Anal. Calcd. for $C_{12}H_{22}O_4Hg$: C, 33.4; H, 5.15. Found: C, 33.8; H, 5.26.

β-2-Chloromercuri-trans-terpin. A solution of 0.6 g. of the acetoxymercuri analog in 6 ml. of chloroform was shaken with saturated aqueous sodium chloride. The crystalline substance (0.48 g.) which precipitated from the nonaqueous layer melted at 120–120.6° and was unchanged in melting point by crystallization (2 ml. per g.) from hot chloroform.

Anal. Calcd. for $C_{10}H_{19}O_2HgCl$: C, 29.5; H, 4.70. Found: C, 29.3; H, 4.51.

Bis-β-2-mercuri-trans-terpin sulfide. A solution of 2.49 g. (0.005 mole) of β-2-iodomercuri-*trans*-terpin in 65 ml. of acetone was treated with 0.4 ml. (0.0066 mole) of acetic acid and then 1.20 g. (0.005 mole) of sodium sulfide nonahydrate in 6 ml. of water was added. After a day the solvent was evaporated leaving a filterable residue; 1.72 g. (88%), m.p. 190°. Solution in dimethylsulfoxide (10 ml. per g.) followed by addition of one-half volume of water raised this melting point to 194–194.5°. After 3 hr. of reflux in methanol 55% was recovered unchanged. Treatment with lead acetate trihydrate in acetic acid precipitated lead acetate at once yielding a complex product, m.p. 134–138°.

Anal. Calcd. for $C_{20}H_{38}Hg_2O_4S$: C, 30.9; H, 4.97; S, 4.13. Found: C, 30.6; H, 4.95; S, 4.30.

By contrast to the preparation of this sulfide the same reaction conditions applied to α-iodomercuri-*trans*-terpin yielded only terpineol.

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TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Model Compounds for Comparison with Lignin.* I. Preparation and Properties of 8-Methoxy-6-methylflavanone and 2'-Hydroxy-3'-methoxy-5'-methylchalcone

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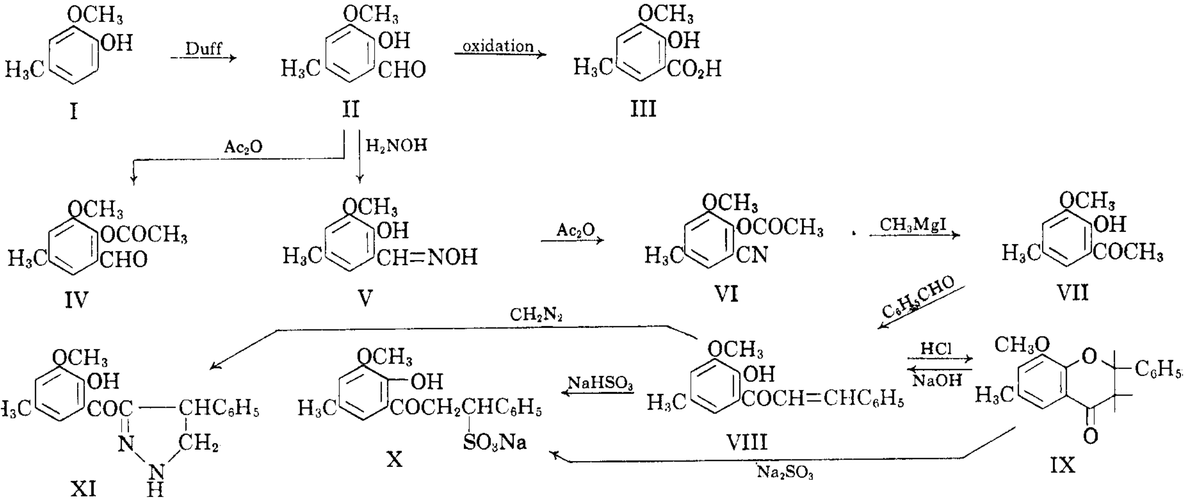
The syntheses of 8-methoxy-6-methylflavanone and 2'-hydroxy-3'-methoxy-5'-methylchalcone are described. These compounds differed from those reported for soft wood lignin with respect to ultraviolet and infrared spectra and also in their chemical properties.

