Anal. Calcd. for $C_8H_6O_5NAsClNa_3 + 8H_2O$: N, 2.69; As, 14.43; H_2O of cryst., 27.71. Found: N, 3.12; As, 14.27; H_2O of cryst., 27.84.

Summary[5]

Improvements have been suggested for the preparation and purification of 3-amino-4-hydroxy-phenylarsonic acid and its acetyl derivative. New compounds have been described which result from the interaction of this acid with lower member fatty acid anhydrides such as formyl, propionyl, butyryl and chloro-acetyl derivatives and their salts.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE BAKER CHEMICAL AND THE ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF RESORCINOL-BENZEIN[1]

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A brief outline of our experimental method and procedure has already been given in an article on the Absorption of Benzaurin.[3] As there explained, it is not always feasible to plot all of the observed points, but in drawing the curves, we have been guided as in the previous paper by all of the observations available.

As resorcinol-benzein[4] is the mother substance of fluorescein, sulfonefluorescein and of the other phthaleins containing a pyrone ring, it was thought highly desirable to study its absorption spectrum in order to compare it with that of fluorescein itself. A preliminary report upon the absorption of resorcinol-benzein in the visible region only has been made by Medhi and Watson.[5] Since they did not make quantitative measurements and since they report contradictory evidence of the existence of certain absorption bands, it is difficult to compare their data with those given below. Moir[6] has also published some results obtained in the visible region,

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[5] This paper was presented at the meeting of the American Chemical Society, at Baltimore, April, 1925.

[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled us to make the measurements described in this report is gratefully acknowledged.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–25.

[3] THIS JOURNAL, **47**, 2767 (1925). Unfortunately an error appears in our previous article. The curves for Figs. 4 and 5, pp. 2774 and 2775, should be interchanged leaving the caption beneath each on the same page as it there appears.

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

[5] Medhi and Watson, *J. Chem. Soc.*, **107**, 1579 (1915).

[6] Moir, *Trans. Roy. Soc. S. Africa*, **7**, 5 (1918).

without the use of a spectrophotometer, on solutions of resorcinol-benzein in aqueous alkali and in concd. sulfuric acid.

Resorcinol-benzein was made and purified by the method of Kehrmann and Dengler.[7] The benzein was dried at 140° and analyzed by Mr. C. Wang with the following result.

Anal. Subs., 0.2067, 0.2215, 0.2168: CO_2, 0.6139, 0.6574, 0.6441; H_2O, 0.0785, 0.0836, 0.0835. Calcd. for $C_{19}H_{12}O_3$: C, 79.15; H, 4.20. Found: C, 79.18, 79.13, 79.20; H, 4.25, 4.22, 4.31.

Our product did not lose one molecule of water when heated to 140° as reported by Meyer and Gerloff.[8] It was well crystallized and melted at 328–329° in a sealed tube. Kehrmann and Dengler[9] assign an *ortho*quinoid formula to resorcinol-benzein, but as this formula is not in accord with all the facts,[10] and as the *para*quinoid formula is more generally accepted, we prefer to use the latter formula in this article.

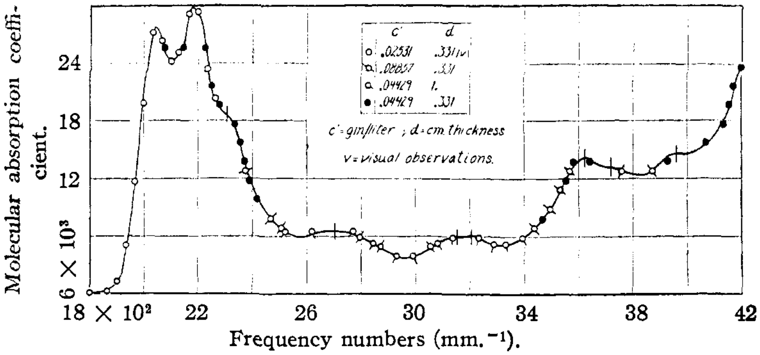

Fig. 1.—Resorcinol-benzein in neutral alcoholic solution.

Fig. 1 gives the absorption curve for resorcinol-benzein in absolute ethyl alcohol. It will be noted that there are nine absorption bands, two in the visible region (at frequency numbers 2040 and 2183) and the others in the ultraviolet. The curve is more complex than that for phenol-benzein (benzaurin)[3] as might be expected from the presence of the pyrone ring in resorcinol-benzein. Attention should also be called to the fact that the color of the alcoholic solution of resorcinol-benzein does not fade on standing as does that of benzaurin. Crystallized resorcinol-benzein has a brick-red color, but its dilute solution in alcohol is yellow with an orange tint and a slight, greenish fluorescence. Its absorption spectrum as well as its chemical conduct indicates that it has the quinoid structure.

