

Anal. Calcd. for $C_{26}H_{14}O_4Br_4$: Br, 45.07. Found: Br, 44.90, 44.45.

Diiodophenoldiphenic.—To 4 g. of phenoldiphenic in 60 cc. of 2 *N* potassium hydroxide are added with stirring during twenty minutes 10.8 g. of iodine and 11.2 g. of potassium iodide in 60 cc. of water and after twenty minutes the solution is made slightly acid with 6 *N* acetic acid. The reaction product is washed with 5% potassium iodide solution, dissolved in 5 *N* potassium hydroxide and reprecipitated with acetic acid. From the crude product, after boiling with 20 cc. of chloroform and recrystallizing from glacial acetic acid, a 20% yield of colorless diiodophenoldiphenic melting at 216–217° results.

Anal. Calcd. for $C_{26}H_{16}O_4I_2$: I, 39.29. Found: I, 39.31, 39.66.

Dinitrophenoldiphenic.—To 1 g. of phenoldiphenic suspended in 10 cc. of glacial acetic acid are added slowly with stirring and below 20° a mixture of 0.56 g. of nitric acid (sp. gr. 1.50) and 1.68 g. of sulfuric acid (sp. gr. 1.84). The reaction mixture is maintained at 45° for five minutes. Recrystallization of the precipitate from absolute alcohol gives yellow crystalline dinitrophenoldiphenic melting at 212.5–213°.

Anal. Calcd. for $C_{26}H_{16}O_6N_2$: N, 5.78. Found: N, 5.96, 5.89.

***o*-Cresoldiphenic.**—Ten grams of diphenic anhydride, 16 g. of *o*-cresol and 15 g. of fuming stannic chloride are heated at 125–135° for ten hours. The precipitate remaining after steam distillation is filtered, washed, extracted with 3 *N* potassium hydroxide and reprecipitated at 0° with 12 *N* hydrochloric acid. From the crude product, after washing with water and recrystallizing from glacial acetic acid, a 50% yield of colorless *o*-cresoldiphenic melting at 218.5–219.5° results.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.8; H, 5.24. Found: C, 79.0, 79.7; H, 5.35, 5.68.

Dibromo-*o*-cresoldiphenic.—To 2 g. of a hot alcoholic solution of *o*-cresoldiphenic are added slowly 5 g. of bromine and the solution refluxed twenty minutes; a product separates which, purified from absolute alcohol gives a 62% yield of colorless dibromo-*o*-cresoldiphenic melting at 203–204°.

Anal. Calcd. for $C_{28}H_{20}O_4Br_2$: Br, 27.54. Found: Br, 27.85, 27.65.

Diiodo-*o*-cresoldiphenic.—To 1 g. of *o*-cresoldiphenic in 15 cc. of 2 *N* potassium hydroxide are added slowly with stirring 2.7 g. of iodine and 2.8 g. of potassium iodide in 15 cc. of water, and after twenty minutes the solution is made slightly acid with 6 *N* acetic acid. The reaction product is dissolved in 10% potassium hydroxide and reprecipitated with 6 *N* hydrochloric acid. From the crude product, after washing with acetone and recrystallizing from absolute alcohol, a 43% yield of colorless diiodo-*o*-cresoldiphenic melting at 206–207° results.

Anal. Calcd. for $C_{28}H_{20}O_4I_2$: I, 37.69. Found: I, 37.80, 37.81.

Dinitro-*o*-cresoldiphenic.—To 1 g. of *o*-cresoldiphenic suspended in 10 cc. of glacial acetic acid are added slowly with stirring and below 20° a mixture of 0.57 g. of nitric acid (sp. gr. 1.50) and 1.70 g. of sulfuric acid (sp. gr. 1.84). The reaction mixture is maintained at 45° for five minutes. Recrystallization of the crude product from benzene and from absolute alcohol gives yellow crystalline dinitro-*o*-cresoldiphenic melting at 212.5–213°.

Anal. Calcd. for $C_{28}H_{20}O_6N_2$: N, 5.46. Found: N, 5.23, 5.40.

Resorcinoldiphenic, tetrabromo- and tetraiodoresorcinoldiphenic have been prepared previously.^{2,4} Crystallization of resorcinoldiphenic from absolute alcohol gave a pale yellow product which melted at 248–249°. Tetrabromoresorcinoldiphenic was prepared as a brownish-yellow powder which melted at 271–272°. Tetraiodoresorcinoldiphenic was obtained as a greenish-yellow powder which melted at 208.5–209.5°.

Summary

1. The preparation of tetrabromo-, diiodo-, dinitrophenoldiphenic and *o*-cresoldiphenic, dibromo-, diiodo- and dinitro-*o*-cresoldiphenic has been described.

2. All of the known substitution products of phenoldiphenic dissolve in dilute sodium hydroxide with the development of a pale yellow color.

(4) A. T. Wilson, Bachelor of Science Thesis, M. I. T., 1932.

