Anal. Calc'd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.50; H, 7.49.

This ester upon saponification gave an acid identical with the one described in the following paragraph.

The reaction of diacetyl peroxide with p-isopropylbenzoic acid. The preparation of 2,3-di-p-carboxyphenyl-2,3-dimethyl-n-butane. The solvent used for this reaction had the following composition: acetic anhydride, 150.0 g., *p*-isopropylbenzoic acid, 237.0 g., acetic acid, 289.5 g., and benzene, 130.0 g. A solution containing diacetyl peroxide, 0.18 mole, dissolved in 587.0 g. of this mixed solvent was introduced one drop at the time beneath the surface of 182.5 g. of the same mixed solvent contained in a 3-liter flask (*see reference* 3) *and held at the reflux temperature*, 105°, of this mixture. The volatile products obtained and identified were carbon dioxide, (12.8 g., 0.30 mole), and methane, (4.74 l., STP., 0.21 mole). The unreacted solvent was removed from the residue in the reaction vessel by distillation at atmospheric pressure. A first fraction, (100.8 g.), b.p., 80–85°, was principally benzene. A section fraction, (450.2 g.), collected at 95–125°, was a mixture of benzene, acetic acid, and acetic anhydride. Upon cooling to room temperature the residue in the still-pot crystallized to a white solid. This white solid (crude dimeric acid, 22.8 g., 0.069 mole) was triturated with hot aqueous 50% ethanol and finally was recrystallized from a 5% solution of acetic acid in benzene, m.p. 275–280° with decomposition.

Anal. Calc'd for $C_{20}H_{22}O_4$: C, 73.62; H, 6.79; Neut. Equiv., 163. Found: C, 73.78; H, 6.89; Neut. Equiv., 163.

A sample of this dimeric acid, 2,3-di-*p*-carboxyphenyl-2,3-dimethyl-*n*-butane, (3.0 g.) was converted into the dimethyl ester, m.p. 212–213°. This ester did not depress the m.p. of the dimeric ester described in the previous paragraph.

The decarboxylation of 2,3-di-p-carboxyphenyl-2,3-dimethyl-n-butane. To a solution containing 3.35 g. of 2,3-di-*p*-carboxyphenyl-2,3-dimethyl-*n*-butane dissolved in 50 ml. of quinoline was added 1.0 g. of powdered copper, and this mixture was refluxed for 25–30 hours.[4] At intervals during this time there was added to the mixture in small samples a total of 1.0 g. of fresh copper powder. The mixture then was taken up in ethyl ether and was extracted repeatedly with 12 *M* HCl, then with H_2O, and finally with 5% NaOH followed by H_2O. After drying over $CaCl_2$, the neutral fraction was isolated by removing the ether on water-bath. The residue, 2.1 g., crystallized upon standing overnight. Recrystallization of this residue from 95% ethanol gave white crystals which melted at 113–114°. These crystals did not depress the m.p. (115°[5]), of authentic 2,3-dimethyl-2,3-diphenyl-*n*-butane. Attempts to decarboxylate the original dimeric acid (II) by fusion with soda-lime gave results that were much less satisfactory.

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Betti Reactions of Some Phenols

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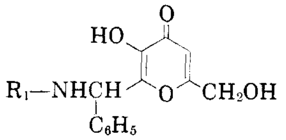
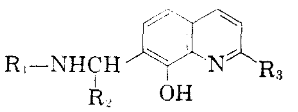
In continuation of previous work[1–3] on the preparation of chelating agents by the reaction of phenols with aromatic aldehydes and primary amines (Betti reaction)[4] some new derivatives of kojic acid, 8-quinolinol, and 8-hydroxyquinaldine have been obtained. Of these three phenols kojic acid is the most reactive; for example, it reacts with benzylideneaniline to precipitate the 6-substituted derivative (formula A) in less than one day at room temperature while 8-quinolinol requires weeks and 8-hydroxyquinaldine months for the corresponding reactions.

Betti reaction products from benzaldehyde and 8-hydroxyquinaldine, using aniline and ethyl anthranilate as the amines, were obtained in poor yields after long standing. On the basis of similarity of ultraviolet and infrared spectra of these two compounds to the spectra of the corresponding 8-quinolinol derivatives,[1] substitution was assumed to have occurred in the 7 position (formula B), although reaction at the active methyl group was a possibility since 8-hydroxyquinaldine is known to condense with benzaldehyde to yield 2-styryl-8-quinolinol.[5] Indeed, use of anthranilic acid as the amine gave a red product that may have resulted from the condensation of benzaldehyde with the active methyl group in addition to the expected Betti reaction; anthranilic acid was the only amine tried that could furnish the necessary acid catalysis for such a condensation. This red product was quite different from the other compounds prepared in this investigation and no further examination of it was made.



