

The values above 130° have been found to be in agreement with those of Kahlbaum. Two of the four values of Niederschulte lie near the vapor-pressure curve of the solid, as determined by us.

The latent heat of fusion as calculated from the difference in slopes of the two curves is in agreement with cryoscopic data.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

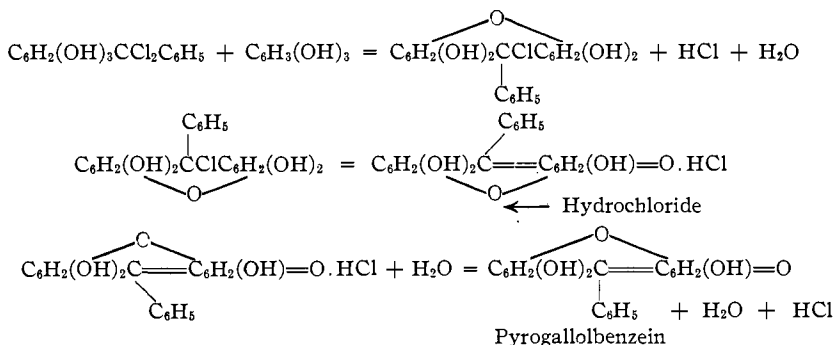
PYROGALLOLBEZEIN AND SOME OF ITS DERIVATIVES

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The method of preparation, purification and the analyses of pyrogallolbenzein have already been given.² The red aqueous extracts obtained in the purification of the benzein² were concentrated and on cooling gave red crystals. Yellow crystals were obtained when these were crystallized from water, after boiling the solution with bone black. Analyses³ showed that this substance was 2,3,4-trihydroxydiphenyl ketone, known commercially as Alizarin Yellow A. The triacetate, sodium and lead salts were also made and analyzed³ and proved that this by-product obtained in the preparation of the benzein was 2,3,4-trihydroxydiphenyl ketone. The pyrogallol probably first reacts with the benzotrichloride to form trihydroxydiphenyldichloromethane, $C_6H_3(OH)_3 + C_6H_5CCl_3 = C_6H_2(OH)_3CCl_2C_6H_5 + HCl$, and this, on boiling with water, gives 2,3,4-trihydroxydiphenyl ketone, $C_6H_2(OH)_3CCl_2C_6H_5 + H_2O = C_6H_2(OH)_3COC_6H_5 + 2HCl$. The formation of the pyrogallolbenzein itself probably takes place as follows.



¹ From a dissertation submitted by Chen Wang to the Faculty of the Graduate School of Cornell University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Orndorff and Wang, *THIS JOURNAL*, **47**, 290 (1925).

³ See *Thesis*, Cornell University Library. International atomic weights for 1925 were used in all calculations.

Sen and his co-workers⁴ claim to have made pyrogallolbenzein, but as their products gave a *yellow* color with sodium hydroxide solution, it is doubtful whether they really had pyrogallolbenzein. The molecular weight of pyrogallolbenzein was determined by the boiling-point method, using anhydrous formic acid as the solvent. The anhydrous formic acid was prepared by dehydrating 85% formic acid by Schierz's method;⁵ molecular rise in the boiling point for anhydrous formic acid 26.61.⁶ Mol. wt. Subs., 2.5145, 2.4138; in HCO₂H, 100,100: Δt , 0.205°, 0.196°. Calcd. for C₁₆H₁₂O₅: mol. wt., 320.1. Found: 326.4, 327.7.

From the analyses² and molecular-weight determinations, the formula for pyrogallolbenzein is C₁₅H₁₂O₅, and not C₃₅H₂₄O₁₁ as given by Doebner and Foerster.⁷ The structural formula of pyrogallolbenzein, showing its relation to resorcinolbenzein and to gallein has already been given.²

The solubility of pyrogallolbenzein in formic acid is over 2.5 g. in 100 g., while in ether, chloroform, acetone, methanol, ethanol and amyl alcohol it is always less than 1 g. in 100 g. It is nearly insoluble in water, petroleum ether, benzene, toluene and carbon tetrachloride. It is soluble with a beautiful blue color in concd. ammonium hydroxide and in 10% solutions of the caustic alkalis. It is readily soluble in concd. sulfuric acid with a dark red color and in concd. hydrochloric acid with an orange-yellow color. Dry pyrogallolbenzein takes up a little less than two molecules of dry ammonia gas, all of which it loses in a vacuum desiccator over concd. sulfuric acid.³

The pyrogallolbenzein forms a crystalline hydrochloride, sulfate and perchlorate, the latter containing three molecules of water of crystallization.