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Absorption Spectra of Diphenicins

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The fact that alkaline solutions of the diphenicins showed only a faint yellow color as compared with the deep colors observed in the phthaleins prompted a study of their absorption spectra. If the supposed quinoid structure of phenolphthalein (alkaline) is responsible for its color, there is the possibility that this characteristic structure is also present in the diphenicins, but

the absorption band is displaced from the visible to the violet. On the other hand, there are the additional possibilities that the structure of the diphenicins is not analogous to that of the phthaleins or that the effect of the diphenic acid group is to minimize the effectiveness of the "quinoid" structure and so give only a weak absorption band in the visible.

Experimental

Apparatus.—The absorption spectra were recorded with a Hilger E316 spectrograph using a Spekker photometer for the measurements in the ultraviolet and calibrated screens for measurements in the visible. A spark (between iron-tungsten electrodes) and a ribbon filament lamp served as the sources of light. Eastman 33 photographic plates were used for the ultraviolet; I11L plates for the longer wave lengths. Cell lengths varied from 0.1 to 2.0 cm.

Materials.—The preparation of the diphenesins has been described.¹ Additional crystallizations, indicated there, which produced no observable changes in the melting points brought the extinction coefficients to limiting values. Absolute alcohol was prepared as previously described.² Potassium hydroxide was of c. p. quality. All solutions were freshly prepared.

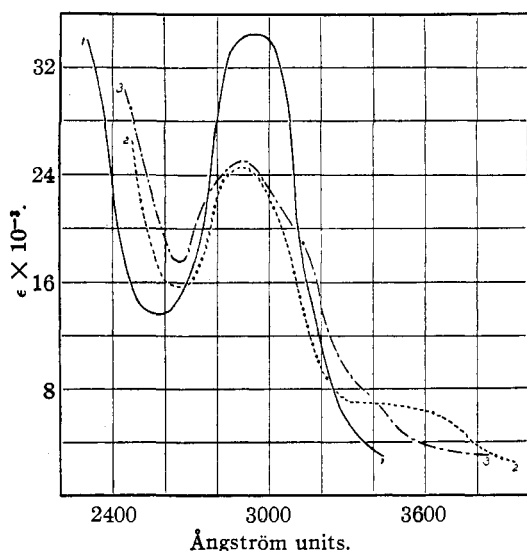


Fig. 1.—Plot of molal extinction coefficients against wave lengths for neutral (absolute alcohol) solutions: 1, phenoldiphenesin; 2, tetrabromophenoldiphenesin; 3, di-iodophenoldiphenesin.

Experimental Results.—The absorption spectra of phenolphthalein and some of its derivatives in neutral and alkaline alcoholic solutions were determined and the values of the molal extinction coefficients found to be in good agreement with the published values.³ The absorption spectra of the phenoldiphenesins in absolute

alcohol are represented in Figs. 1, 2 and 3. Figure 4 shows the absorption after 200 mols. of potassium hydroxide, per mol. of diphenesin, have been added.

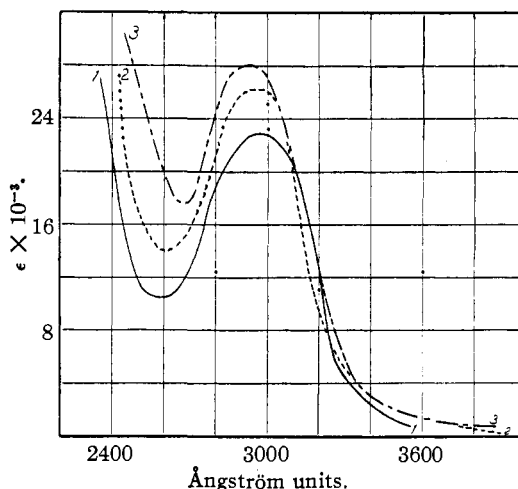


Fig. 2.—Plot of molal extinction coefficients against wave lengths for neutral (absolute alcohol) solutions: 1, *o*-cresoldiphenesin; 2, dibromo-*o*-cresoldiphenesin; 3, di-iodo-*o*-cresoldiphenesin.

Discussion of Results

Neutral Solutions.—The diphenesin series is characterized by an absorption band at 2950 Å., of high extinction coefficient. Substitution of bromine or iodine into the phenol residue of phenoldiphenesin causes a decrease in absorption. In comparison, absorption in the probably comparable band of phenolphthalein at 2800 Å., is increased by substitution of bromine or iodine. Substitution displaces this band of the phenolphthalein toward the red,^{3a} in phenoldiphenesin the displacement is toward the shorter wave lengths. The introduction of bromine or iodine causes an accentuation of a band at 3000 Å. in the phthaleins. The effect of the halogens is much less for the corresponding (3300 Å.) band of the diphenesins. The effect of substituent halogens on the absorption spectra of the diphenesins of substituted phenols is different from their effect in the case of the halogenated phenoldiphenesins. The maximum of the 2950 Å. band of *o*-cresoldiphenesin is displaced to shorter wave lengths, while the maximum of the resorcinoldiphenesin band is displaced toward longer wave lengths with the substitution of bromine or iodine in the phenolic ring. Substitution in the former compound increases the absorption while substitution in the latter decreases the absorption. The

(1) Underwood and Barker, *THIS JOURNAL*, **58**, 642 (1936).