A



B

The chelating properties of 7-(α-anilinobenzyl)-8-hydroxyquinaldine and 7-[α-(*o*-carbethoxyanilino)benzyl]-8-hydroxyquinaldine (compounds V and VI in Table I) were unusual in that both compounds gave fluorescent yellow precipitates with aluminum ion in a neutral solution. All previously prepared 2-substituted 8-quinolinols have been characterized by failure to form an insoluble chelate compound with aluminum, presumably as a result of steric hindrance from the group in the 2 position.[6] The fact that the spectrum of the aluminum compound of VI is almost identical with the spectrum of VI itself rather than shifted to much longer wavelengths as is usual with the chelate compounds

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(2) Phillips, Keown, and Fernando, *J. Org. Chem.*, **19**, 907 (1954).

(3) Phillips and Duckwall, *J. Am. Chem. Soc.*, **77**, 5504 (1955).

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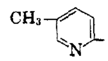
TABLE I

ANALYSES OF BETTI REACTION PRODUCTS

No.	Formula	R_1	R_2	R_3	Empirical Formula	Nitrogen Calc'd	Nitrogen Found
I	A	C_6H_5	—	—	$C_{19}H_{17}NO_4$[a]	—	—
II	A	*m*-ClC_6H_4	—	—	$C_{19}H_{16}ClNO_4$	3.91	3.88
III	A		—	—	$C_{19}H_{18}N_2O_4$	8.28	7.95
IV	A	*o*-$CH_3OC_6H_4$	—	—	$C_{20}H_{19}NO_5$	3.96	4.03
V	B	C_6H_5	C_6H_5	CH_3	$C_{23}H_{20}N_2O$	8.23	8.11
VI	B	*o*-$C_2H_5OOCC_6H_4$	C_6H_5	CH_3	$C_{26}H_{24}N_2O_3$	6.79	6.58
VII	B	C_6H_5	*p*-$NO_2C_6H_4$	H	$C_{22}H_{17}N_3O_3$	11.32	11.49
VIII	B	C_6H_5	*p*-$iPrC_6H_4$	H	$C_{25}H_{24}N_2O$	7.60	7.56

[a] Previously prepared by this reaction.[11]

of 8-quinolinol[7] suggests the possibility that the structure is either a salt or a relatively unstable chelate compound. To establish whether the side chain nitrogen was involved in the chelation a sample of 2-(α-anilinobenzyl)-1-naphthol was prepared,[8] but this compound did not give the fluorescent yellow product with aluminum and apparently gave no chelate at all.

Although attempts to use secondary amines in the Betti reaction have been successful with α-naphthol,[9,10] 8-quinolinol and benzaldehyde gave only resinous materials with the amines piperidine, diethylamine, and diisopropylamine. Some primary amines that gave no products with 8-quinolinol and benzaldehyde were glycine, glycine ethyl ester hydrochloride, and 2,6-dimethylaniline.

EXPERIMENTAL

Preparation of compounds. In 50 to 100 ml. of 95% ethanol 0.05 mole of aldehyde and 0.05 mole of amine were dissolved. Then 0.05 mole of the phenol (kojic acid, 8-quinolinol, or 8-hydroxyquinaldine) was added and the mixture was stoppered and allowed to stand. The kojic acid derivatives precipitated within one day and were filtered after a week but the other compounds required considerably longer times (Table II), as observed in previous work with this reaction.[1,2] All compounds were recrystallized from ethanol.

6-(α-Anilinobenzyl)kojic acid was made from benzylideneaniline and kojic acid by essentially the same procedure.

Spectra. Ultraviolet spectra were determined on 95% ethanol solutions in the range 220–360 mμ using a Beckman DU Spectrophotometer.