In Fig. 2 is shown the effect of the addition of different amounts of dry hydrogen chloride gas to the alcoholic solution of resorcinol-benzein. The type of curves is entirely different from that of resorcinol-benzein in

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[7] Kehrmann and Dengler, *Ber.*, **42**, 873 (1909).

[8] Meyer and Gerloff, *Ber.*, **57**, 591 (1924).

[9] Kehrmann and Dengler, *Ber.*, **41**, 3440 (1908).

[10] See Kropp and Decker, *Ber.*, **42**, 578 (1909); and Pope and Howard, *J. Chem. Soc.*, 97, 1023 (1910); 99, 545 (1911).

neutral alcohol, showing that a chemical change has taken place, namely, the formation of a hydrochloride. This is also shown by the disappearance of the slight, greenish fluorescence of the neutral alcoholic solution of resorcinol-benzein. F. G. Pope[4] has made and analyzed the hydrochloride of resorcinol-benzein. A study of the curves shows that the band at 2040 in the neutral alcoholic solution of resorcinol-benzein (see Fig. 1) persists on the addition of four and of twenty-three molecules of hydrogen chloride, but has disappeared in Curve C for 234 molecules of the acid. The bands at frequency numbers 3152 and 3624 of the neutral alcoholic solution of resorcinol-benzein do not completely disappear in the solution containing four molecules of hydrogen chloride, although they are absent from the solutions of a higher concentration. New bands have appeared at frequency numbers 2243, 2871, 3394, 3820 and 3991 (see Curve C, Fig. 2). The last two bands in the ultraviolet (3820 and 3991) are very characteristic of the salts of resorcinol-benzein and its derivatives with the acids, analogous bands being found in the concd. sulfuric acid solution of resorcinol-benzein (see Fig. 3) and in solutions of fluorescein, sulfonefluorescein and eosin in acid (unpublished data). They may be ascribed to the presence of the pyrone ring in these substances, as similar bands do not occur in the curves representing the absorption of benzaurin[3] and of phenolphthalein in acids.

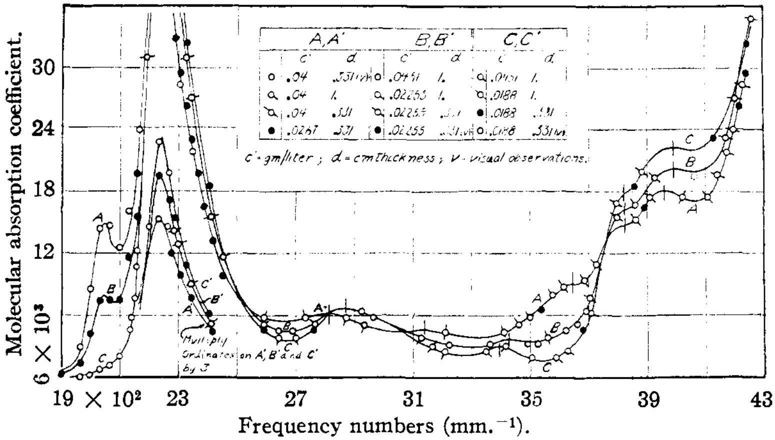

Fig. 2.—Resorcinol-benzein in alcoholic HCl solution.
A,A'—1 molecule : 4 molecules of HCl.
B,B'—1 molecule : 23 molecules of HCl.
C,C'—1 molecule : 234 molecules of HCl.

Fig. 3 gives the curves for resorcinol-benzein in solution in 93% sulfuric acid and in 5% aqueous potassium hydroxide, the curves being given on one plate to bring out their differences and resemblances and so that they may be compared with the curves for benzaurin[3] in the corresponding solvents. The solution in concd. sulfuric acid has a lemon-yellow color with a slight, greenish fluorescence, the solution in potassium hydroxide is yellow-orange with a very marked, greenish fluorescence. The type of the curves is very different from that of the neutral alcoholic solution of resorcinol-benzein, showing again that a chemical change has taken place, in the one case a sulfate is formed, in the other a potassium salt.[11] Attention should be called to the two characteristic bands in the ultraviolet (in this case at frequency numbers 3911 and 3988) in the curve for the sulfuric acid solution of resorcinol-benzein, due we believe to the formation of the sulfate just as the bands at 3820 and 3991 in Curve C, Fig. 2 are due to the formation of a hydrochloride. The curve for the sulfuric acid solution of resorcinol-benzein is more complex than that for benzaurin[3] in the same solvent, due we believe to the presence of the pyrone ring.

