[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Studies on Lignin and Related Products. XIV.[1] Spectral and Chromatographic Data on Lignin Model Compounds in the Phenylpropane Series

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The R_f value in two solvent systems and the infrared absorption spectra of twenty-five lignin model compounds are reported. These model compounds comprise phenylpropane derivatives with 4-hydroxy-, 4-hydroxy-3-methoxy-, and 3,5-dimethoxy-4-hydroxy-substitution. Many of these compounds were prepared by new procedures, and in other cases many intermediates were new or were prepared by new procedures.

During the past few years, in connection with our studies on the isolation and identification of individual compounds from lignin reaction mixtures, pulping spent liquors, and wood extracts, we had the occasion to prepare many phenylpropane derivatives with 4-hydroxy-, 4-hydroxy-3-methoxy-, and 3,5-dimethoxy-4-hydroxy- substitution. These compounds have proved invaluable for compound identification in these isolation studies. The use of paper chromatographic, electrophoretic, and countercurrent distribution techniques in recent years has enabled investigators in many laboratories to isolate from lignin and wood mixtures individual compounds in amounts much too small for identification by conventional procedures. Under such conditions R_f values in several developing systems together with color reactions of spray reagents known for individual functional groups serve for preliminary identification, and infrared spectra serve admirably for positive identification of isolated compounds. The present paper reports infrared absorption spectra and R_f data for the butanol saturated with 2% aqueous ammonia and 10:3:3 butanol-pyridine-water systems at 20° for a number of phenylpropane derivatives with the above noted substitution. Many of these compounds were prepared by known procedures and others required new procedures or intermediates prepared by new procedures. New compounds, new intermediates, and new procedures are noted in the experimental portion.

4-Hydroxy-3-methoxyphenylpropane was prepared by hydrogenation at room temperature over palladium on charcoal catalyst of either eugenol or isoeugenol. 3,5-Dimethoxy-4-hydroxyphenylpropane was prepared by similar hydrogenation of 4-allyl-2,6-dimethoxyphenol[2] and 4-hydroxyphenylpropane by hydrogenation of anethole followed by demethylation with hydrobromic acid.

Ferulic acid, *p*-coumaric acid, and sinapic acid were prepared by condensation with malonic acid in the presence of piperidine of vanillin, *p*-hydroxybenzaldehyde, and syringaldehyde,[3] respectively, in accordance with an earlier described procedure.[4] Hydrogenation of ferulic and *p*-coumaric acids yielded dihydroferulic and dihydro-*p*-coumaric acids, respectively. Similar hydrogenation of sinapic acid failed to yield the dihydro acid, but dihydrosinapic acid was prepared simply by reduction of sinapic acid with Raney nickel alloy in alkaline solution.

Coniferyl alcohol was prepared by the lithium aluminum hydride reduction of ethyl acetylferulate according to Allen and Byers,[5] and *p*-coumaryl alcohol was prepared by similar reduction of ethyl acetyl-*p*-coumarate in accordance with Freudenberg and Gehrke.[6] The procedure of Freudenberg and co-workers[7,8] was also employed for the preparation of sinapyl alcohol from ethyl acetylsinapate. Dihydroconiferyl alcohol was prepared by low-pressure hydrogenation of coniferyl alcohol and by lithium aluminum hydride reduction of ethyl acetyldihydroferulate at room temperature. Attempted hydrogenation of *p*-coumaryl alcohol and sinapyl alcohol failed to give the desired dihydroalcohols, but dihydro-*p*-coumaryl alcohol was readily prepared by lithium aluminum hydride reduction of methyl acetyldihydro-*p*-coumarate at room temperature, and dihydrosinapyl alcohol was prepared by sodium and ethanol reduction of methyl dihydrosinapate according to Brewer, Cooke, and Hibbert.[9]

Coniferaldehyde and *p*-coumaraldehyde were prepared by reduction with lithium tri-*t*-butoxyaluminohydride of acetylferuoyl chloride and acetyl-*p*-coumaroyl chloride, respectively, and hydrolysis of the acetylated aldehydes as described earlier.[10] Similar reaction with acetylsinapoyl chloride

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[1] For paper XIII of this series, see I. A. Pearl, *J. Am. Chem. Soc.*, **78**, 5672 (1956).

