in hexane solution, which agrees substantially with our results for an alcoholic solution.

Summary

1. The absorption curves of diphenylmethane and diphenyl carbinol, and of triphenylmethane, triphenyl carbinol and triphenylmethyl chloride in neutral absolute alcohol solution have been determined and their relations discussed.

2. A table has been prepared, showing the frequency numbers of the peaks of the absorption bands of the various substances studied.

ITHACA, NEW YORK

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

THE ABSORPTION SPECTRA OF FUCHSONE, BENZAURIN AND AURIN[1]

BY W. R. ORNDORFF, R. C. GIBBS, S. ALICE MCNULTY[2] AND C. V. SHAPIRO[3]

RECEIVED DECEMBER 27, 1926 PUBLISHED JUNE 7, 1927

In continuation of our work on the absorption spectra of triphenylmethane derivatives,[4] we are reporting now on fuchsone, *p*-hydroxytriphenyl carbinol and aurin, together with some further data on benzaurin.[4a] Fuchsone has been investigated by Meyer and Fischer,[5] who found two bands in its neutral alcoholic solution at frequency numbers (estimated from their curves) 2630 and 3850. Schlenk and Marcus[6] and Hantzsch[7] each located but one band in the neighborhood of 2600. Aurin has been studied by Hartley,[8] whose data indicate three bands at 2640, 2800 and 3700 in the neutral solution. However, none of these investigators have made any study of the fading of neutral alcoholic solutions of fuchsone and aurin which have been allowed to stand for some time in the dark. Ghosh and Watson[9] have reported two bands in the visible region at frequency numbers 1830 and 2000 for an alkaline solution of aurin.

---

[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, 1921–1923. (Now Mrs. H. F. Vieweg.)

[3] Heckscher Research Assistant in Physics and Chemistry, Cornell University, **1923–1926.**

[4] (a) Orndorff and co workers, THIS JOURNAL, **47**, 2767 (1925); (b) **48**, 1327; (c) 1994 (1926); (d) **49**, 1541 (1927).

[5] Meyer and Fischer, *Ber.*, **46**, 70 (1913).

[6] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[7] Hantzsch, *Ber.*, **52**, 509 (1919).

[8] Hartley, *J. Chem. Soc.*, **51**, 152 (1887).

[9] Ghosh and Watson, *ibid.*, **111**, 815 (1917).

Fuchsone was prepared by Dr. Snow[10] by dehydrating yellow *p*-hydroxytriphenyl carbinol[11] at 95°, and was recrystallized first from benzene and ether, and then from acetone. Its melting point was 166–167°. Aurin was prepared by the condensation of carbon tetrachloride and phenol,[12] and after purification it was recrystallized from acetone.

Fuchsone dissolves in alcohol with a bright yellow color which gradually fades to a pale yellow. Gomberg[13] has shown that fuchsone readily takes up a molecule of water to form the quinoid hydrate, which can be recrystallized from 50% acetic acid as a yellow compound. The quinoid hydrate is unstable in alcoholic solution, going over partially to the white form, *p*-hydroxytriphenyl carbinol. This change is only complete in the presence of ammonium hydroxide. Hence a neutral alcoholic solution of fuchsone, after standing for some time, contains an equilibrium mixture of the quinoid hydrate and the carbinol, a fact which is strikingly brought out by the absorption curves of these several compounds. Aurin dissolves in alcohol with a deep orange color, which rapidly fades to a paler shade of orange. The evidence from its absorption curves indicates that it, too, takes up a molecule of water and goes over to quinoid hydrate and carbinol forms.