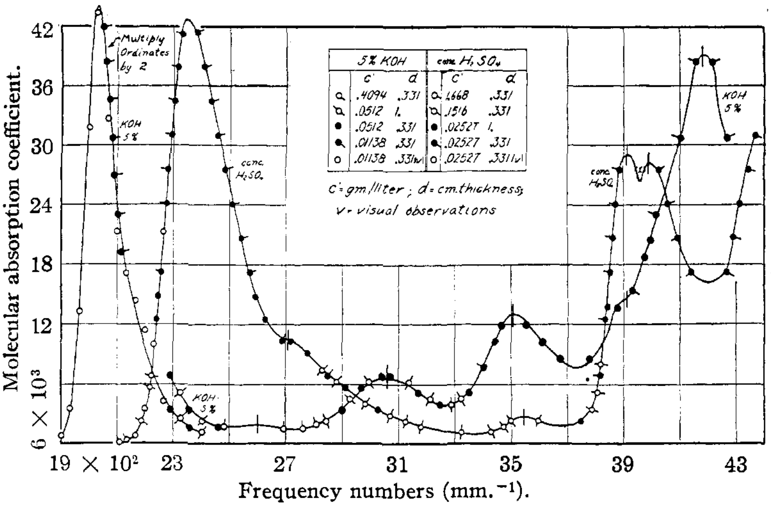

Fig. 3.—Resorcinol-benzein in concd. (93%) sulfuric acid. Resorcinol-benzein in aqueous 5% KOH solution.

The curve for the solution of resorcinol-benzein in 5% potassium hydroxide solution is of an entirely different type from that of the neutral alcoholic solution of the same substance due to the formation of a potassium salt, as resorcinol-benzein itself is insoluble in water. It was impossible to dissolve resorcinol-benzein in a more concentrated solution of potassium hydroxide owing to the fact that it is insoluble in alkaline solutions stronger than 5% and the addition of strong alkali solution to the 5% potassium hydroxide solution of resorcinol-benzein precipitates the potassium salt. The two most pronounced bands in the 5% potassium hydroxide solution are the very intense one entirely in the visible at fre-

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[11] Pope (Ref. 4) has made and analyzed the sodium and barium salts of resorcinol-benzein.

quency number 2031 and the intense one in the extreme ultraviolet at frequency number 4180. The absorption in the aqueous alkali is analogous to that in an alcoholic solution of potassium hydroxide (see Fig. 4), but there is a slight displacement of the bands due to the fact that water is the solvent in the one case and alcohol in the other. The absorption curve of resorcinol-benzein for the solution in 5% potassium hydroxide is somewhat similar to the corresponding one for benzaurin,[3] as will be seen by a comparison of the curves.

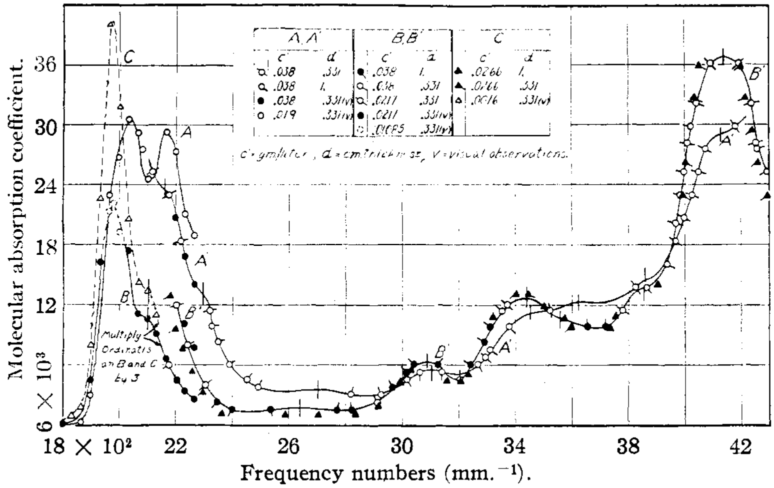

Fig. 4.—Resorcinol-benzein in alcoholic KOH solution.
A,A'—1 molecule : 1 molecule of KOH.
B,B'—1 molecule : 2 molecules of KOH.
C—1 molecule : 20 molecules of KOH