Substance	ANALYSES	
	Calcd., %	Found, %
Hydrochloride	Cl, 9.94	9.91 9.98
Sulfate	S, 7.67	7.71 7.64
Perchlorate	H ₂ O, 11.39	11.31 11.28
Dry perchlorate	Cl, 8.43	8.37 8.38

Triacetate of Pyrogallolbenzein.—The triacetate was made by boiling 5 g. of the dry benzein with 100 g. of freshly distilled acetic anhydride. Part of the acetic anhydride was distilled off. On cooling, orange-brown needles crystallized out. These were filtered off and repeatedly crystallized from acetic anhydride, dried in a vacuum and analyzed.

Anal. Subs., 0.1931, 0.2064: CO₂, 0.4605, 0.4926; H₂O, 0.0751, 0.0813. Calcd. for C₁₅H₉O₅(COCH₃)₃ + 0.5(CH₃CO)₂O: C, 65.17; H, 4.26. Found: C, 65.04, 65.09; H, 4.35, 4.41.

⁴ Sen and Sinha, *THIS JOURNAL*, **45**, 2984 (1923). Sen and Sarker, *ibid.*, **47**, 1079 (1925).

⁵ Schierz, *ibid.*, **45**, 447 (1923).

⁶ J. Castell-Evans, "Physico-Chemical Tables," 1911, vol. 2, p. 1032.

⁷ Doebner and Foerster, *Ann.*, **257**, 61 (1890).

When heated to 110–120° the triacetate lost the half molecule of acetic anhydride.

Anal. Subs., 0.1736, 0.1828: loss in wt., 0.0182, 0.0193. Calcd. for $C_{19}H_9O_5(COCH_3)_3 + 0.5(CH_3CO)_2O$: $(CH_3CO)_2O$, 10.25. Found: 10.48, 10.56.

Analyses of the triacetate after heating to 110° gave the following results.

Anal. Subs., 0.1891, 0.1957: CO_2 , 0.4664, 0.4824; H_2O , 0.0677, 0.0719. Calcd. for $C_{19}H_9O_5(COCH_3)_3$: C, 67.24; H, 4.07. Found: C, 67.27, 67.24; H, 4.01, 4.11.

Tetra-acetate of the Carbinol of Pyrogallolbenzein.—Meyer and Gerloff⁸ obtained a yellow diacetate of resorcinolbenzein by boiling the benzein with acetic anhydride and a little sulfuric acid. It was thought possible to prepare the colorless tetra-acetate of the carbinol of pyrogallolbenzein in this way. Five g. of the dry benzein was boiled with 50 g. of acetic anhydride and 0.5 cc. of concd. sulfuric acid. The solution turned from red to dark orange-brown, indicating the formation of the triacetate, and then to brownish-black. The solution was heated until a test portion, when mixed with glacial acetic acid and a large amount of water, gave a sandy precipitate and a colorless aqueous solution. If the solution was not boiled long enough, the precipitate was orange and the aqueous solution showed a yellow fluorescence which indicated the presence of some of the triacetate. If boiled too long the precipitate was black, indicating some decomposition. The solution was cooled; some water was then added and it was boiled for some time. After cooling, the mixture was poured into a large volume of water, when the tetra-acetate was precipitated as a sandy colored product. This was dissolved in glacial acetic acid and the solution boiled with bone black and precipitated with a large quantity of water, until the product was nearly colorless. The yield of the product was small. It was finally dissolved in chloroform, precipitated with dry petroleum ether, filtered off, washed with dry petroleum ether, and dried in a vacuum. This product was nearly colorless.

Anal. Subs., 0.2075, 0.1841: CO_2 , 0.4846, 0.4295; H_2O , 0.0876, 0.0765. Calcd. for $C_{19}H_9O_5(OH)(COCH_3)_4$: C, 64.01; H, 4.38. Found: C, 63.69, 63.63; H, 4.72, 4.65.