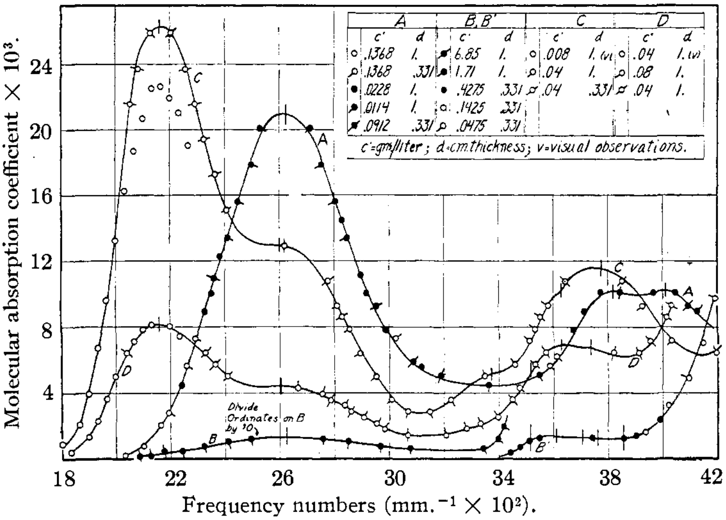

Fig. 1.—Neutral absolute alcohol solution. *A*, fuchsone; *B,B'*, solution A after standing for three months; *C*, aurin; *D*, solution C after standing for four days.

Fig. 1 gives the absorption curves for the fresh and faded solutions of

---

[10] Heckscher Research Assistant, Cornell University, **1922**.

[11] Gomberg and Jickling, This Journal, **37**, 2575 (1915).

[12] Gomberg and Snow, *ibid.*, **47**, 198 (1925).

[13] Gomberg, *ibid.*, **35**, 1035 (1913).

fuchsone and aurin in neutral, absolute alcohol. Curve *A* shows the absorption of a freshly prepared solution of fuchsone and is characterized by the presence of three bands at frequency numbers 2625, 3820 and 4012. After standing for three months, its absorption (Curve *B*,*B'*) has decreased considerably and there is a marked change in the character of the absorption in the further ultraviolet. The band at 2625 still remains, although its intensity is but $^1/_{150}$th of the original, while an entirely new set of bands has appeared at 3515, 3610, 3707, 3761 and 3855. These five bands are identical in intensity and position with the bands for both the yellow quinoid hydrate and the colorless *p*-hydroxytriphenyl carbinol (see Fig. 3, where the ordinates have been multiplied by 10 in order to bring out the detail of these absorption bands). Curve *A* on Fig. 1 thus represents the absorption of fuchsone proper, while Curve *B*,*B'* represents the equilibrium mixture of the two hydrated forms. Similarly for aurin, Curve *C* shows the absorption of the freshly prepared solution, with bands at 2160, 2600, 3372, 3628 and 3777, which are characteristic of aurin in the quinoid state, while Curve *D* represents the same solution after four days. The first two bands at 2160 and 2600 are unchanged in position but have only one-fourth and one-half, respectively, of their original intensity. The band at 3372 has completely disappeared while, further in the ultraviolet, new bands have appeared at 3524, 3628 and 3736. The latter are ascribed to the presence of the quinoid hydrate and carbinol forms of aurin.

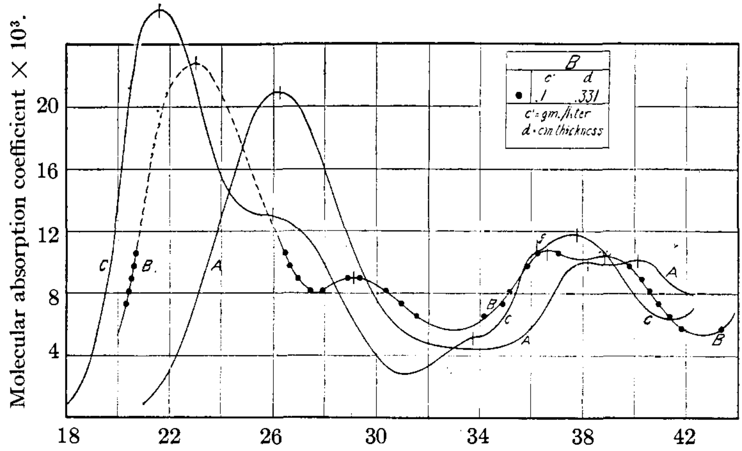

Fig. 2.—Fresh neutral alcohol solution. *A*, fuchsone; *B*, benzaurin; *C*, aurin.