[2] G. Hahn and H. Wassmuth, *Ber.*, **67**, 702 (1934).

[3] I. A. Pearl, *J. Org. Chem.*, **22**, 1229 (1957).

[4] I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, **16**, 216 (1951).

[5] C. H. F. Allen and J. R. Byers, Jr., *J. Am. Chem. Soc.*, **71**, 2683 (1949).

[6] K. Freudenberg and G. Gehrke, *Chem. Ber.*, **84**, 443 (1951).

[7] K. Freudenberg and R. Dillenburg, *Chem. Ber.*, **84**, 70 (1951).

[8] K. Freudenberg, R. Kraft, and W. Heimberger, *Chem. Ber.*, **84**, 472 (1951).

[9] C. P. Brewer, L. M. Cooke, and H. Hibbert, *J. Am. Chem. Soc.*, **70**, 57 (1948).

[10] I. A. Pearl and S. F. Darling, *J. Org. Chem.*, **22**, 1266 (1957).

yielded sinapaldehyde. Sinapaldehyde was also prepared by reduction of acetylsinapoyl chloride with sodium trimethoxyborohydride and hydrolysis of the resulting acetylated aldehyde.

Propiovanillone was prepared by oxidation of 1-(4-hydroxy-3-methoxyphenyl)-1-propanol with alkaline silver oxide,[11] propiosyringone by Fries rearrangement of the propionate of pyrogallol 1,3-dimethyl ether[12] and 4-hydroxypropiophenone was obtained commercially. Propiovanillone and propiosyringone were converted to their α-bromo derivatives by direct bromination, and these bromo compounds were converted to α-hydroxypropiovanillone and α-hydroxypropiosyringone, respectively, by the procedures of Hibbert and co-workers.[13,14] Copper sulfate and pyridine oxidation of these α-hydroxypropiophenones according to Hibbert and co-workers[15,16] yielded vanilloyl methyl ketone and syringoyl methyl ketone, respectively.

R_f values determined at 20° by the descending technique in butanol saturated with 2% aqueous ammonia and in 10:3:3 butanol-pyridine-water developers are given in Table I. Infrared absorption spectra are given in Figs. 1–9.

TABLE I

R_f VALUES AT 20°[a]

Compound	Butanol–2% Aqueous Ammonia	10:3:3 Butanol-Pyridine-Water
4-Hydroxy-3-methoxyphenylpropane	0.79	0.90
4-Hydroxyphenylpropane	0.93	0.89
3,5-Dimethoxy-4-hydroxyphenylpropane[b]	0.86	0.84
Ferulic acid[c]	0.13	0.48
p-Coumaric acid	0.18	0.57
Sinapic acid[c]	0.06	0.36
Dihydroferulic acid	0.20	0.42
Dihydro-*p*-coumaric acid	0.25	0.50
Dihydrosinapic acid[c]	0.13	0.47
Coniferyl alcohol	0.81	0.79
p-Coumaryl alcohol	0.84	0.88
Sinapyl alcohol	0.70	0.75
Dihydroconiferyl alcohol	0.87	0.81
Dihydro-*p*-coumaryl alcohol	0.89	0.85
Dihydrosinapyl alcohol	0.85	0.78
Coniferaldehyde[c]	0.55	0.84
p-Coumaraldehyde	0.65	0.84
Sinapaldehyde[c]	0.47	0.80
Propiovanillone	0.76	0.84
p-Hydroxypropiophenone	0.61	0.88
Propiosyringone	0.60	0.81
α-Hydroxypropiovanillone	0.45	0.82
α-Hydroxypropiosyringone[c]	0.33	0.78
Vanilloyl methyl ketone	0.53	0.87
Syringoyl methyl ketone[d]	0.40	0.81

[a] R_f values were located by means of bis-diazotized benzidine spray. [b] An immediate red spot appears, but disappears after a few moments. [c] Blue fluorescence under ultraviolet light before spraying. [d] Negative fluorescence under ultraviolet light before spraying.

