4. The benzoyl-benzoic acid formed by the condensation of hemipinic anhydride with *o*-cresol methyl ether proved not to be identical with the benzoyl-benzoic acid produced by condensing opianic acid with *o*-cresol methyl ether and oxidation of the product. This is further evidence that in hemipinic anhydride the carbonyl adjacent to the methoxyl group forms the ketone group in the benzoyl-benzoic acids.

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

PYROGALLOLBENZEIN AND ITS HYDROCHLORIDE

Preliminary Paper

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Pyrogallolbenzein was first made by Doebner and Förster[1] by heating pyrogallol with benzotrichloride. They give it the formula, $C_{38}H_{24}O_{11} + 5H_2O$. As it seemed probable from the work done in this Laboratory on gallein and on pyrogallol-sulfonephthalein that this formula was not correct, the work of these chemists has been repeated and it has been shown that the formula of pyrogallolbenzein is $C_{19}H_{12}O_5$.

Preparation of Pyrogallolbenzein.—A mixture of pyrogallol (2 molecular equivalents) and benzotrichloride (1 equivalent) was heated in a 1-liter distilling flask in a boiling water-bath until the evolution of hydrogen chloride stopped. The flask was then connected with a vacuum pump and the heating at the boiling point of water continued for about four hours longer. Water was then added and the mixture boiled to decompose the hydrochloride formed and remove the pyrogallol and benzotrichloride left. After repeatedly extracting the benzein with water until free from hydrochloric acid, it was filtered off, dried and purified by crystallization of its hydrochloride (see below). The dark red crystals of the *pure* hydrochloride were repeatedly boiled with water until all of the hydrochloric acid was removed. The benzein thus obtained was *crystalline*. It was recrystallized from a mixture of equal parts of 95% ethyl alcohol and benzene and the dark green crystals, which lost no weight when heated, were analyzed.

Anal. Subs., 0.1808, 0.1832, 0.1838: CO_2, 0.4723, 0.4778, 0.4799; H_2O, 0.0627, 0.0646, 0.0651. Calcd. for $C_{19}H_{12}O_5$: C, 71.24; H, 3.78. Found: C, 71.26, 71.15, 71.23; H, 3.88, 3.95, 3.96.

Pyrogallolbenzein does not melt, but begins to decompose at about 200°.

The benzein, purified by means of its hydrochloride as above described, was also recrystallized from methyl alcohol a number of times until the crystals were uniform. These crystals contained 3 molecules of water of

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[1] Doebner and Förster, *Ann.*, **257**, 61 (1890).

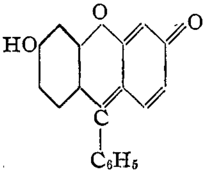
crystallization, which were driven off when the crystals were heated to 120° for 1.5 hours.

Anal. Subs., 0.2084, 0.2162: loss, 0.0302, 0.0314. Calcd. for $C_{19}H_{12}O_5 + 3H_2O$: H_2O, 14.44. Found: 14.49, 14.52.

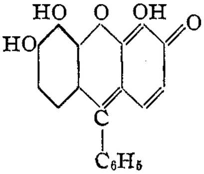
Subs. (dry), 0.1782, 0.1848: CO_2, 0.4647, 0.4826; H_2O, 0.0622, 0.0620. Calcd. for $C_{19}H_{12}O_5$: C, 71.24; H, 3.78. Found: C, 71.14, 71.25; H, 3.91, 3.75.

Doebner and Förster[1] crystallized their pyrogallolbenzein from glacial acetic acid, but it is quite evident from their analyses that they did not have a pure product.

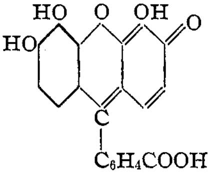
Pyrogallolbenzein resembles gallein[2] very closely in its properties and chemical conduct. Its structure is similar to that of resorcinolbenzein[3] and of gallein:[2]



Resorcinolbenzein



Pyrogallolbenzein



Gallein

Like gallein and resorcinolbenzein, pyrogallolbenzein combines very readily with hydrochloric acid to form a well-crystallized hydrochloride.