When powdered, the yellowish product decomposed at 150–155°. The tetra-acetate is insoluble in water and petroleum ether, moderately soluble with a yellow color in ether, acetone, methanol and ethanol and readily soluble with a yellow to orange-red color according to concentration in chloroform, benzene and glacial acetic acid. It is slowly saponified with a 10% solution of sodium hydroxide, giving a yellow solution.

By the use of benzoyl chloride, a tetrabenzoate of the carbinol was prepared in colorless crystals; m. p., 185–187°.

Anal. Calcd. for $C_{19}H_9O_5(OH)(COC_6H_5)_4$: C, 74.78; H, 4.01. Found: C, 74.73, 74.70; H, 4.13, 4.09.

Dibromopyrogallolbenzein.—Two g. of pyrogallolbenzein was dissolved in 120 cc. of hot formic acid, and 2.2 g. of bromine in 20 cc. of formic acid was slowly added, with constant stirring. Crystallization began on cooling. The powdered crystals lost 3.27% of formic acid on heating at 110° for two hours.

Anal. Subs. (after heating at 110°), 0.1921, 0.1864. AgBr, 0.1497, 0.1451. Calcd. for $C_{19}H_{10}Br_2O_5$: Br, 33.36. Found: 33.18, 33.14.

Dibromopyrogallolbenzein decomposes at about 260–263°. It is insoluble in water, petroleum ether, chloroform, benzene and toluene; very slightly soluble in formic acid with a faint yellow color; slightly soluble with a purplish color in ether, methanol, 95% ethanol and glacial acetic acid; readily soluble with a purplish-red color in absolute ethanol, acetone and phenol. It is soluble in 10% solutions of the caustic alkalies and concd. ammonium hydroxide with a beautiful blue color.

⁸ Meyer and Gerloff, *Ber.*, **57**, 598 (1924).

Action of Ammonia on Dibromopyrogallolbenzein.⁸—Dibromopyrogallolbenzein absorbs about two molecules of dry ammonia and turns from purplish-red to brownish-black with a greenish surface color, but on standing in a vacuum desiccator containing concd. sulfuric acid, this product loses all of the ammonia.

Action of Dry Hydrochloric Acid on Dibromopyrogallolbenzein.⁸—When the powdered dibromo product, after being heated to 110°, was treated with dry hydrogen chloride it absorbed a little more than two molecules of the gas and turned from purplish-red to red. This product lost hydrochloric acid in a desiccator containing solid sodium hydroxide and then contained one molecule of hydrochloric acid. All of the hydrochloric acid was lost when this hydrochloride was heated to 110–120°, as was the case also with the pyrogallolbenzein hydrochloride.

The dibromopyrogallolbenzein forms a bluish-green, crystalline triacetate which contains a mole of acetic acid and hydrobromic acid of crystallization.

Anal. Calcd. for $C_{19}H_7Br_2O_6(COCH_3)_3 + HBr + CH_3COOH$: $CH_3COOH + HBr$, 18.91; Br, 32.17. Found: $CH_3COOH + HBr$: 19.14, 19.06; Br, 32.21, 32.18.

Anal. (dried at 150°). Calcd. for $C_{19}H_7Br_2O_6(COCH_3)_3$: Br, 26.44. Found: 26.31, 26.36.

Dinitropyrogallolbenzein.—Two g. of pyrogallolbenzein was dissolved in a liter of boiling glacial acetic acid, and 1.2 g. of fuming nitric acid (d., 1.5) dissolved in 20 cc. of glacial acetic acid was slowly added. The mixture was heated on the water-bath until a test portion gave a yellowish-orange color with water. The solution was distilled to a small volume. On cooling, a yellowish-brown powder was obtained. After filtering, the dinitro product was precipitated by the addition of benzene and petroleum ether. As the substance could not be crystallized it was dissolved in acetone and precipitated with petroleum ether as a yellowish-brown powder. It was dried first in a vacuum and then by heating to 100–105°.