Brauns[2] and Harris[3] have reviewed the various structures proposed for spruce lignin. One of the polymeric structures incorporated a substituted chalcone unit in equilibrium with the flavanone unit.[4,5] For purposes of comparison, two model compounds, 2'-hydroxy-3'-methoxy-5'-methylchalcone (VIII) and 8-methoxy-6-methylflavanone (IX) have been prepared and their properties compared with some of the reactions reported for lignin. Chart I summarizes the reactions and inter-



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* A contribution in honor of Lyndon F. Small and a tribute to his services as former Editor of this Journal, as Chairman and member of the Executive Committee of the Division of Organic Chemistry and for his outstanding investigations in organic chemistry.

(1) From the Ph.D. Thesis submitted to the Graduate College of the State University of Iowa.

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(3) E. E. Harris, *Progress in the Chemistry of Lignin*, Report No. 2020, Forest Products Laboratory, Madison, Wis. (1955).

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mediates involved in the syntheses of these two compounds. Each step paralleled reactions previously described in the literature and the procedures are given in the experimental part.

Comparison of the properties of these two model compounds with those reported in the literature[2,3] for soft wood lignin preparations showed marked differences in the following respects:

(*1*) The colorless flavanone (IX) was insoluble in dilute aqueous alkali but dissolved in 24% sodium hydroxide solution in 50% ethanol or dioxane to form a beautiful red solution of the sodium salt of the chalcone (VIII). Careful acidification precipitated the orange-red crystals of the chalcone. Alcoholic hydrochloric acid readily converted the chalcone to the flavanone. Lignin preparations dissolve in alkali to give a yellow to brown color and give no indication of behavior paralleling the above.

(*2*) The ultraviolet absorption spectra of lignin preparations[6] show a rather broad maximum at about 276 mμ to 280 mμ which is not shown by either the chalcone or flavanone. Maxima for the chalcone were found at 325 mμ ($\epsilon = 28 \times 10^3$); 323 m$\mu$ ($\epsilon = 17 \times 10^3$) and about 207 m$\mu$ ($\epsilon = 33 \times 10^3$). The flavanone had maxima at 218 mμ ($\epsilon = 27 \times 10^3$); 268 m$\mu$ ($\epsilon = 18 \times 10^3$) and 242 m$\mu$ ($\epsilon = 7 \times 10^3$). The curves for VIII and IX were quite different from those for lignin preparations.

(*3*) The chemistry of the reaction of lignin with bisulfite solutions has been extensively investigated.[2,3] The reaction appears to be a sulfonation accompanied by hydrolysis. The chalcone (VIII) reacted with aqueous alcoholic sodium bisulfite to form the sodium sulfonate, X, but the flavanone (IX) failed to react under the same conditions. With alkaline aqueous-alcoholic sodium sulfite the ring of IX was opened and the same sulfonate (X) was formed.

(*4*) Lignin preparations have been methylated by methyl sulfate and aqueous alkalies. Brauns[7] used a reaction mixture kept slightly alkaline and Russell[4a] used 10% alkali. The chalcone (VIII) did undergo methylation with an excess of methyl sulfate and 17% aqueous sodium hydroxide solution at 60–70° but a pure product with the theoretical methoxyl content could not be isolated. Treatment of the flavanone (IX) with the same methylation procedure resulted in a 93% recovery of the flavanone. This was somewhat surprising in view of the opening of the flavanone ring by alcoholic alkali mentioned above. However, the flavanone was insoluble in aqueous alkali and the reaction between methyl sulfate and alkali formed methanol and sodium methyl sulfate which reduced the alkalinity of the reaction mixture.

(*5*) Spencer and Wright[8] found that diazomethane methylated the phenolic group in lignin and also formed a nitrogen containing methoxylated lignin which had about 1% nitrogen. This may be due to the addition of the diazomethane to a conjugated system. The flavanone (IX) did not react with diazomethane but the chalcone (VIII) reacted rapidly (within 4 min.) to give high yields of a substituted pyrazoline XI. This product gave a greenish tan color with ferric chloride solution and analysis showed that the phenolic hydroxyl of VIII was not methylated.

Because of its high melting point (207–208°), and yellow color, it seems probable that the diazomethane reaction product has the conjugated Δ^2-pyrazoline structure by analogy to the structure assigned by Smith and Pings[9] for the high-melting product obtained from chalcone and diazomethane.