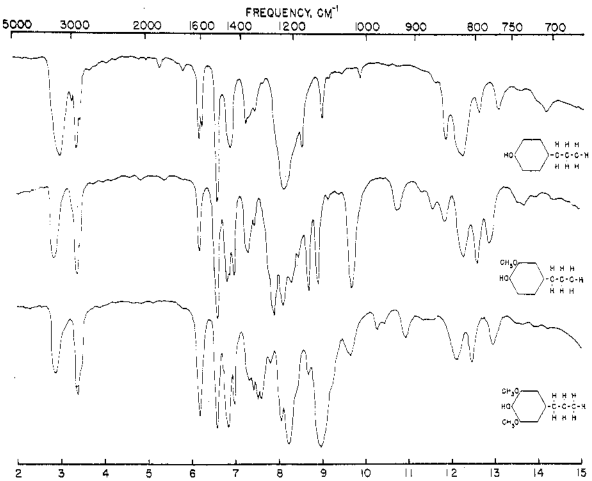

Fig. 1. Infrared absorption spectra for 4-hydroxyphenylpropane, 4-hydroxy-3-methoxyphenylpropane, and 3,5-dimethoxy-4-hydroxyphenylpropane

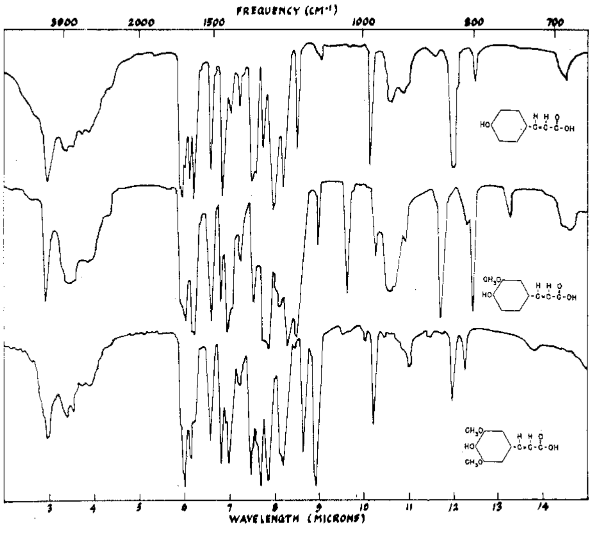

Fig. 2. Infrared absorption spectra for *p*-coumaric acid, ferulic acid, and sinapic acid

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(11) I. A. Pearl, *J. Am. Chem. Soc.*, **78**, 4433 (1956).

(12) M. J. Hunter, A. B. Cramer, and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 516 (1939).

(13) A. B. Cramer and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 2204 (1939).

(14) M. J. Hunter and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 2190 (1939).

(15) L. Brickman, W. L. Hawkins, and H. Hibbert, *J. Am. Chem. Soc.*, **62**, 2149 (1940).

(16) M. Kulka, W. L. Hawkins, and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 2371 (1941).

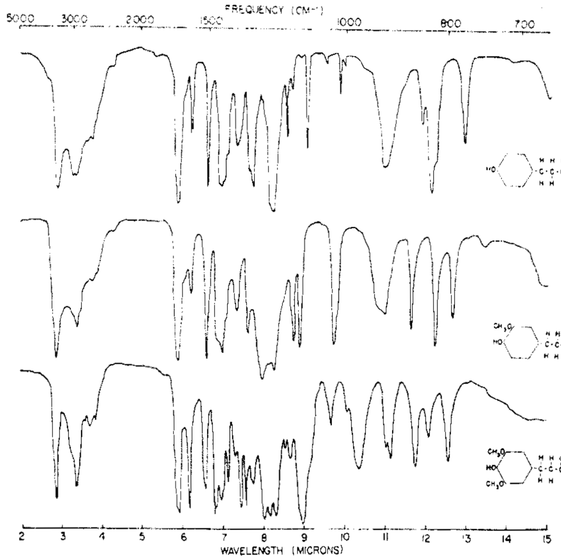

Fig. 3. Infrared absorption spectra for dihydro-*p*-coumaric acid, dihydroferulic acid, and dihydrosinapic acid