Our previous report[4a] on benzaurin showed that the absorption curves for the fresh and faded alcoholic solutions were entirely parallel. Further experimentation with benzaurin now indicates that the preliminary change

—the assumption of a molecule of water to form the quinoid hydrate—proceeds with great rapidity, while the succeeding change, which involves the setting up of an equilibrium between the quinoid hydrate and carbinol forms, is a much slower process. By working at the utmost speed compatible with obtaining accurate results, it was found that a fresh solution of benzaurin possessed absorption entirely analogous to that of a fresh solution of fuchsone. Fig. 2 gives the absorption curves for the fresh solutions of fuchsone, benzaurin and aurin. On Curve *B* for benzaurin, the upper part of the band at 2300 is drawn in with a broken line on the assumption that it lies intermediate between fuchsone and aurin, since attempts to obtain further data on this portion of the curve were fruitless, due to the almost instantaneous fading of the solution at the lower concentrations. It is evident that as hydroxyl groups are introduced, the absorption spectrum becomes more complex; thus, fuchsone, benzaurin and aurin have, respectively, three, four and five bands each in their fresh alcoholic solutions.

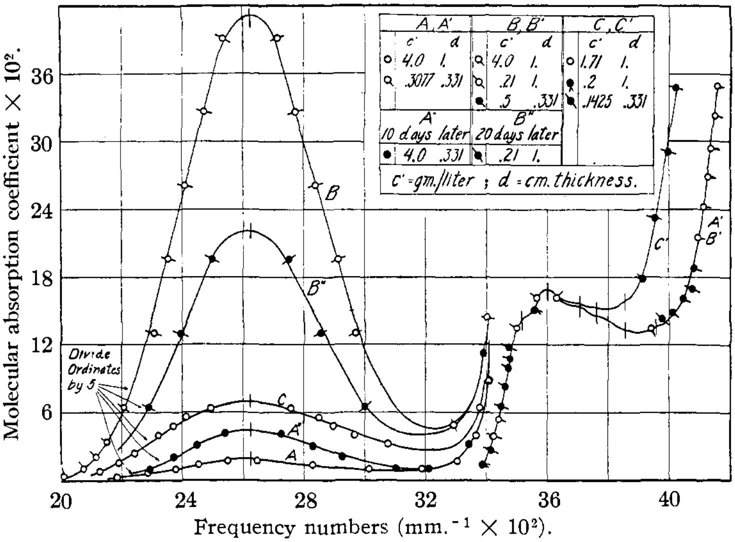

Fig. 3.—Neutral absolute alcohol solution. *A,A'*, *p*-hydroxytriphenyl carbinol, white form; *A"*, solution A after standing for 10 days; *B,B'*, *p*-hydroxytriphenyl carbinol, yellow form; *B"*, solution B after standing for 20 days; *C,C'* fuchsone after standing for three months.

Since fuchsone changes over in alcoholic solution to an equilibrium mixture of the quinoid hydrate and carbinol forms, it should be possible, by starting with either one of these forms, to arrive at the same equilibrium. The yellow and white forms of *p*-hydroxytriphenyl carbinol were prepared by the method of Gomberg[13] and purified by recrystallization. The colorless form of the *p*-hydroxytriphenyl carbinol dissolves in alcohol with a very *pale yellow* color, which at once begins to increase in intensity. The yellow form dissolves with a *very bright* yellow color, which then begins to fade fairly rapidly. The absorption of the freshly prepared solutions and of the same solutions after they had stood several days is shown in Fig. 3. The changes in intensity of the band at 2625 corroborate in a striking manner the theory postulated above. Curve *A* for the fresh solution of the colorless form goes over in ten days to Curve *A″*, while Curve *B* for the fresh solution of the yellow form changes over to Curve *B″* in 20 days. Intermediate between these two sets of curves lies the curve for the faded solution of fuchsone, Curve *C*. From the relative positions of these curves, it is estimated that the equilibrium mixture contains approximately 13% of the yellow form and 87% of the colorless.