Hydrochloride.—Ten g. of the crude benzein was suspended in 500 cc. of methanol and the mixture heated to boiling on a steam-bath. Thirty cc. of concd. hydrochloric acid was added, when the benzein dissolved as the hydrochloride. The solution was filtered and about two-thirds of the methanol was distilled. On cooling, well-formed, red crystals of the hydrochloride separated. These were recrystallized four or five times in this manner from methanol and then analyzed for chlorine by the Parr bomb method.

Anal. Subs., 0.1630, 0.1851, 0.1773, 0.1901: AgCl, 0.0572, 0.0637, 0.0620, 0.0655. Calcd. for $C_{19}H_{12}O_5 + HCl + 3H_2O$: Cl, 8.63. Found: 8.68, 8.50, 8.65, 8.52.

When dried at 110° this hydrochloride lost 3 molecules of water.

Anal. Subs., 0.6927, 0.2908: loss, 0.0910, 0.0382. Calcd. for $C_{19}H_{12}O_5 + HCl + 3H_2O$: H_2O, 13.16. Found: 13.14, 13.14.

It was impossible to dry the hydrochloride at this temperature without driving off a trace of the acid.

As the hydrochloride is completely hydrolyzed by boiling with water, it was analyzed by boiling about 0.3 g. with a liter of water, filtering off the benzein, washing it with water until free from hydrochloric acid, drying it at 105–110° and weighing it.

Anal. Subs., 0.3060, 0.3320: loss, 0.0686, 0.0726. Calcd. for $C_{19}H_{12}O_5 + HCl + 3H_2O$: $HCl + 3H_2O$, 22.04. Found: 22.42, 21.87.

In the second analysis the hydrochloric acid was determined as silver chloride.

Anal. Subs., 0.3320: AgCl, 0.1141. Calcd. for $C_{19}H_{12}O_5 + HCl + 3H_2O$: Cl, 8.63. Found: 8.51.

The anhydrous hydrochloride was made by treating the benzein crystallized from

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[2] Orndorff and Brewer, *Am. Chem. J.*, **46**, 97 (1901).

[3] Kehrmann and Loth, *Ber.*, **47**, 2271 (1914). Pope, *J. Chem. Soc.*, **105**, I, 251 (1914).

ethanol and benzene with dry hydrogen chloride. The hydrochloride was allowed to stand in a desiccator with solid sodium hydroxide until it came to constant weight and was then analyzed.

Anal. Subs., 0.3449: wt. of HCl absorbed, 0.0389. Calcd. for $C_{19}H_{12}O_5$ + HCl: HCl, 11.39. Found: 11.28.

Anal. Subs., 0.2746: AgCl, 0.1094. Calcd. for $C_{19}H_{12}O_5$ + HCl: Cl, 9.94. Found: 9.86.

This hydrochloride is very hygroscopic and did not melt when heated to 300°.

Professor Vieweg of the Department of Geology has kindly furnished the following description of the crystals.

Pyrogallolbenzein from Methanol.—This forms irregularly shaped crystals, somewhat resembling fuchsin in appearance. They show a yellow-green surface color and in smaller fragments transmit a red-orange color.

Pyrogallolbenzein from Alcohol and Benzene.—This material is a crystalline powder very similar to the pyrogallolbenzein from methanol. The surface color is also yellow-green, but the transmission color in thin pieces is a purple-red.

Pyrogallolbenzein Hydrochloride from Methanol.—This substance forms in bladed crystals. They show a steel blue surface color. Most of the crystals are too thick to be translucent, but in thin sections they transmit a red-brown color.

Summary

It has been shown in this paper that the formula, $C_{38}H_{24}O_{11} + 5H_2O$, given to pyrogallolbenzein by Doebner and Förster is not correct. When crystallized from ethyl alcohol and benzene, pyrogallolbenzein has the formula $C_{19}H_{12}O_5$. When crystallized from methyl alcohol, it contains 3 molecules of water of crystallization and has the formula $C_{19}H_{12}O_5 + 3H_2O$. A well-crystallized hydrochloride having the formula $C_{19}H_{12}O_5 + HCl + 3H_2O$ has been obtained. It has also been shown that pyrogallolbenzein combines with dry hydrogen chloride to form a hydrochloride having the formula, $C_{19}H_{12}O_5 + HCl$. The structure of pryogallolbenzein is similar to that of resorcinolbenzein and of gallein.

ITHACA, NEW YORK

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