Evidently the diazomethane added rapidly to the conjugated system of the chalcone to precipitate the pyrazoline. The methylation of the phenolic group is hindered by the strong hydrogen bonding of the *ortho*-hydroxyl group with the carbonyl group. Evidence of this chelation was found in the infrared absorption spectrum of the chalcone which does not show a typical hydroxyl peak. The chalcone has a carbonyl band at 1638 cm.$^{-1}$ indicating hydrogen bonding. The flavanone (IX) has a strong carbonyl band at 1691 cm.$^{-1}$ The infrared bands for the two model compounds differ from those reported for lignin.[10]

EXPERIMENTAL

2-Hydroxy-3-methoxy-5-methylbenzaldehyde (II). This aldehyde was made from *o*-creosol (I) by the Duff[11] reaction using the general method of Manske and Ledingham[12] with the modification suggested by Liggett and Diehl.[13] Yields of 40 to 50% were obtained of light yellow needles melting at 76° (Manske and Ledingham[12] reported 77°). A small sample of this aldehyde was oxidized to the acid (III) using alkali and a suspension of silver oxide. The acid melted at 190° which agreed with that previously reported by Wacek and Nittner.[14]

When 2.5 g. of the aldehyde (II) was refluxed with 15 ml. of acetic anhydride for 45 min., then cooled and poured into water, the acetyl derivative (IV) separated. Recrystallization from 50% ethanol-water gave 2.3 g. (74%) of colorless needles melting at 115–117°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.48; H, 5.81. Found: C, 63.38; H, 5.78.

2-Hydroxy-3-methoxy-5-methylbenzaldoxime (V). A solution of 125 g. of the aldehyde (II) and 65 g. of hydroxyl-

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(6) Ref. 3, p. 14.

(7) F. E. Brauns, *J. Am. Chem. Soc.*, 61, 2120 (1939).

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(10) Ref. 3, pp. 14, 15.

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(12) R. H. F. Manske and A. E. Ledingham, *Can. J. Res.*, **22B**, 115 (1944).

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(14) A. v. Wacek and E. Nittner, *Cell. Chem.*, **18**, 29 (1940).

amine hydrochloride in 500 ml. of pyridine and 500 ml. of absolute ethanol was refluxed for 12 hr. The solvents were removed under reduced pressure in a stream of nitrogen gas. Addition of 300 ml. of water to the residual mass caused the oxime to separate as dark greenish crystals. They were collected on a filter, washed well with ice water, and recrystallized from 25% ethanol. Pale yellow needles of the oxime weighing 117 g. (87%) and melting at 162–164° were obtained (Manske and Ledingham[12] reported m.p. 165°).

Anal. Calcd. for $C_9H_{11}NO_3$: C, 59.70; H, 6.07; N, 7.73. Found: C, 59.56; H, 6.05; N, 7.98.

2-Acetoxy-3-methoxy-5-methylbenzonitrile (VI). A mixture of 117 g. of the oxime (V), 2 g. of anhydrous sodium acetate, and 500 ml. of acetic anhydride was refluxed 3 hr. The mixture was decomposed with 500 g. of ice and 2 l. of water and after standing several hours the oil solidified. The solid was collected on a filter, dried, and recrystallized from ligroin (60–100°). A yield of 117 g. (88%) of white prisms of the nitrile (VI) melting at 76–78° was obtained.

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.35; H, 5.40; N, 6.90.

2-Hydroxy-3-methoxy-5-methylacetophenone (VII). A solution of 50.0 g. (0.24 mole) of the above nitrile in 750 ml. of benzene was distilled until 600 ml. of benzene had been collected. To the remaining anhydrous solution of the nitrile was added 1.5 l. of absolute ether and then with vigorous stirring was added 800 ml. of ether containing 202 g. (1.22 moles) of methyl magnesium iodide. After refluxing with stirring for 12 hr. 20 ml. of water was cautiously added dropwise and then a solution of 70 g. of ammonium chloride in 400 ml. of water was added. Emulsions which formed in some runs were broken by adding 100 to 600 ml. of ethanol. Concentrated hydrochloric acid was added slowly with vigorous stirring until the mixture was acid to litmus. The ether was removed from a water bath and the aqueous solution concentrated to about 400 ml. and cooled. The tan precipitate was collected on a filter, washed with a little ice water, and dried. The crude product (42 g. 95%) was recrystallized from 80% ethanol to give 32 g. (72%) of pale greenish prisms melting at 82–84°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.31; H, 6.65.

In only 0.3 mole of the Grignard reagent to 0.2 mole of the nitrile was used in the above reaction, the acetoxy group was hydrolyzed but the nitrile group was not attacked. The product melted sharply at 123° and analyzed for 2-hydroxy-3-methoxy-5-methylbenzonitrile.

Anal. Calcd. for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.59. Found: C, 65.98; H, 5.51; N, 8.65.