Fig. 4 gives the absorption curves for resorcinol-benzein in alcoholic solutions of potassium hydroxide. Curves A and A′ represent solutions containing one molecule of potassium hydroxide to one of resorcinol-benzein. The solution used in determining the A′ curve was so highly absorbing in the visible part of the spectrum that it had to be diluted with alcohol to enable us to determine the absorption in this region. It will be noted that this addition of alcohol brings about almost complete reversion to the absorption curve for the neutral alcoholic solution (see Fig. 1) thus failing to follow Beer's law. It is interesting to note that this effect of dilution was not noticeable in the case of the alcoholic hydrogen chloride solutions, indicating that the basic properties of resorcinol-benzein are more pronounced than the acid properties. Had it been possible to measure the absorption in the visible of the solution used to determine the curve A′, there is every reason to believe that the band at 2040 would not have appeared and we should have found a band corresponding to the one at

1980 in the solution containing a *higher concentration* of the potassium hydroxide. The addition of the alcohol removes the potassium from the potassium salt of resorcinol-benzein and replaces it with hydrogen, thus regenerating resorcinol-benzein which gives its characteristic spectrum. In the A′ curve the bands at 2160, 2295, 2702 and 3625 are evidently remnants of the corresponding bands of resorcinol-benzein in neutral alcoholic solution, while the bands at 3103, 3452, 3860 and 4128 are new ones as they also occur in the higher concentrations of the potassium hydroxide. The addition of two molecules of potassium hydroxide to one of resorcinol-benzein produces an almost complete change to the characteristic alkaline absorption (see Curves **B** and **B**′). However, the visible band at 1980 is still affected by dilution, the dash portion of the curve obtained with a solution containing 0.01085 g. per liter being probably lower than would have been obtained by the higher concentration (0.0217 g. per liter). The further addition of potassium hydroxide to 20 molecules produces no appreciable change in the ultraviolet region with the exception

TABLE I

FREQUENCY NUMBERS OF ABSORPTION BANDS OF RESORCINOL-BENZEIN

In neutral abs. alc.		In alc. HCl		In concd. H_2SO_4
	4 *m.*	23 *m.*	234 *m.*	
2040	2051	2044		
2183				
	2235	2241	2243	
2307				2349
2704				2709
	2814	2869	2871	
3152	3139			
3205				
		3428	3394	3545
3624	3647			
3718				
	3826	3825	3820	3911
3960	3958	3992	3991	3988
In neutral abs. alc.		**In alc. KOH**		**In 5% aq. KOH**
	1 *m.*	**2 *m.***	**20 *m.***	
	(1980)?	1980	1980	2031
2040	(2040)			
2183	2160	2102	2105	
2307	2295			
2704	2702	2639	2639	2601
3152	3103	3085	3083	3061
3205				
	3452	3440	3430	3507
3624	3625	3560		
3718				
	3860	3854	3863	3912
3960				
	4128	4137	4129	4180

of the disappearance of the weak band at 3560 (which may be only a remnant of the neutral band at 3624). No attempt has been made to draw in this part of the curve for 20 molecules of potassium hydroxide, as it lies so close to the curve for two molecules of the alkali and in fact is identical with it in some portions. In the visible region of the curve, however, the addition of 20 molecules of the alkali has increased the absorption tremendously, the molecular absorption coefficient at 1980 rising to a maximum of 120×10^3. However, dilution effects are still appreciable, a rough estimate of the absorption of a more concentrated solution (0.0133 g. per liter) giving a value of the absorption coefficient of over 144×10^3. This portion of the curve has, therefore, been drawn in with a broken line.

Summary

1. The absorption curves of solutions of resorcinol-benzein in absolute ethyl alcohol, in alcoholic hydrochloric acid, in aqueous and in alcoholic potassium hydroxide and in concd. (93%) sulfuric acid have been determined.

2. When hydrogen chloride gas is added to the alcoholic solution of resorcinol-benzein, the absorption curves are of an entirely different type from that obtained with the neutral alcoholic solution, due to the formation of the hydrochloride of resorcinol-benzein.

3. The absorption curve of resorcinol-benzein in concd. (93%) sulfuric acid is similar to that obtained when hydrochloric acid is added to the neutral solution of resorcinol-benzein and indicates the formation of the sulfate of resorcinol-benzein.

4. The absorption curve of resorcinol-benzein in 5% aqueous potassium hydroxide is entirely different from that of the neutral alcoholic solution of resorcinol-benzein, indicating the formation of the potassium salt of resorcinol-benzein.

5. The absorption curves for resorcinol-benzein in solutions of potassium hydroxide in alcohol are similar to that obtained with the aqueous alkaline solution.

6. A table of frequency numbers indicating the positions of the maxima of the absorption bands of resorcinol-benzein in the various solvents is given.

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