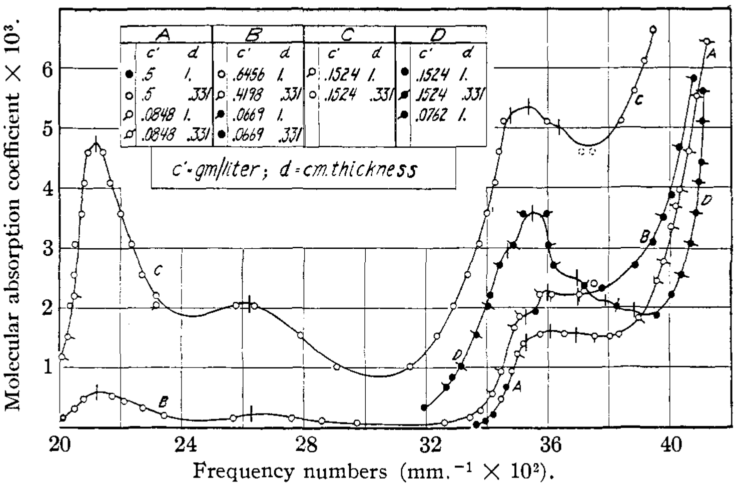

Fig. 4.—Fuchsone in alcoholic HCl solution. Fuchsone:HCl, *A*, 1:5; *B*, 1:1000; *C*, 1:10,000; *D*, solution *C* after standing for three days.

In the further ultraviolet, both forms give identical absorption. Curve *C′* for the faded solution of fuchsone coincides with the curve for the carbinol forms up to frequency number 3650, after which it exhibits a constantly increasing intensity of absorption with respect to *A′*,*B′*, resulting in the apparent wiping out of the band at 3956. A comparison of the bands for *p*-hydroxytriphenyl carbinol and for triphenyl carbinol (see Fig. 9) indicates that the set of bands for the former is shifted bodily toward the red.

Fig. 4 shows the effect of adding various amounts of dry hydrogen chloride gas to a solution of fuchsone in absolute alcohol. The presence of five molecules of hydrogen chloride to one of fuchsone, Curve *A*, and of 1000 molecules, Curve *B*, yields absorption similar to that of faded neutral solutions of fuchsone, with some increase in intensity. With the addition of 10,000 molecules of hydrogen chloride, Curve *C*, the solution becomes intensely yellow, as indicated by the strong increase in absorption at 2120 and 2625. Further in the ultraviolet, the absorption has also increased greatly, while the bands have shifted toward lower frequency numbers, their locations now being 3478, 3537 and 3637. On standing for three days, the solution became entirely colorless and its absorption is represented by Curve *D*. There are now five bands in the ultraviolet at 3468, 3549, 3696, 3789 and 3885, which no longer correspond to the bands in faded fuchsone. However, as in the case of benzaurin in alcoholic solution containing a large amount of hydrogen chloride,[4a] reduction has probably taken place with the formation of the hydroxytriphenylmethane or its ethyl ether. These five bands closely resemble

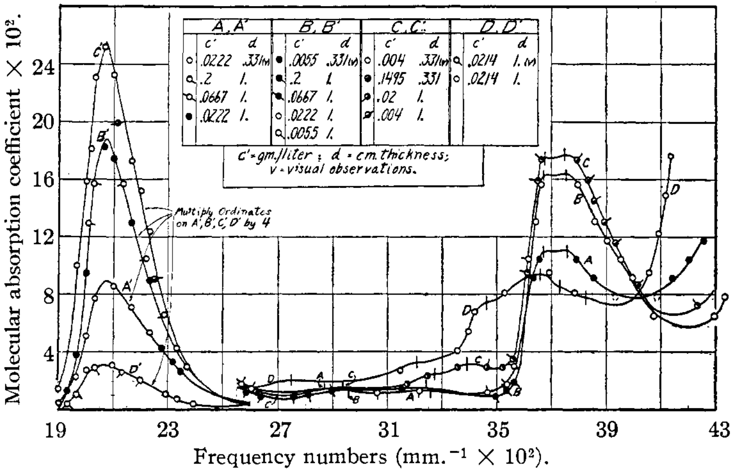

Fig. 5.—Aurin in alcoholic HCl solution. Aurin:HCl, *A,A'*, 1:16; *B,B'*, 1:329; *C,C'*, 1:10,000; *D,D'*, solution C after standing for four months.

the five bands that are found in di-*p*-dihydroxytriphenylmethane[4a] (see Fig. 9). The first effect of the hydrogen chloride is apparently to increase the velocity of the change from fuchsone to the equilibrium mixture of quinoid hydrate and carbinol.[13] With more hydrogen chloride, salt formation takes place and finally at very high concentrations of hydrogen chloride, reduction occurs.