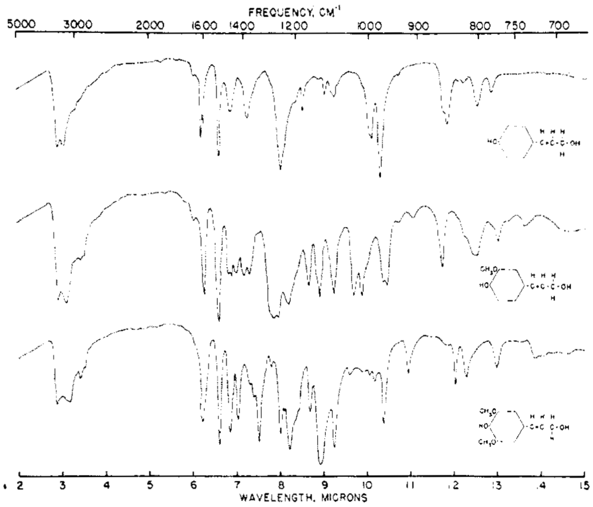

Fig. 4. Infrared absorption spectra for *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol

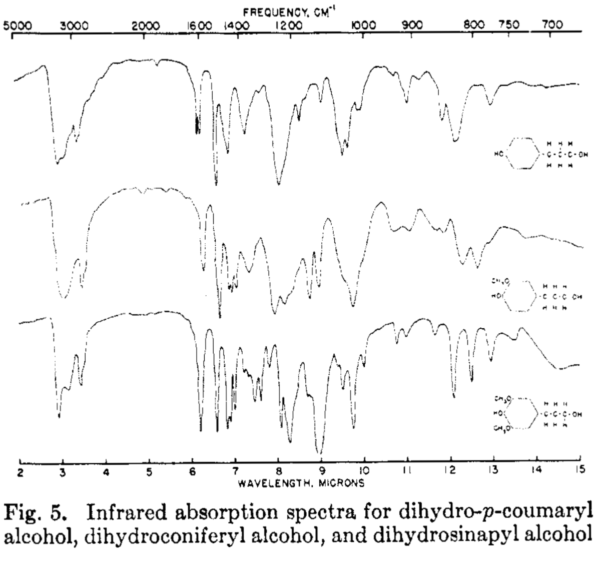

Fig. 5. Infrared absorption spectra for dihydro-*p*-coumaryl alcohol, dihydroconiferyl alcohol, and dihydrosinapyl alcohol

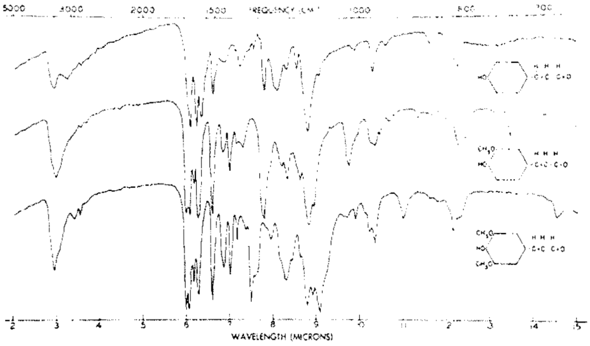

Fig. 6. Infrared absorption spectra for *p*-coumaraldehyde, coniferaldehyde, and sinapaldehyde

