propenylphenoxy)acetoveratrone (XIX) was prepared easily by condensation of ω-bromoacetoveratrone (XX) with isoeugenol in acetone and in the presence of anhydrous potassium carbonate. However, subsequent hydroxymethylation with formaldehyde to yield 2 - (3,4 - dimethoxybenzoyl) - 2 - (2 - methoxy - 4-propenylphenoxy)ethanol (XXI) could not be accomplished.

Experimental[7]

Ethyl α-Bromo-α-veratroylacetate (II).—A solution of 45 g. (0.186 mole) I[8] in 180 ml. of chloroform was treated dropwise with stirring with 30 g. (0.37 mole) of bromine in 85 ml. of chloroform while maintaining the temperature at 20–25°. After the addition was complete, the mixture was washed with saturated sodium bicarbonate solution and then with water. The chloroform solution was dried with anhydrous sodium sulfate and evaporated under reduced pressure to leave 57 g. of brown oil which solidified on standing. Recrystallization from 1:3 benzene–petroleum ether (b.p. 30–60°) and decolorizing carbon gave colorless crystals of II melting at 65–67°.

Anal. Calcd. for $C_{13}H_{15}O_5Br$: C, 47.15; H, 4.58. Found: C, 46.84, 46.95; H, 4.66, 4.78.

Ethyl α-(2-Methoxyphenoxy)-α-veratroylacetate (III).—A solution of 16 g. (0.048 mole) of II in 200 ml. of dimethylformamide was treated at room temperature with 10.4 g. (0.072 mole) of sodium guaiacol.[9] After stirring at room temperature for 30 min., the mixture was poured into 200 ml. of water and extracted with chloroform. The chloroform was washed with *N* sodium hydroxide solution and then with water, and then dried with anhydrous sodium sulfate. The chloroform was evaporated under reduced pressure, and the residual oil was diluted with a little petroleum ether (b.p 30-60°) and cooled below 0°. Scratching caused crystallization. The crystals were filtered and washed with 3:1 hexane–benzene to yield 10.8 g. (60%) of III as colorless crystals melting at 103° before and after recrystallization from 3:1 hexane–benzene. The infrared absorption curve contained bands at 3.41, 5.66, 5.96, 6.29, 6.64, 6.87, 7.02, 7.28, 7.42, 7.58, 7.88, 8.00, 8.35, 8.47, 8.62, 8.89, 9.10, 9.25, 9.46, 9.87, 10.70, 11.00, 11.31, 11.84, 12.31, 13.01, 13.50, 13.85, and 14.05 μ.

Anal. Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.21, 64.43; H, 5.95, 5.95.

III was also prepared by boiling under reflux for 1 hr. a mixture of 16.6 g. (0.05 mole) of II, 12.4 g. (0.1 mole) of guaiacol, 13.8 g. (0.1 mole) of anhydrous potassium carbonate, and 70 ml. of anhydrous acetone. The mixture was diluted with water and extracted with chloroform. Further processing as noted for the other preparation yielded III as crude crystals in only 44% yield which gave pure III on recrystallization from 3:1 hexane–benzene in the presence of decolorizing carbon. The recrystallized material melted at 101–102° and did not depress the melting point of a mixture with authentic III above.

Veratrylglycerol β-Guaiacyl Ether (IV).—A solution of 5.2 g. (0.014 mole) of III in 10 ml. of purified tetrahydrofuran was added dropwise with stirring to a suspension of 0.8 g. (0.021 mole) of lithium aluminum hydride in 20 ml. of purified tetrahydrofuran at a rate to maintain gentle reflux. Stirring was continued at room temperature for 20 min. The mixture was cooled in ice water and treated cautiously with 5 ml. of water. The hydroxide mud which formed was filtered and washed with tetrahydrofuran. The combined filtrate and washings were dried with anhydrous sodium sulfate and distilled under diminished pressure to yield 4 g. (87%) IV as a colorless, viscous sirup. Its infrared absorption spectrum was identical to that of IV prepared by the procedure of Adler, Lindgren, and Saeden[5] ($\lambda_{\max\,(\mu)}^{\text{KBr}}$ 2.90, 3.44, 6.27, 6.65, 6.86, 7.05, 7.99, 8.50, 8.66, 8.80, 8.91, 9.76, 10.85, 11.70, 12.35, and 13.35).

For maximum yield of pure product the tetrahydrofuran was purified by treating with 30% by weight solid potassium hydroxide for 1 week, distilling, treating with 0.05% lithium aluminum hydride for 12 hr., and distilling again.