Infrared spectra were run on potassium bromide pellets using a Baird Associates Spectrophotometer with salt prism in the range 2–15 μ. For comparative purposes infrared spectra of 8-hydroxyquinaldine, 7-(α-anilinobenzyl)-8-quinolinol, 7-[α-(o-carbethoxyanilino)benzyl]-8-quinolinol, as well as compounds V and VI, were determined. All showed OH bands at approximately 3.0 μ and aromatic C—C linkages at 6.22, 6.35, 6.63 μ. The three compounds having a methyl group at the 2 position of the quinoline ring had bands at 7.53 and 11.98 μ which were absent from the other two compounds. The two anthranilic ester derivatives showed carbonyl bands at 6.0 μ. Additional strong absorption bands were observed as follows: 8-hydroxyquinaldine; 6.78, 6.97, 7.92, 8.40, 8.60, 13.15, 13.30, 13.82 μ; 7-(α-anilinobenzyl)-8-quinolinol: 6.81, 7.00, 7.17, 7.25, 7.79, 8.08, 8.45, 9.19, 11.53, 12.13, 12.58, 13.35, 13.57, 14.38 μ; 7-[α-(o-carbethoxyanilino)benzyl]-8-quinolinol: 6.87, 6.95, 7.12, 7.23, 7.92, 8.07, 8.60, 8.72, 9.17, 9.32, 12.13, 12.63, 13.45, 13.62, 14.30 μ; V, 6.90, 7.95, 8.20, 8.52, 9.19, 13.42, 14.47 μ; VI, 6.87, 7.31, 7.92, 8.50, 8.72, 8.92, 9.25, 13.55, 14.35 μ. Wavelength assignments are estimated to be correct to the nearest 0.05 μ.

TABLE II

SPECTRA AND PROPERTIES OF BETTI REACTION PRODUCTS

No.	M.p., °C.	Yield	Time, days[a]	Absorption Maxima, mμ[b]
I	176	84	7	242 (16,000); 280 (9800)
II	184	75	7	249 (17,000); 280 (12,000)
III	168	78	7	242 (20,000); 280 (12,000)
IV	168	75	7	241 (14,000); 280 (12,400)
V	145	12	60	250 (67,000); 294[c]
VI	156	29	15	249 (52,000); 350 (7400)
VII	127	70	90	247 (50,000)
VIII	122	22	100	249 (54,000); 291 (4300)

[a] Total time elapsed before product was filtered. [b] Numbers in parentheses are molar absorbancies. [c] Shoulder.

Chelate compounds. The aluminum compound of V and the aluminum and copper compounds of VI were made by adding an ethanol solution of the reagent to the dilute metal ion solutions followed by adjustment with ammonium acetate to the *p*H necessary for complete precipitation. After standing for 30 minutes the precipitates were filtered, washed thoroughly with water, and finally with a small portion of ethanol. The dried precipitates then were analyzed for metal by ignition of weighed samples to the oxides.

Anal. Calc'd for $Al(C_{23}H_{19}N_2O)_3$: Al, 2.59. Found: Al, 2.61.
Calc'd for $Al(C_{26}H_{23}N_2O_3)_3$: Al, 2.13. Found: Al, 2.17.
Calc'd for $Cu(C_{26}H_{23}N_2O_3)_2$: Cu, 7.15. Found: Cu, 7.00.

The ultraviolet spectra of the compounds of VI in ethanol showed maxima at 249 and 350 mμ for the aluminum derivative and at 274 mμ for the copper compound.

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Acid Resistant Portion of Corn Fiber Gum[1]

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Recently[2] the partial acid hydrolysis of corn fiber gum[3] was described and the structures of the two main oligosaccharides were determined. An investigation of the structure of a residual polysaccharide is here described. Complete acid hydrolysis of the residual polysaccharide produces xylose and traces of arabinose, galactose, and uronic acid material which indicates that the residual polysaccharide is essentially a xylan.

Hydrolysis of the fully methylated residual polysaccharide produces approximately 14 parts of 2,3,4-tri-O-methyl-D-xylose, 47 parts of 2,3-di-O-methyl-D-xylose, 19 parts of 2-O-methyl-D-xylose, 2 parts of D-xylose, and barium salts of methylated aldobiouronic or uronic acids.

Isolation and identification of methylated sugars from the hydrolysate of a methylated polysaccharide do not permit extensive deductions concerning the structure of the polysaccharide. Yet, in the present instance, the recovery of large amounts of 2-O-methyl-D-xylose and of some D-xylose suggests a highly branched chain. Since the initial corn fiber gum readily lost L-arabinose upon mild hydrolysis, it is presumed that L-arabofuranose units were attached to the branched chain to give an added degree of ramification. It has already been shown[2] that to some of the L-arabinose units are attached units of D-xylose and to others are attached units of D-xylose and L-galactose. No information is yet available on the location of the aldobiouronic or uronic acid units in the polysaccharide structure.