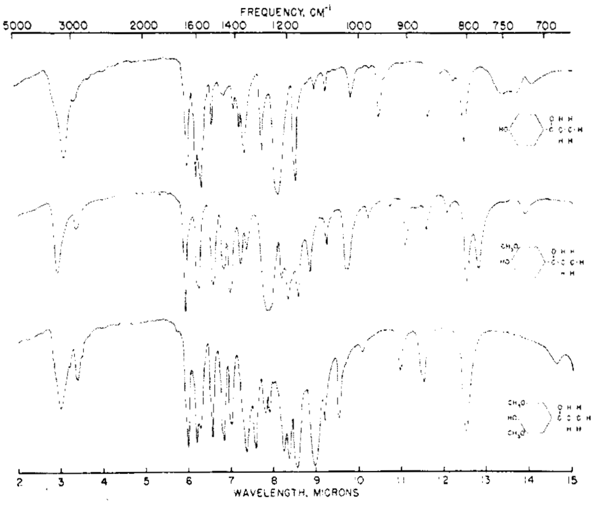

Fig. 7. Infrared absorption spectra for *p*-hydroxypropiophenone, propiovanillone, and propiosyringone

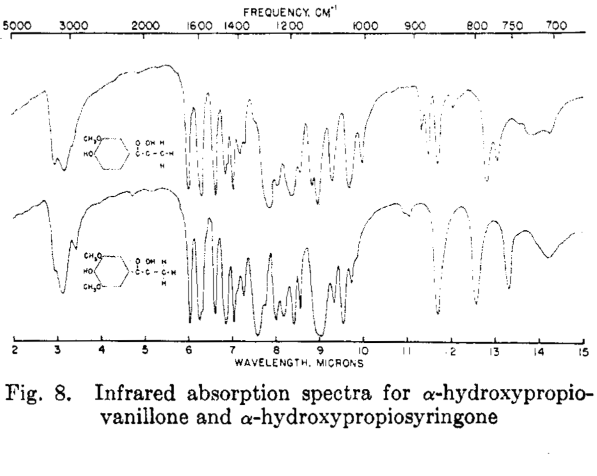

Fig. 8. Infrared absorption spectra for α-hydroxypropiovanillone and α-hydroxypropiosyringone

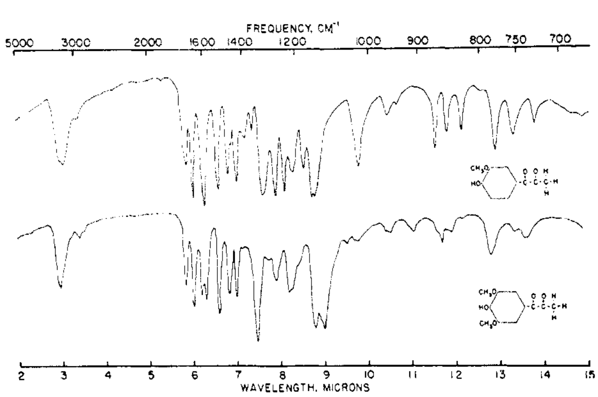

Fig. 9. Infrared absorption spectra for vanilloyl methyl ketone and syringoyl methyl ketone

EXPERIMENTAL

All melting points are uncorrected, and ultraviolet spectral data are for solutions in 95% ethanol (concentration, 0.02 g. per liter).

4-Hydroxy-3-methoxyphenylpropane. A solution of 50 g. (0.3 mole) of eugenol (or isoeugenol) in 200 ml. of absolute ethanol was treated with 0.5 g. of 10% palladium on carbon catalyst and hydrogenated at 24° with an initial pressure of 48 p.s.i. After 15 min., 0.3 mole of hydrogen had been absorbed, and no further pressure drop was observed. The mixture was filtered, and the clear filtrate was concentrated to dryness to yield 50 g. of oil which was distilled under reduced pressure to yield 4-hydroxy-3-methoxyphenylpropane as a colorless oil boiling at 110° at 3.5 mm. and having an index of refraction n_D^{24} 1.5196. The product was identical with that produced according to Brochet and Bauer[17] by hydrogenating eugenol at 60° over active nickel.