Ethyl α-(2-Methoxy-4-propylphenoxy)-α-veratroylacetate (V).—A mixture of 10 g. of II, 10 g. of dihydroeugenol,[10] 8.2 g. of anhydrous potassium carbonate, and 50 ml. of anhydrous acetone was boiled under reflux and then processed as described for the preparation of III. The residual brown oil solidified to a crystalline mass which was recrystallized from 3:1 hexane–benzene in the presence of decolorizing carbon to give 9 g. (70%) of V as colorless crystals melting at 73° and having bands in its infrared absorption spectrum at the following wave lengths: 3.41, 5.70, 5.91, 6.25, 6.60 6.81, 6.88, 7.03, 7.27, 7.45, 7.93, 8.23, 8.61, 8.75, 9.21, 9.77, 11.38, 11.86, 12.32, 12.45, 13.45, and 13.64 μ.

Anal. Calcd. for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78. Found: C, 66.10, 66.35; H, 6.83, 6.80.

A similar experiment employing freshly distilled dimethylformamide as the solvent at 55–60° resulted in only 20% yield of V.

Veratrylglycerol β - (2 - Methoxy - 4 - propylphenyl) Ether (VI).—Under nitrogen atmosphere and with vigorous stirring, a solution of 6.2 g. (0.015 mole) of V in 50 ml. of purified tetrahydrofuran was added dropwise to a suspension of 1.1 g. (0.030 mole) of lithium aluminum hydride in 80 ml. of tetrahydrofuran maintained at 40–45°. Stirring was continued for 3 hr. at room temperature, and the mixture was allowed to stand for 16 hr. at room temperature. The mixture was cooled in a freezing mixture and treated carefully under carbon dioxide atmosphere with 5 ml. of *N* hydrochloric acid. The precipitate was filtered and washed with chloroform. The combined filtrate and washings were dried with anhydrous sodium sulfate and evaporated under reduced pressure. The residual oil was dissolved in chloroform, dried again, and evaporated to yield 5.0 g. (89%) of VI as an almost colorless sirup. The infrared absorption spectrum ($\lambda_{\max\,(\mu)}^{\text{KBr}}$ 2.90, 3.42, 6.28, 6.61, 6.83, 7.05, 7.92, 8.14, 8.67, 8.80, 9.74, 11.75, 12.39, 13.09, and 14.35) con-

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[7] All melting points are uncorrected. Analyses were performed by Huffman Microanalytical Laboratories, Wheatridge, Colo., and by Geller Microanalytical Laboratories, Bardonia, N. Y. Infrared spectra were determined by Mr. Lowell Sell.

[8] R. Robinson and J. P. Rose, *J. Chem. Soc.*, **1933**, 1469.

[9] A. W. Meldrum and M. M. Patel, *J. Indian Chem. Soc.*, **5**, 91 (1928).

[10] I. A. Pearl, *J. Org. Chem.*, **24**, 736 (1959).

firmed the complete reduction of V with the absence of bands for both ester and carbonyl groups.

VI was acylated with 3,5-dinitrobenzoyl chloride in pyridine, and the reaction mixture was poured into water. The semisolid precipitate was recrystallized from ethanol in the presence of decolorizing carbon to give yellow crystals of the bis-3,5-dinitrobenzoate of VI melting at 90–92°.

Anal. Calcd. for $C_{35}H_{32}O_{16}N_4$: CH_3O, 12.18. Found: CH_3O, 12.13, 12.25.

1-(3,4-Dimethoxyphenyl)-1,3-propanediol (VII).—I was reduced directly with lithium aluminum hydride in a manner identical with that described for the preparation of VI. The reaction mixture, after acidification, was filtered, and the precipitate was washed thoroughly with tetrahydrofuran and then with ethanol. The combined filtrate and washings were evaporated under reduced pressure in a nitrogen atmosphere, and the residual oil was dissolved in chloroform and dried. The chloroform was evaporated to leave 6 g. (94%) of VII as a slightly orange-colored oil soluble in water, ethanol, and methanol and insoluble in ether and petroleum ether. Complete reduction of the ester and carbonyl groups was confirmed by the infrared absorption spectrum ($\lambda_{\max(\mu)}^{\mathrm{KBr}}$ 2.97, 3.43, 6.00, 6.28, 6.60, 6.84, 7.05, 7.95, 8.13, 8.80, 9.76, 11.66, 12.35, and 13.10).