Fig. 5 represents the absorption of aurin with various ratios of hydrogen chloride in alcoholic solution. A solution containing 16 molecules of hydrogen chloride to one of aurin is yellow in color and shows bands Curve *A,A'*, at 2075, 2869, 3257, 3671 and 3759. Increasing the ratio of hydrogen chloride to 329 molecules, Curve *B,B'*, results in a general increase in absorption throughout the spectrum, with the bands now at 2075, 2958, 3241, 3671 and 3755. A further addition of hydrogen chloride to 10,000 molecules, Curve *C,C'*, increases the absorption markedly at 2075 with only slight changes in intensity in the ultraviolet and the bands are now located at 2938, 3272, 3390, 3675 and 3746. On allowing this solution to stand, it faded very gradually, but even after four months it had not become entirely colorless.[14] Its absorption, Curve *D,D'*, shows that the band at 2075 has decreased to one-eighth its original intensity, while marked changes in the character of the absorption in the ultraviolet have occurred. The two bands in the neighborhood of 3675 and 3746 have disappeared and in their place we find three bands at 3659, 3732 and 3826, recalling the type of bands found in the faded alcoholic hydrochloric acid solutions of fuchsone and benzaurin.[4a] Aurin is apparently more stable than these two, and less susceptible to reduction under similar circumstances. Unlike these two, also, aurin appears to form a hydrochloride readily at the lowest concentration of hydrogen chloride used, namely, 16 molecules.

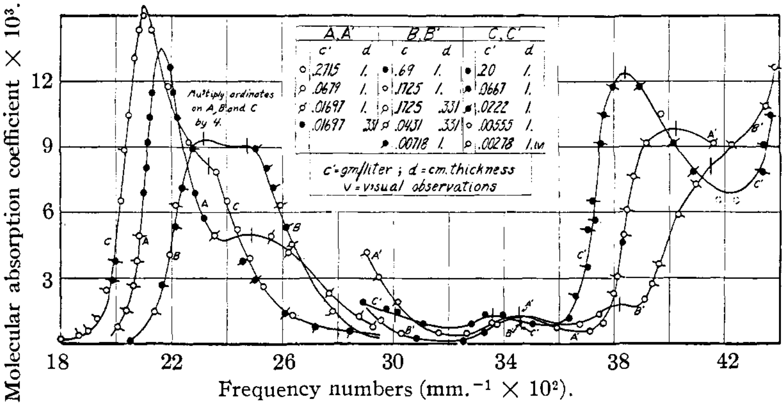

Fig. 6.—Concentrated (93%) sulfuric acid solution. *A,A'*, fuchsone; *B,B'*, triphenyl carbinol; *C,C'*, aurin.

Fig. 6 shows the absorption curves for triphenyl carbinol, fuchsone and aurin in concd. sulfuric acid. Triphenyl carbinol dissolves in concd. sulfuric acid with a yellow color, and its absorption (Curves *B,B'*) shows two bands near the visible region at 2318 and 2476. There are bands at 3460 and 3820 and a weak shoulder at 4150. Fuchsone gives a bright yellow solution in concd. sulfuric acid, which exhibits absorption bands (Curves *A,A'*) at 2165, 2490, 3455 and 4025 while aurin, which dissolves with an orange-yellow color, has absorption bands (Curves *C,C'*) at 2100, 2335, 3006, 3360, 3463 and 3842. It is apparent from a study of the absorption curves of these three substances and that of benzaurin[4a] in concd. sulfuric acid, that the presence of the benzenoid state in triphenyl carbinol clearly differentiates itself from the quinoid condition

---

[14] We shall continue to observe the absorption of this solution from time to time and will report upon its behavior later.