3,5-Dimethoxy-4-hydroxyphenylpropane. Similar hydrogenation of 2,6-dimethoxy-4-allylphenol[2] yielded 3,5-dimethoxy-4-hydroxyphenylpropane as a viscous light-colored oil boiling at 160° at 6.0 mm. and having an index of refraction n_D^{25} 1.5259. Melting points of its acetate and benzoate agreed with recorded values.[9,18]

4-Methoxyphenylpropane. Hydrogenation of anethole under the same conditions yielded 4-methoxyphenylpropane as a colorless oil boiling at 67° at 2.0 mm. and having an index of refraction n_D^{23} 1.5024. Klages[19] reported a boiling point of 215–216° at atmospheric pressure and an index of refraction n_D^{20} 1.5045 for the compound prepared by reduction of anethole with sodium and ethanol.

4-Hydroxyphenylpropane. A solution of 60 g. of 4-methoxyphenylpropane in 600 ml. of acetic acid was heated to boiling under reflux and treated over a period of 1 hr. with 120 ml. of 48% hydrobromic acid. The solution was boiled an additional 4 hr., concentrated under reduced pressure to 200 ml. volume, and stirred into excess water. The aqueous mixture was neutralized with a slurry of sodium bicarbonate and extracted with ether, and the ether was dried and distilled to leave an oil. Redistillation under reduced pressure yielded 49 g. of pure 4-hydroxyphenylpropane boiling at 90° at 3.0 mm. and having an index of refraction n_D^{23} 1.5231. The benzoate melted at 36–37°, agreeing with the benzoate prepared by Coulthard, Marshall, and Pyman[20] from 4-hydroxyphenylpropane obtained by Clemmenson reduction of 4-hydroxypropiophenone.

Dihydroferulic acid. A solution of 19.4 g. (0.10 mole) of ferulic acid in 125 ml. of tetrahydrofuran was treated with 0.1 g. of platinum oxide and hydrogenated at 27° with an initial pressure of 49 p.s.i. Hydrogen uptake was complete after 90 min. The mixture was filtered, and the clear filtrate was concentrated to dryness under reduced pressure. The white residue was recrystallized from water to give white crystals of dihydroferulic acid melting at 90–91° and not depressing a mixed melting point with authentic dihydroferulic acid prepared by alkaline hydrolysis of ethyl acetyldihydroferulate.[21]

Dihydro-p-coumaric acid. Similar reduction of *p*-coumaric acid and recrystallization of the product from benzene gave dihydro-*p*-coumaric acid melting at 125–126° and not depressing a mixed melting point with authentic material prepared by alkaline hydrolysis of ethyl acetyldihydro-*p*-coumarate.

Dihydrosinapic acid. A solution of 10 g. of sinapic acid in 400 ml. of 4% sodium hydroxide solution was treated with stirring with 10 g. of Raney nickel alloy in 1-g. amounts over a period of 15 min. After stirring an additional 15 min., the mixture was filtered, and the filtrate was stirred into a mixture of ice and excess hydrochloric acid. The clear solution was extracted with ether, and the ether was dried and distilled. The white residue was recrystallized from benzene to give crystals of pure dihydrosinapic acid melting at 102–103°.

Anal. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.54; H, 6.34.

Dihydrosinapic acid was also prepared by alkaline hydrolysis of ethyl dihydrosinapate.

Methyl dihydrosinapate. Esterification of dihydrosinapic acid with absolute methanol and sulfuric acid yielded methyl dihydrosinapate as a viscous colorless oil boiling at 165–167° at 0.5 mm. and having an index of refraction n_D^{25} 1.5302; λ_{max} 264 mμ, ε 866.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.99; H, 6.71.