Ethyl 3,4,5-Trimethoxybenzoylacetate (VIII).—VIII was prepared by the procedure of Bradley and Robinson[11] and was obtained in 91% yield. Its infrared absorption spectrum ($\lambda_{\max(\mu)}^{\mathrm{KBr}}$ 3.43, 5.75, 5.99, 6.32, 6.65, 6.85, 7.08, 7.44, 7.85, 8.14, 8.40, 8.72, 8.91, 9.73, 10.00, 11.15, 11.65, 11.91, and 12.95) contained strong bands for both carbonyl and ester functions.

1-(3,4,5-Trimethoxyphenyl)-1,3-propanediol (IX).—VIII was reduced with lithium aluminum hydride in the manner described for the preparation of VII to yield 87% IX as an almost colorless oil having an infrared absorption spectrum ($\lambda_{\max(\mu)}^{\mathrm{KBr}}$ 2.95, 3.41, 6.27, 6.64, 6.84, 7.04, 7.52, 8.10, 8.89, 9.51, 9.95, 11.96, and 12.91), indicating complete absence of ester and carbonyl functions.

Ethyl 4-Benzyloxy-3,5-dimethoxybenzoylacetate (X).—X was prepared by the method of Bradley and Robinson[11] and was obtained as colorless crystals from methanol melting at 50–51°, whereas the earlier authors reported a melting point of 64–66°. The infrared absorption spectrum indicated carbonyl and ester functions and contained bands at 3.39, 3.42, 5.80, 5.98, 6.31, 6.65, 6.85, 7.09, 7.48, 7.69, 7.76, 8.03, 8.13, 8.43, 8.58, 8.61, 8.86, 9.65, 10.30, 10.96, 11.21, 11.75, 12.19, 13.20, 13.67, and 14.41 μ.

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from 3:1 ethyl acetate–ethanol to give red-orange needles melting at 138–140°.

Anal. Calcd. for $C_{26}H_{26}O_9N_4$: N, 1041. Found: N, 10.25, 10.24.

1-(4-Benzyloxy-3,5-dimethoxy)-1,3-propanediol (XI).—XI was prepared from X as described for the preparation of VII and was obtained in 91% yield as a slightly yellow viscous oil which solidified to a semisolid mass upon standing. The infrared absorption spectrum indicated no carbonyl or ester groups.

Ethyl 4-Acetoxy-3,5-dimethoxybenzoylacetate (XII).—Ethyl syringoylacetate[11] was acetylated with acetic anhydride in pyridine, and the product was recrystallized from dilute ethanol to yield XII as colorless crystals melting at 86–88° with infrared absorption bands at the following wave lengths: 3.40, 5.64, 5.83, 6.07, 6.24, 6.63, 6.83, 7.06, 7.30, 7.44, 7.65, 8.04, 8.28, 8.65, 8.84, 9.29, 9.69, 9.88, 10.59, 10.99, and 11.99 μ.

Anal. Calcd. for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found: C, 57.93, 57.73; H, 5.86, 5.97.

1-(4-Hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol (XIII).—A suspension of 5.3 g. (0.140 mole) of lithium aluminum hydride in 100 ml. of purified tetrahydrofuran was treated dropwise with a solution of 11 g. (0.035 mole) of XII at a rate to maintain gentle reflux, and the reaction mixture processed as described for the preparation of VI. The final product was dried by covering with benzene and distilling under reduced pressure to yield a white crystalline product. The product (5.2 g., 65%) was recrystallized from methanol in the presence of decolorizing carbon to yield pure XIII as colorless crystals melting at 109–110° and having the following bands in its infrared absorption spectrum at the following wave lengths: 2.99, 3.40, 6.00, 6.20, 6.30, 6.57, 6.84, 7.00, 7.38, 7.59, 7.83, 7.92, 8.25, 8.37, 8.56, 8.99, 9.22, 9.55, 10.09, 10.98, 11.52, and 12.52 μ, thus confirming the absence of ester and carbonyl groups.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07. Found: C, 57.51, 57.69; H, 6.91, 7.13.