as it exists in the other three compounds. This is even more evident from Fig. 9 which gives a schematic diagram of the absorption bands of all of these related compounds. It will be seen that the bands for fuchsone, benzaurin and aurin uniformly follow Hartley's law, that is, with increasing molecular weight there is a steady shifting of the bands toward the red, while triphenyl carbinol gives bands which do not fall in line with this regularity. While it is generally assumed that in quinoid substances like fuchsone the quinoid oxygen carries basic properties, thus giving rise to *oxonium* salts, Baeyer[15] has suggested that triphenyl carbinol forms a colored *carbonium* salt in concd. sulfuric acid. This distinction appears to be confirmed by the evidence at hand. Attention may also be called to the fact that with the first three compounds, the addition of successive hydroxyl groups results in the appearance of more bands; fuchsone has four, benzaurin five and aurin six.

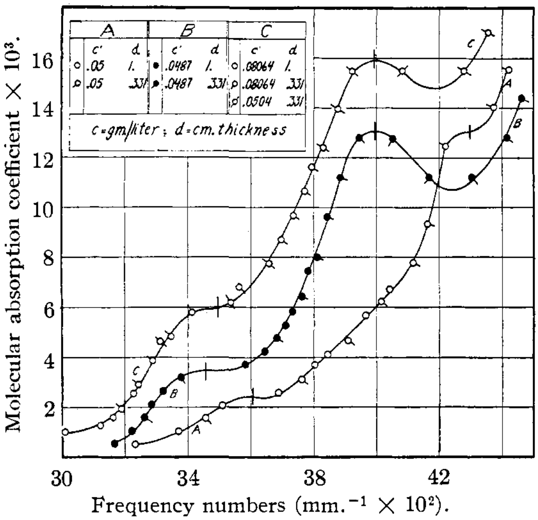

Fig. 7.—Fuchsone in alcoholic KOH solution. *A*, 1 molecule : 2 molecules of KOH; *B*, 1 molecule : 50 molecules of KOH; C, 1 molecule : 325 molecules of KOH.

Fig. 7 shows the absorption curves for solutions of fuchsone in absolute alcohol containing various amounts of potassium hydroxide. Curve *A* for a ratio of two molecules of potassium hydroxide to one of fuchsone shows bands at 3605 and 4298. Increasing the ratio of potassium hydroxide to 50 and 325 molecules results in a general increase of absorption and a shift of the bands, first to 3455 and 3995 and then with the higher ratio of potassium hydroxide to 3496 and 3993. Since all three of these solutions are colorless, there seems to be a fair indication that the

---

[15] Baeyer, *Ber.*, **38**, 569, 1156 (1905).

fuchsone goes over in alkaline solution to the carbinol form with the formation of the potassium salt.

Fig. 8 shows the absorption of aurin in alcoholic solutions containing various amounts of potassium hydroxide and in concentrated aqueous potassium hydroxide. At low ratios of potassium hydroxide to aurin in alcoholic solution, the type of absorption curve obtained depends on the exact method that is followed in the preparation of the solution. If the necessary amount of potassium hydroxide in alcohol be added to an aurin solution of the proper dilution and the absorption of the resulting solution determined, a curve is obtained which is consistent in its general features with the type of curve found for higher ratios of potassium hydroxide. Thus, Curve *A*,*A*′ for four molecules of potassium hydroxide shows two bands at frequency numbers 1865 and 3560, and a shoulder at 2000. If, however, the required amount of potassium hydroxide be added to a more concentrated solution of aurin and the resulting alkaline solution then diluted with alcohol to bring it down to a concentration where it could be photographed, the absorption curve so obtained is invariably of the type shown in broken lines on Curve *B*,*B*′. There are in this case four bands at 1810, 2400, 3230 and 3590. This peculiar phenomenon was checked several times and, although the absorption was very sensitive to change in absolute intensity, the bands still reappeared in the same unexpected positions. Possibly the second procedure furnishes a more favorable condition for reversion to the neutral type of absorption than does the first. Reversions of this character have been very definitely found in alcoholic alkaline solutions of resorcinolbenzein[4b] and phenolphthalein.[4c] Increasing the ratio of potassium hydroxide to 11.4 molecules, Curve *C*,*C*′, produces absorption similar to that for four molecules,