EXPERIMENTAL

Paper chromatography. Chromatographic separations were made on strips of Whatman No. 1 filter paper with one of the following commonly used irrigating solutions. (A) ethyl acetate-pyridine-water (10:4:3 v/v), (B) azeotropic mixture of methyl ethyl ketone and water, b.p. 74–75°, and (C) butanol-pyridine-water (6:4:3 v/v). The positions of the components were revealed by spraying the papers with *p*-anisidine hydrochloride.[4]

Preparation of acid-resistant residue. Corn fiber hemicellulose was hydrolyzed with *N* sulfuric acid as previously described.[2] The polysaccharide precipitated by the addition of alcohol to the neutralized hydrolysate had $[\alpha]_D^{25}$ $-53.3°$ (*c*, 2.0 in water). Complete hydrolysis of the polysaccharide produced xylose and uronic acids together with trace amounts of arabinose and galactose as indicated by chromatographic comparison in solvent A.

Methylation of residue. A solution of 25 g. of residue in 100 ml. of water was placed in a three-neck flask and was flushed with nitrogen for 15 minutes. To the rapidly stirred solution was added 185 ml. of oxygen-free 30% sodium hydroxide solution followed by the alternate addition of six portions each of 95 ml. of 30% sodium hydroxide and 45 ml. of dimethyl sulfate. The reaction flask was cooled in a water-bath until after the last addition, and then the stirring was continued at room temperature for a further 18 hours. The solution was then neutralized with glacial acetic acid, dialyzed and concentrated for remethylation.

The polysaccharide was methylated three times by this method with the exception that during the second and third methylations, acetone was added to dissolve the partially methylated product. After the third methylation the precipitated methylated polysaccharide was freed from the neutralized solution and stirred with three 250-ml. portions of water. It was then dried by azeotropic distillation with alcohol and benzene to give 31.4 g. of a glassy product. The methylated xylan was refluxed for 18 hours with 150 ml. of methyl iodide and 20 g. of silver oxide, and then the solution was filtered from the silver oxide which was washed with hot chloroform. The combined filtrates were concentrated to a glass which was remethylated in a similar manner to give a methylated xylan having $[\alpha]_D^{25}$ $-52.1°$ (*c*, 1.0 in chloroform); methoxyl content 36.2%. No increase in methoxyl content occurred in the final methylation treatment.

Hydrolysis of methylated residue and isolation of the components. A sample of 3.225 g. of the methylated xylan was refluxed with 60 ml. of 2% methanolic hydrogen chloride for 18 hours at which time the optical rotation was constant. The solution was neutralized with silver carbonate, filtered, and concentrated to 3.294 g. of sirup. The sirup was dissolved in 100 ml. of *N* sulfuric acid and refluxed for 3 hours when constant rotation was reached. After neutralization of the acid with barium carbonate, the filtered solution was concentrated to 2.760 g. of sirup. A sample of 0.896 g. of the sirup was separated into its components on 24 sheets of 6 × 20-inch paper, using solvent B as the irrigant. The two leading components were extracted from the paper with hot acetone, the next component with hot alcohol, and the remaining two components with water at room temperature.

The leading component was 0.099 g. of clear sirup, $[\alpha]_D^{25}$ $+15.2°$ (*c*, 1.0 in water). In solvent B it was chromatographically identical to 2,3,4-tri-O-methyl-D-xylose. The sirup crystallized on seeding with the trimethyl ether to give crystals m.p. 83°. After recrystallization from ether-light petroleum ether the crystals had m.p. 89–90°, undepressed on admixture with an authentic sample.

The second and main component of 0.307 g. of clear sirup, $[\alpha]_D^{25}$ $+21.0°$ (*c*, 1.0 in water) was chromatographically identical to 2,3-di-O-methyl-D-xylose in solvent B. On refluxing 0.100 g. of the sirup with 0.2 ml. of aniline in 5 ml. of methanol, 2,3-di-O-methyl-*N*-phenyl-D-xylosylamine was obtained, m.p. 124–125°, undepressed on admixture with an authentic sample.

The third component of 0.115 g. of sirup crystallized on seeding with 2-O-methyl-D-xylose. After recrystallization

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[1] Journal Paper No. *925* of the Purdue Agricultural Experiment Station, Lafayette, Indiana. The corn fiber gum was kindly supplied by the Corn Products Refining Company.

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