Ethyl α-Bromo-α-(4-acetoxy-3,5-dimethoxybenzoyl)acetate (XIV).—A solution of 21.0 g. (0.068 mole) of XII in 140 ml. of chloroform was treated during the course of 2 hr. with a solution of 10.8 g. (0.136 mole) of bromine in 60 ml. of chloroform while maintaining the temperature at 2–10°. The mixture was extracted with chloroform, and the chloroform was washed with saturated aqueous sodium bicarbonate and then with water. The chloroform extract was dried with anhydrous sodium sulfate and evaporated under reduced pressure to yield 23 g. of product melting at 98–100°. Recrystallization from 3:1 hexane–benzene in the presence of decolorizing carbon yielded colorless crystals of XIV melting at 100–102°.

Anal. Calcd. for $C_{15}H_{17}O_7Br$: C, 46.24; H, 4.40. Found: C, 45.27, 45.17; H, 4.43, 4.33.

Ethyl α-Acetoxy-α-(4-acetoxy-3,5-dimethoxybenzoyl)-acetate (XV).—A solution of 4.4 g. (0.045 mole) of anhydrous potassium acetate in a mixture of 90 ml. of glacial acetic acid and 30 ml. of acetic anhydride was treated with 11.7 g. (0.03 mole) of XIV, and the clear solution was boiled under reflux for 9 hr. The mixture was cooled and filtered to recover 3.5 g. (95%) of potassium bromide. The precipitate was washed with ether, and the combined filtrate and washings were distilled under reduced pressure. The residual oil was stirred with 20 ml. of water and extracted with chloroform. The chloroform extract was washed with saturated aqueous sodium bicarbonate and then with water. The extract was dried with sodium sulfate and evaporated under reduced pressure to yield 11 g. (99%) crude product melting at 70–80°. The product was recrystallized three times from methanol in the presence of decolorizing carbon to yield 7.5 g. (68%) of pure XV melting at 90–92° and having the following bands in its infrared absorption spectrum: 3.39, 5.70, 5.90, 6.24, 6.64, 6.84, 7.05, 7.30, 7.50, 8.00, 8.19, 8.32, 8.70, 8.84, 9.13, 9.54, 9.86, 11.06, 11.74, 12.05, 12.32, and 13.10 μ.

Anal. Calcd. for $C_{17}H_{20}O_9$: C, 55.43; H, 5.47. Found: C, 55.28, 55.35; H, 5.53, 5.81.

An attempt to prepare XV from XIV by the exchange reaction of Adler and Yllner[12] with silver acetate resulted in complete recovery of starting material.

The 2,4-dinitrophenylhydrazone of XV was prepared and recrystallized from ethanol to yield orange-yellow crystals melting at 80–85°.

Anal. Calcd. for $C_{23}H_{24}O_{12}N_4$: N, 10.24. Found: N, 9.78, 9.85.

α-(3,5-Dimethoxy-4-hydroxyphenyl)glycerol (XVI).—A solution of 10.0 g. (0.027 mole) of XV in 100 ml. of purified tetrahydrofuran was added with vigorous stirring and under nitrogen atmosphere to a suspension of 3.8 g. (0.10 mole) of lithium aluminum hydride in 100 ml. of tetrahydrofuran at a rate to maintain gentle reflux. After addition was complete (45 min.), boiling under reflux was continued 45 min. The mixture was cooled to −5° and treated cautiously under carbon dioxide atmosphere with 70 ml. of ice cold *N* hydrochloric acid. The mixture was filtered, and the hydroxide mud was washed with 70 ml. of water and then with 240 ml. of ethanol. The combined filtrate and washings

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[11] W. R. Bradley and R. Robinson, *J. Chem. Soc.*, **1928**, 1541.

[12] E. Adler and S. Yllner, *Acta Chem. Scand.*, **7**, 570 (1953).

were centrifuged, and the centrifugate was evaporated under reduced pressure in an atmosphere of carbon dioxide below 25°. Water was removed from the residue by repeated addition of ethanol and benzene and continued evaporation under reduced pressure. During this treatment, a white waxy material separated. It was filtered, washed with a few milliliters of ice-cold ethanol, and boiled under reflux with anhydrous ether for 10 min. to yield 2 g. of XVI as an ether-insoluble white amorphous solid melting at 95–102°. Complete absence of ester and carbonyl functions was demonstrated by its infrared absorption spectrum ($\lambda_{\max}^{\mathrm{KBr}}(\mu)$ 2.94, 6.19, 6.56, 6.83, 7.00, 7.24, 7.55, 8.11, 8.98, 9.57, 9.80, 10.45, 12.00, and 14.24).