(2) L. Harris, *ibid.*, **55**, 1940 (1933).

(3) (a) Howe and Gibson, *Phys. Rev.*, **10**, 767 (1917); (b) Gibbs and Shapiro, *THIS JOURNAL*, **50**, 2798 (1928); (c) Orndorff, Gibbs and Shapiro, *ibid.*, **50**, 819 (1928).

3300 Å. band is much more pronounced in the case of resorcinoldiphenin than in the other compounds studied.

Alkaline Solutions

The outstanding feature of these solutions is the strong absorption band at 3550 Å. which seems to have no counterpart in the phthaleins. Cresol- and resorcinoldiphenins and their bromine and iodine derivatives have practically the same absorption. Absorption bands are present in alkaline solutions of both the phenolphthaleins and diphenins at 2500 Å. However, the extinction coefficients of the diphenins are about four times as large. An absorption band in the visible comparable to that found in alkaline solutions of the phenolphthaleins is absent in the diphenins. The yellow coloration of these solutions is due to absorption of blue light as indicated by the absorption wing. No absorption bands, further to the red (as far as 8000 Å.), were observed.

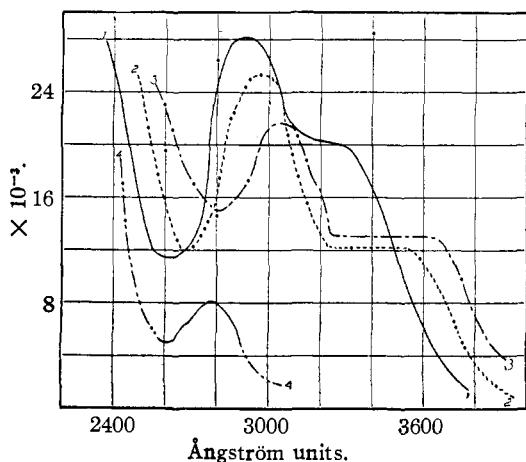


Fig. 3.—Plot of molal extinction coefficients against wave lengths for neutral (absolute alcohol) solutions: 1, resorcinoldiphenin; 2, tetrabromoresorcinoldiphenin; 3, tetraiodoresorcinoldiphenin; 4, fluorescein.

Conclusions

It is apparent that whatever configuration of atoms in the diphenins is responsible for the specific absorption in neutral solutions, the struc-

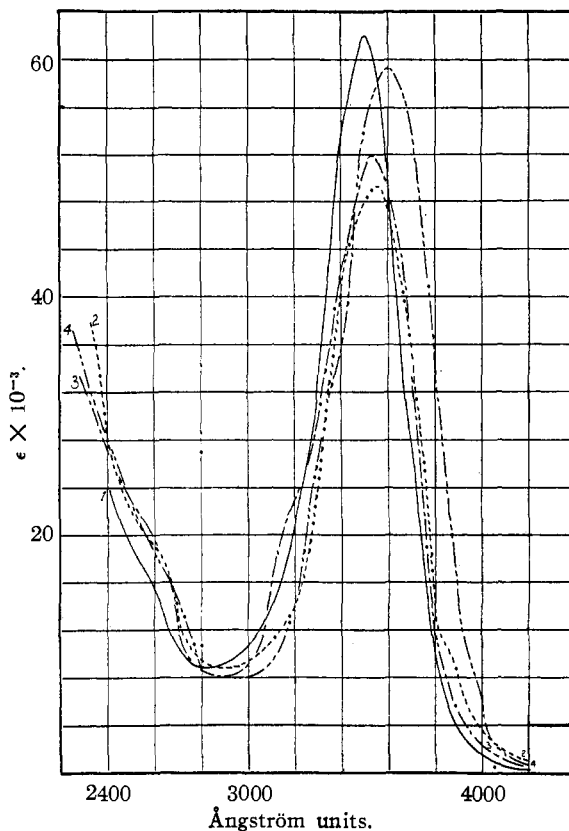


Fig. 4.—Plot of molal extinction coefficients of alkaline solutions against wave lengths: 1, phenoldiphenin; 2, tetrabromophenoldiphenin; 3, resorcinoldiphenin; 4, *o*-cresoldiphenin.

ture undergoes a marked change when the solutions are made alkaline. These absorption spectra do not permit a choice between the possible structures of the diphenins in neutral or alkaline solutions.

Summary

The absorption spectra of neutral and alkaline solutions of phenoldiphenin and several of its derivatives have been obtained. Absorption bands characteristic of the diphenins have been noted. In both neutral and alkaline solutions the absorption spectra of the diphenins are quite different from the phthaleins. All the diphenin derivatives tested showed essentially the same absorption spectra in alkaline solution.

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