Ethyl dihydrosinapate. A solution of 19.7 g. of ethyl acetylsinapate[8] in 150 ml. of acetic acid was treated with 10 ml. of water and then with 20 g. of zinc dust. The mixture was heated to boiling under reflux with occasional shaking for 2 hr. and filtered hot. The precipitate was washed with hot acetic acid, and the combined filtrate and washings were stirred into 1 l. of mixed cracked ice and water. The white precipitate which separated was filtered, washed with water, and recrystallized to give 12 g. of ethyl dihydrosinapate as colorless crystals melting at 48–49°. Brewer, Cooke, and Hibbert[9] recorded only a boiling point of 178–179° at 1 mm.

Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.40; H, 7.14. Found: C, 61.25; H, 6.99.

Ethyl dihydrosinapate was also prepared by esterification of dihydrosinapic acid with absolute ethanol in the presence of sulfuric acid.

Acetyldihydroferulic acid. Acetylferulic acid[22] was hydrogenated in tetrahydrofuran with platinum oxide at 25°, and the product was recrystallized from Skellysolve "C" to give white crystals of acetyl dihydroferulic acid melting at 93–94°; λ_{max} 273 mμ, ε 2,785.

Anal. Calcd. for $C_{12}H_{14}O_5$; C, 60.50; H, 5.92. Found: C, 60.68; H, 6.04.

Acetyldihydro-p-coumaric acid. Similar hydrogenation of acetyl-*p*-coumaric acid[23] and recrystallization from petroleum ether (88–95°) yielded acetyldihydro-*p*-coumaric acid melting at 94–95°; λ_{max} 265 mμ, ε 500.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.53; H, 5.86.

Ethyl acetyldihydro-p-coumarate. Hydrogenation of ethyl acetyl-*p*-coumarate[6] in tetrahydrofuran in the presence of palladium oxide at 28° and distillation of the resulting oil

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[17] A. Brochet and M. Bauer, *Compt. rend.*, **159**, 192 (1914).

[18] A. W. Hoffman, *Ber.*, **11**, 331 (1878).

[19] A. Klages, *Ber.*, **37**, 3987 (1904).

[20] C. F. Coulthard, J. Marshall, and F. L. Pyman, *J. Chem. Soc.*, **1930**, 280.

[21] M. Granath and C. Schuerch, *J. Am. Chem. Soc.*, **75**, 707 (1953).

[22] K. Kratzl and G. Billek, *Monatsh.*, [2] **84**, 413 (1953).

[23] F. E. King, M. F. Grundon, and K. G. Neill, *J. Chem. Soc.*, 1952, 4580.

under reduced pressure gave an 85% yield of ethyl acetyldihydro-*p*-coumarate as a colorless oil boiling at 145–146° at 0.5 mm. and having an index of refraction n_D^{25} 1.4950; λ_{max} 266 mμ, ϵ 1,110; λ_{max} 210 mμ, ϵ 9,650.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.10; H, 6.89.

Methyl acetyldihydro-p-coumarate. Similar hydrogenation of methyl acetyl-*p*-coumarate[6] in the presence of platinum oxide and distillation under reduced pressure gave 90% of methyl acetyldihydro-*p*-coumarate as a sweet smelling oil boiling at 149–150° at 0.5 mm. and having an index of refraction n_D^{25} 1.5010; λ_{max} mμ, ϵ 695.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.85; H, 6.36.

Dihydroconiferyl alcohol. Hydrogenation of coniferyl alcohol in tetrahydrofuran in the presence of palladium oxide at 28° gave a quantitative yield of dihydroconiferyl alcohol as a viscous colorless oil boiling at 155° and having a refractive index n_D^{25} 1.5518, identical with an authentic sample prepared according to Granath and Schuerch[21] by lithium aluminum hydride reduction at low temperature of ethyl acetyldihydroferulate. Dihydroconiferyl alcohol was also prepared in almost quantitative yield by the reduction of ethyl acetyldihydroferulate at room temperature with lithium aluminum hydride according to the procedure described for the preparation of dihydro-*p*-coumaryl alcohol and by the reduction of acetyldihydroferuoyl chloride with sodium trimethoxyborohydride in tetrahydrofuran.