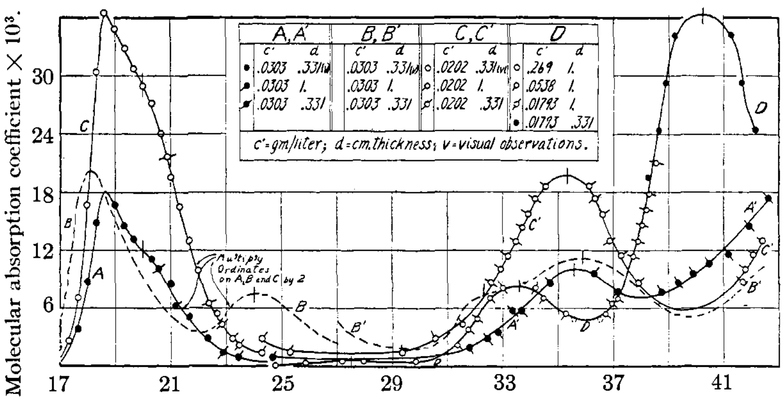

Fig. 8.—Aurin in alcoholic alkaline solution. Aurin:KOH; *A*,*A*′, 1:4; *B*,*B*′, 1:4; *C*,*C*′, 1:11.4; *D*, concd., aqueous KOH.

(Curve *A*,*A*′) except for a uniformly greater intensity, with the bands now located at 1865, 2000 and 3535. This solution can be prepared by either of the two methods described above, without affecting the type of absorption produced. Aurin dissolved in concentrated aqueous po-

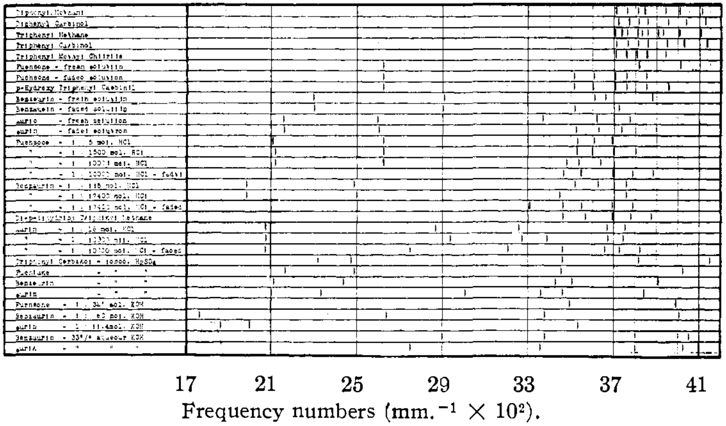

Fig. 9.—Relative positions of the absorption bands of di- and triphenylmethane and some of their derivatives in neutral, acid and alkaline solution.

TABLE I

FREQUENCY NUMBERS OF BANDS IN SOLUTIONS

Solvent	*p*-Hydroxytriphenyl carbinol	Fuchsone	Benzaurin	Aurin	Triphenyl carbinol[a]
Abs. alcohol, fresh soln.			2300	2160	
	2625	2625	2910	2600	
				3372	
	3516				
	3602	3820	3662	3629	
	3706				
	3762	4012	3883	3777	
	3855				
	3956				
Abs. alcohol, faded soln.			2300	2160	
	2625	2625	2902	2600	
	3516	3515	3520	3514	
	3602	3610	3613	3628	
	3706	3707	3727 (?)	3736	
	3762	3761			
	3855	3855			
	3956				
Concd. H_2SO_4		2165		2100	2318
		2490		2335	2476
				3006	
		3455		3360	3460
				3463	3820
		4025		3842	4150

Table I (*Concluded*)

Fuchsone

Alcoholic HCl				Alcoholic KOH		
5 m.	1000 m.	10,000 m.	10,000 m. (faded)	2 m.	50 m.	325 m.
2108	2120	2120				
2625	2625	2625		3605	3455	3496
3530	3528	3479	3468	4298	3997	3993
		3537	3549			
3610	3600	3637	3696			
3693	3700		3789			
			3885			