Anal. Subs. (dry), 0.1829, 0.2557: N_2 , 11.38 cc. (21°, 730 mm.), 15.49 cc. (20°, 734 mm.). Calcd. for $C_{19}H_{10}(NO_2)_2O_6$: N, 6.83. Found: 6.76, 6.66.

Dinitropyrogallolbenzein decomposes at 195–200°. It is insoluble in petroleum ether, slightly soluble with yellow color in chloroform and in benzene; moderately soluble with orange-yellow color in water and in ether, readily soluble in acetone, methanol and ethanol, and very readily soluble with dark red color in glacial acetic acid. It is also soluble with yellow color in concd. hydrochloric acid and readily soluble with orange-red color in 10% sodium hydroxide solution and in concd. sulfuric acid. It is readily decomposed by concd. nitric acid.

Trimethyl Ether of Pyrogallolbenzein.—No ethers of pyrogallolbenzein were obtained by boiling it with absolute methanol or absolute ethanol containing 3% of hydrogen chloride or concd. sulfuric acid. The trimethyl ether of pyrogallolbenzein was prepared by the Claisen method.⁹ Two g. of the benzein was dissolved in 2.5 liters of acetone by heating. After cooling, 2.8 g. of potassium carbonate and 2.8 g. of methyl iodide were added. On boiling, the solution turned from dark purplish-red to blue and then to red. The boiling was continued until a test portion no longer gave a blue color with a 10% solution of sodium hydroxide. The solution was then concentrated to a small volume by distillation and water was added. The trimethyl ether which precipitated was dried and repeatedly extracted with ether. The ether extracts were dried with potassium carbonate, filtered and distilled to a small volume. The trimethyl ether, in the form of red crystals with a slight greenish surface color, separated on cooling.

It was repeatedly recrystallized from ether, dried in a vacuum and lost no weight at 60°. It was analyzed by the modified Zeisel method.¹⁰ The Hempel tube was sur-

⁹ Claisen, *Ann.*, **401**, 29 (1913).

¹⁰ Hewitt and Moore, *J. Chem. Soc.*, **81**, 318 (1902).

rounded with cold water during the experiment. Ten cc. of acetic anhydride was used in addition to the 16 cc. of concd. hydriodic acid and the solution was kept gently boiling.

Anal. Subs., 0.2178, 0.2074: AgI, 0.4221, 0.4008. Calcd. for $C_{19}H_9O_2(OCH_3)_3 \cdot CH_3O$, 25.70. Found: 25.61, 25.53.

The trimethyl ether was also crystallized from methanol. It melts to a red liquid at 187–189°. It is insoluble in water, concd. ammonium hydroxide and 10% sodium hydroxide solution, slightly soluble with an orange tint in petroleum ether, moderately soluble with an orange color in benzene, toluene and glacial acetic acid and readily soluble with orange-red color in ether, chloroform, acetone, methanol and ethanol. It gives a yellow color in concd. hydrochloric acid and an orange color with concd. sulfuric acid, in which it is readily soluble. As it is colored, it has a quinoid structure like the benzein.² Professor Gill reported on these crystals as follows. "The sample is composed of dark, brick-red, crystalline masses loosely grouped together. They appear to have monoclinic or triclinic shape, although double refraction was not observed even in the 0.03mm. grains which transmitted light of a less deep color than the substance in mass."

Trisodium Salt of Pyrogallolbenzein.—Two g. of pyrogallolbenzein was dissolved in 2.5 liters of boiling absolute ethanol, and a solution of 1 g. of sodium in absolute ethanol was added. The color of the solution changed from dark red to dark reddish-purple. The trisodium salt was precipitated with a large volume of anhydrous ether as a crystalline powder with a reddish-bronze surface color. This was washed with anhydrous ether and dried in a vacuum. The substance lost but little weight on heating to 80°.

Anal. Subs., 0.2075, 0.1911; Na_2SO_4 , 0.1142, 0.1025. Calcd. for $C_{19}H_9O_5Na_3$: Na, 17.87. Found: 17.83, 17.77.

Professor Gill gives the following crystallographic data. "This substance occurs in somewhat equidimensional crystals which appear to be triclinic in shape. They reach 0.3 mm. in diameter. The reddish-bronze surface color may be due to fine, red particles on the surface of a yellow-reflecting crystal."