Ethyl α-Vanilloylacetate (XVII).—Acetylvanilloyl chloride[13] was converted to ethyl 4-acetoxy-3-methoxybenzoylacetoacetate by the procedure employed by Bradley and Robinson for the preparation of the analogous ethyl 4-acetoxy-3,5-dimethoxybenzoylacetoacetate,[11] and was obtained as a viscous oil. This oil (65 g.) was added to a mixture of 1300 ml. of water, 80 ml. of concd. aqueous ammonia, and 110 g. of ammonium chloride with vigorous stirring. Within a few minutes, the ester dissolved, and a new substance was formed. After stirring for 30 min., the colorless solution was acidified with dilute hydrochloric acid and extracted with ether. The ether was washed with aqueous sodium bicarbonate, then with water, and dried with anhydrous sodium sulfate. The ether was evaporated under reduced pressure to leave 55 g. of XVII as an almost colorless semisolid having the following bands in its infrared absorption spectrum: 2.96, 3.40, 5.75, 5.96, 6.28, 6.60, 6.82, 7.00, 7.30, 7.76, 8.40, 9.73, 11.91, 13.04, and 14.60 μ.

Ethyl α-(4-Acetoxy-3-methoxybenzoyl)acetate (XVIII).—XVII was acetylated with acetic anhydride and pyridine at room temperature, and the product was recrystallized from dilute ethanol in the presence of decolorizing carbon to give colorless crystals of XVIII melting at 117–122° and having the following bands in its infrared absorption spectrum: 3.41, 5.67, 6.08, 6.21, 6.60, 6.80, 7.05, 7.29, 7.45, 7.75, 8.05, 8.20, 8.36, 8.60, 8.79, 9.39, 9.70, 9.90, 11.06, 11.83, and 13.28 μ.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 60.26, 60.46; H, 4.97, 4.89.

ω-(2-Methoxy-4-propenylphenoxy)acetoveratrone (XIX).—A mixture of 10 g. (0.04 mole) of ω-bromoacetoveratrone,[14] 13 g. (0.08 mole) of freshly distilled isoeugenol, 10 g. (0.08 mole) of anhydrous potassium carbonate, and 70 ml. of anhydrous acetone was boiled under reflux with vigorous stirring for 1 hr. The mixture was cooled, diluted with 70 ml. of water, and filtered. The crystalline precipitate was washed with water and dried to yield 6.5 g. crude XIX melting at 144–145°. An additional 1.4 g. was obtained by extracting the filtrate and washings with chloroform followed by washing the chloroform with *N* sodium hydroxide solution and with water, drying, and evaporating. Recrystallization of the crude product from acetone yielded colorless crystals of pure XIX melting at 146–147°. The yield was 55%.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48. Found: C, 70.20, 70.13; H, 6.51, 6.63.

Infrared Spectra.—Infrared absorption spectra were obtained with a Perkin-Elmer Model 21 recording spectrophotometer using a sodium chloride prism and potassium bromide pellets prepared by hand grinding with sample before pressing.

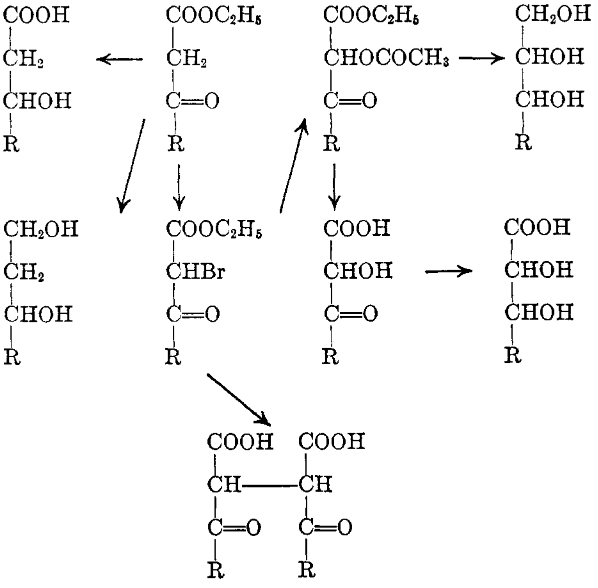

Fig. 1.—Some possible lignin models from substituted ethyl benzoylacetates. R = free or protected 3,4-dihydroxyphenyl or 3,4,5-trihydroxyphenyl.

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(13) K. W. Rosenmund and F. Zetzsche, *Ber.*, **56**, 1481 (1923).

(14) H. Erdtman and B. Leopold, *Acta Chem. Scand.*, **3**, 1358 (1949).