Aurin

Alcoholic HCl[a]				Alcoholic KOH		Concd. aq. KOH
16 m.	1000 m.	10,000 m.	10,000 m. (faded)	4 m.	11.4 m.	
2075	2075	2075	2074	1865	1865	
2869	2958	2938	2746			
3257	3241	3272	3207	2000	2000	2750
		3390	3463			
3671	3671	3675	3659	3560	3535	3360
3759	3755	3746	3732			
			3826			4025

[a] The data on then eutral alcohol solution of triphenyl carbinol will be found in the preceding article (Ref. 4d).

tassium hydroxide yields a colorless solution, whose absorption is shown in Curve *D*. There are three bands at 2750, 3360 and 4025, the curve being very similar in form to that for benzaurin in a 33% solution of potassium hydroxide,[4a] with the bands shifted uniformly toward lower frequency numbers. It is evident, therefore, that the aurin is present as a tripotassium salt of the carbinol form.

Table I gives the frequency numbers of the bands in the various solutions of fuchsone, benzaurin, aurin and triphenyl carbinol. In Fig. 9 there is summarized in a graphic form all of the data published thus far by us on the absorption of triphenylmethane derivatives.[4]

Summary

1. The absorption curves of fuchsone, benzaurin, aurin and *p*-hydroxytriphenyl carbinol in freshly prepared, neutral alcoholic solutions have been determined. It seems likely that the first three are present initially in the quinoid condition, but then pass over to an equilibrium mixture of the quinoid hydrate and carbinol forms. This is corroborated by the changes in absorption on aging of an alcoholic solution of *p*-hydroxytriphenyl carbinol.

2. The effect on the absorption of fuchsone and aurin in alcoholic solutions due to the addition of various amounts of hydrogen chloride has been studied. It is believed that salt formation first occurs, followed

on standing by more or less complete reduction of these compounds in the more concentrated acid solutions.

3. The absorption curves of fuchsone, aurin and triphenyl carbinol in concd. sulfuric acid have been determined.

4. The absorption curves of fuchsone and aurin in alcoholic solution containing various amounts of potassium hydroxide, and of the latter compound in concentrated aqueous potassium hydroxide have been obtained.

5. A table showing the frequency numbers of the peaks of the absorption bands of the various solutions studied has been prepared.

6. A chart, showing graphically the results of our studies on di- and triphenylmethane and some of their derivatives, and on fuchsone, benzaurin and aurin, has been prepared.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

IDENTIFICATION OF SOME OF THE PRODUCTS FORMED BY BACTERIUM PRUNI IN MILK

BY S. L. JODIDI

RECEIVED FEBRUARY 12, 1927 PUBLISHED JUNE 7, 1927

Dr. Erwin F. Smith, who was the first to study and to name *Bacterium pruni*, the microbe that causes a disease of plum and peach trees,[1] has made the observation that when the organism is grown in milk, crystals are formed in the culture medium. Because of their characteristic form and interest, Dr. Smith requested me to try to ascertain their chemical nature.

Available for identification were four flasks which contained pure cultures of *Bacterium pruni* grown in skim milk for about four months at room temperature. The crystals formed were separated from the wine-red, slimy fluid by filtration, after which they were spread on porous, unglazed porcelain. A preliminary macroscopic examination of the dry substance showed it to contain chiefly white, star-like needles mixed with some globular aggregates. Under the microscope one could see fine, transparent, prismatic needles partly arranged in bunches. The needles gave the Millon, Mörner and xanthoprotein reactions, indicating the presence of tyrosine. A melting point of the repeatedly purified crystals taken simultaneously with the melting point of tyrosine, a Kahlbaum preparation, showed them to decompose, respectively, at 294–299° and 295–300°, with evolution of gas.

---

[1] Smith, *Science*, [N. S.] **17**, 456 (1903); **30**, 224 (1909). "Bacteria in Relation to Plant Diseases," *Carnegie Inst. Wash. Publ.*, **1911**, vol. II, pp. 57–60. See also Rorer, *Mycologia*, **1**, 23 (1909). Rolfs, *Cornell Agr. Exptl. Sta. Memoir* No. 8, **1915**. Roberts, *U. S. Dept. Agr. Bull.*, 543, **1917**.