The trisodium salt is insoluble in petroleum ether, ether, chloroform and benzene; very slightly soluble with pink color in acetone; readily soluble with red color in methanol and ethanol and very readily soluble with dark red color in water. Addition of 10% sodium hydroxide solution to the alcoholic solution of the trisodium salt changes the red color to purplish-red. On standing, the dark red, aqueous solution of the salt changes to orange and slowly hydrolyzes, precipitating some pyrogallolbenzein. This colored trisodium has the quinoid structure.

Reduction Product of Pyrogallolbenzein.—It was found impossible to obtain a colorless reduction product by reducing pyrogallolbenzein by Doebner and Foerster's method.⁷ It was obtained in colorless crystals by using formic acid as the solvent. Four g. of the benzein was dissolved in about 200 cc. of boiling formic acid, and 10 g. of zinc dust was added. The solution was decolorized in five minutes. It was filtered hot in an atmosphere of carbon dioxide. On cooling, minute, colorless needles separated. A colorless, crystalline powder was obtained when the filtrate was diluted with water. The reduction product was recrystallized from 50% formic acid and dried in carbon dioxide.

Anal. Subs., 0.1874, 0.1705: CO_2 , 0.4162, 0.3785; H_2O , 0.0921, 0.0826. Calcd. for $C_{19}H_{14}O_6 + 3H_2O$: C, 60.61; H, 5.36. Found: C, 60.57, 60.55; H, 5.50, 5.42.

The colorless crystals of the reduction product lost three molecules of water when heated to 105–110° in a current of carbon dioxide.

Anal. Subs., 0.2206, 0.2075: loss of wt., 0.0316, 0.0299. Calcd. for $C_{19}H_{14}O_5 + 3H_2O$: H_2O , 14.37. Found: H_2O , 14.33, 14.41.

The analyses of the dried product gave results corresponding to the formula $C_{19}H_{14}O_5$.

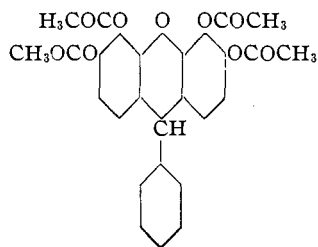
Anal. Subs. (dry), 0.1889, 0.1776: CO_2 , 0.4902, 0.4607; H_2O , 0.0737, 0.0698. Calcd. for $C_{19}H_{14}O_5$: C, 70.78; H, 4.38. Found: C, 70.77, 70.75; H, 4.36, 4.40.

When exposed to the air, this reduction product readily takes up oxygen and becomes red, due to the formation of pyrogallolbenzein.

The reduction product forms a colorless, crystalline tetra-acetate which melts at 225–226° to a red liquid.

Anal. Calcd. for $C_{19}H_9O_5(H)(COCH_3)_4$: C, 66.11; H, 4.52. Found: C, 66.18, 66.15; H, 4.63, 4.70.

The following structure is assigned to this compound.



Summary

The results of this investigation may be summarized as follows.

1. The condensation of pyrogallol and benzotrichloride to give pyrogallolbenzein is best brought about at the temperature of boiling water and under reduced pressure, instead of at 160°, as recommended by Doebner and Foerster. It has been shown that 2,3,4-trihydroxydiphenyl ketone is a by-product in this preparation of pyrogallolbenzein.

2. The formula $C_{38}H_{24}O_{11} + 5H_2O$, given to pyrogallolbenzein by Doebner and Foerster, is not correct. Analyses and molecular-weight determinations show that the formula is $C_{19}H_{12}O_5$.

3. Pyrogallolbenzein has basic properties, as is shown by the preparation of the hydrochloride, sulfate and perchlorate. These salts are colored compounds and may be represented as oxonium or carbonium salts.

4. Pyrogallolbenzein, its trisodium salt, trimethyl ether, triacetate, dibromo compound, the triacetate of the dibromo compound and the dinitro derivative are all colored compounds and have the quinoid structure. A colorless tetra-acetate and tetrabenzoate of the carbinol form of the benzein have been prepared.

5. The colorless reduction product of pyrogallolbenzein and its tetra-acetate have been prepared.