2'-Hydroxy-3'-methoxy-5'-methylchalcone (VIII). While nitrogen gas was bubbled through a solution of 120 g. of sodium hydroxide in one liter of 50% ethanol-water, there was added with stirring, 60 g. (0.33 mole) of 2-hydroxy-3-methoxy-5-methylacetophenone followed by 60 g. (0.56 mole) of freshly distilled benzaldehyde. The solution turned red and set to a thick slurry in about 20 min. It was allowed to stand 12 hr., and 250 ml. of water followed by 250 ml. of concentrated hydrochloric acid were added slowly with stirring. The still basic solution was cooled in an ice bath and saturated with carbon dioxide. Red crystals of the chalcone separated first and were quickly filtered, and washed with water. The chalcone was recrystallized from 95% ethanol. The yield was 10 g. (11%) of red crystals melting at 95–96°.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.08; H, 5.97.

The acetyl derivative was prepared by refluxing 1 g. of the chalcone with 15 ml. of acetic anhydride for 3 hr. After pouring into 100 ml. of water, the solid was collected and recrystallized from 95% ethanol to give pale yellow needles melting at 85–86°. This derivative gave no color with ferric chloride solution.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85; Acetyl, 13.85. Found: C, 73.34; H, 5.81; Acetyl, 13.53%.

When the filtrate from the chalcone preparation was cooled and allowed to stand, crystals of the flavanone separated. To recover as much flavanone as possible, the above filtrate was mixed with 250 ml. of concentrated hydrochloric acid, refluxed for 3 hrs., and then cooled. The crude flavanone was collected on a filter and recrystallized from ethanol. There was obtained 33 g. of flavanone (IX) melting at 142–143° identical with that obtained below.

8-Methoxy-6-methylflavanone (IX). A solution of 3.5 g. of the chalcone (VIII) in 150 ml. of 95% ethanol and 37 ml. of concentrated hydrochloric acid was refluxed 5.5 hr. The volume was reduced to about 80 ml. by distillation, 50 ml. of water added, and the solution chilled in an ice bath. The flavanone which separated was recrystallized from ethanol and then from petroleum ether. Colorless needles, melting at 142–143° and amounting to 2.5 g. (72%) were obtained. This product gave no color with ferric chloride solution.

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 76.11; H, 5.91.

4-Phenyl-3-(2-hydroxy-3-methoxy-5-methylbenzoyl)Δ^2-pyrazoline (XI). A 100 ml. ether solution containing 2.8 g. (0.066 mole) of diazomethane was added to 2.7 g. (0.01 mole) of the chalcone in 100 ml. of ether. A light yellow precipitate formed in 4 min. but the mixture was allowed to stand overnight. The precipitate was collected on a filter and recrystallized from 95% ethanol to give 1.5 g. (48%) of golden needles melting with decomposition at 207–208°. In 95% ethanol this pyrazoline gave the same greenish-tan color with a drop of 10% ferric chloride as was observed for the chalcone.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.34; H, 6.00; N, 8.92.

Reaction of the chalcone (VIII) *with sodium bisulfite.* A mixture of 20 ml. of saturated sodium bisulfite solution, 30 ml. of 95% ethanol, 10 ml. of water, and 1 g. of the chalcone was heated on a steam bath until the volume was reduced to 25 ml. When cooled, the solid was collected on a filter and recrystallized from 10 ml. of water. Light yellow needles were obtained which melted at 65° after air drying. When dried in a vacuum pistol they melted at 121° and the weight (2 g.) indicate a hydrate. A sample was dried at 100° over phosphorus pentoxide for 24 hr. to obtain an anhydrous sample of the salt which decomposed over a range of 166–176°. It gave a blue green color with ferric chloride solution.

Anal. Calcd. for $C_{17}H_{17}O_6SNa$: C, 54.83; H, 4.60; Na, 6.18. Found: C, 53.03; H, 4.66; Na, 6.02.

The carbon analyses on this salt were low due to retention by the copper oxide of sodium carbonate along with sodium sulfate. To check the composition, this sodium sulfonate (X) was converted back to the chalcone (VIII) by refluxing a sample with 24% sodium hydroxide solution which gave the typical red solution of the salt of the chalcone. Acidification with acetic acid precipitated the chalcone which melted at 94–95° after recrystallization from 95% ethanol.

The flavanone (IX) was recovered unchanged when subjected to the reaction with sodium bisulfite using the same conditions as above. However, when 1 g. of the flavanone, 30 ml. of water, 20 ml. of saturated sodium sulfite solution, and 30 ml. of 95% ethanol were boiled and concentrated on a steam bath light yellow needles of the hydrate of the sodium sulfonate salt were obtained identical with those obtained above.

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