Dihydro-p-coumaryl alcohol. A mixture of 3.5 g. of powdered lithium aluminum hydride and 400 ml. of anhydrous ether was placed in a one-liter 3-neck flask fitted with a gas inlet tube, reflux condenser, silicone oil-sealed stirrer, and dropping funnel. Nitrogen was introduced, and stirring was begun. After 1 hr. of stirring at room temperature a solution of 7.6 g. of methyl acetyldihydro-*p*-coumarate in 500 ml. of anhydrous ether was added dropwise over a period of 2 hr. After addition was complete, the mixture was stirred an additional hour, treated dropwise with 100 ml. of water, and then with 150 ml. of 2*N* sulfuric acid. The ether layer was removed, and the slightly acid aqueous layer was extracted twice with ether. All ether solutions were combined, dried, and concentrated to dryness to yield 5.5 g. crude dihydro-*p*-coumaryl alcohol as a white crystalline solid. Two recrystallizations by solution in a little anhydrous ether, addition of petroleum ether (b.r. 30–60°) to incipient turbidity, and freezing yielded colorless crystals melting at 54–55°. This is the melting point recorded by Braun and Deutsch[24] for dihydro-*p*-coumaryl alcohol prepared by reaction of *p*-hydroxyphenylpropyl chloride with acetic acid and sodium acetate and hydrolysis of the reaction product with sodium hydroxide.

Acetylsinapaldehyde. Reduction of 14.2 g. of acetylsinapoyl chloride in diglyme (diethylene glycol dimethyl ether) with lithium tri-*t*-butoxyaluminohydride as described earlier[10] for acetylconiferyl aldehyde yielded 4.8 g. crude acetylsinapaldehyde melting at 132–134° which, upon recrystallization from methanol, gave colorless crystals melting at 134–135°; λ_{max} 230 mμ, ϵ 16,430; λ_{max} 310 mμ, ϵ 18,410.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.44; H, 5.64.

Reduction of acetylsinapoyl chloride in tetrahydrofuran with sodium trimethoxyborohydride at −5° and then at room temperature gave a 30% yield of acetylsinapaldehyde melting at 134–135° and not depressing a mixed melting point with the authentic aldehyde prepared above.

Sinapaldehyde. Acetylsinapaldehyde was reduced with sodium methylate in methanol-chloroform solution as described for coniferaldehyde[10] to give an almost quantitative yield of sinapaldehyde which was recrystallized from benzene to give slightly yellow needles melting at 107–108°. This agrees with the melting point reported by Freudenberg and Hübner[25] who prepared the compound by Rósenmund reduction of acetylsinapoyl chloride and that reported by Pauly and Strassberger[26] who condensed methoxymethylsyringaldehyde with acetaldehyde and hydrolyzed the resulting methoxymethylsinapaldehyde. Sinapaldehyde gives a very strong violet-red color with phloroglucinol-hydrochloric acid reagent.

Sinapaldehyde was prepared directly by reduction of acetylsinapoyl chloride in tetrahydrofuran by lithium tri-*t*-butoxyaluminohydride. Acetylsinapoyl chloride was prepared from 10 g. of acetylsinapic acid with thionyl chloride and recrystallized from xylene. The chloride was dissolved in 150 ml. of tetrahydrofuran and treated at room temperature with a solution of 15 g. of lithium tri-*t*-butoxyaluminohydride in 100 ml. of tetrahydrofuran. The mixture was allowed to stand at 20° for 6 hr. and then poured into 1 l. of cold water. The mixture was filtered, and the filtrate was concentrated to a small volume in a rotating evaporator. The crystals which separated were recrystallized from benzene to give 3.4 g. of yellow sinapaldehyde melting at 106–107° and not depressing the melting point of a mixture with the authentic material prepared above.

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APPLETON, WIS.

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[24] J. von Braun and H. Deutsch, *Ber.*, **45**, 2513 (1912).

[25] K. Freudenberg and H. H. Hübner, *Chem. Ber.*, **85**, 1181 (1952).

[26] H. Pauly and L. Strassberger, *Ber.*, **62**, 2277 (1929).