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An Investigation of The Iodine Derivatives of Certain Meta-Substituted Phenols

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AN INVESTIGATION OF THE IODINE DERIVATIVES OF
CERTAIN META-SUBSTITUTED PHENOLS

being

A thesis presented to the Graduate Faculty
of the Fort Hays Kansas State College in
partial fulfillment of the requirements for
the Degree of Master of Science

by

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Fort Hays Kansas State College

Date

May 15, 1951

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Sept

Author

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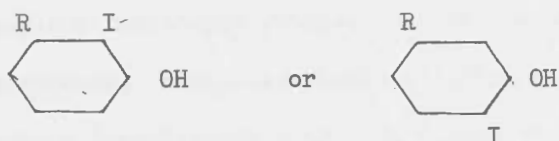
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INTRODUCTION

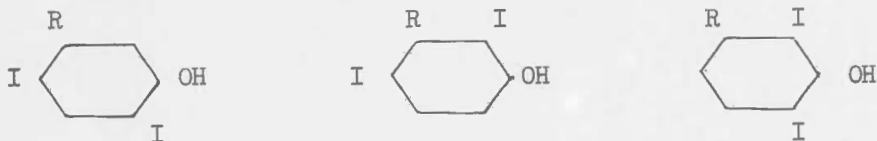
Phenol and derivatives of phenol are widely used today in industry and medicine. Phenol is a powerful germicide, and was first introduced into medicine by Lister. It has the advantage of being more stable than many other germicides; it is not injurious to metals or fabrics in the strength commonly used. In recent years, however, phenol has been largely replaced by its derivatives and by other coal-tar products which are more effective, cheaper and less toxic (37), (2).

The antibacterial action of substituted phenols depends upon the experimental conditions and the nature of the substituent groups. It has been shown that the bactericidal power of a phenol is stronger in an acid solution than in an alkaline solution (39). Fogg and Lodge made a study of the antibacterial action of phenol, m-chlorophenol, resorcinol, m-cresol, m-nitrophenol and m-hydroxybenzoic acid, with somewhat controversial results. The investigators studied the distribution of phenols between olive oil and aqueous buffer as a model for the distribution between bacteria and liquid culture medium. It was concluded that the antibacterial activity of the phenols studied was due largely to their distribution relationships and to their ability to precipitate protein, and that their structure, apart from its effect on the distribution coefficient, was relatively unimportant (23). In general, halogen substitution increases the bactericidal power of substituted phenols (36).

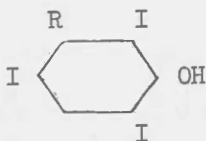
The purpose of this investigation was to prepare a series of iodinated meta-substituted phenols, and, if time permitted, to determine the structures of the compounds prepared. The situation was complicated somewhat by the prevailing controversy regarding the mechanism of iodination of phenols and the uncertainty involved in controlling iodine substitution in the aromatic nucleus. If only one iodine were substituted in the benzene ring, the compound would be expected to be of the type



If two iodine atoms entered the ring, the compound probably would be one of the types



Three iodine atoms probably would give the form



Proof of structure of the prepared compounds could be carried out by reference to literature citing chemical and physical properties of the compounds being investigated and of their

derivatives, or by transforming the compounds, by accepted methods, into new materials for which physical and chemical properties were readily available.

The compounds investigated included m-cresol, m-nitrophenol, m-aminophenol, m-chlorophenol, and m-hydroxybenzoic acid. Other m-substituted phenols were not readily available.

Ultraviolet absorption spectra of the iodinated compounds were to be examined with the possibility of providing a means of identification of various functional groups. Bacteriological properties of the compounds, including phenol coefficients, have been assigned to another investigator with a more adequate knowledge of bacteriology, and will not be discussed further.

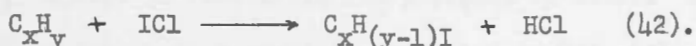
THEORY AND METHOD OF INVESTIGATION

Unlike chloro- and bromobenzene, iodobenzene cannot be prepared by direct iodination of benzene because the hydriodic acid formed acts as a reducing agent to reduce the iodobenzene back to benzene. To iodinate aromatic organic compounds it is necessary to add an oxidizing agent, such as nitric acid, a binding agent, or a basic substance, such as ammonium hydroxide (8), (43).

A variety of methods have been employed in the iodination of phenols, resulting in almost as many theories of the mechanisms involved when iodine enters the benzene ring. Dains and co-workers succeeded in iodinating methyl cresol ethers and nitroanisoles by direct substitution, using nitric acid as an oxidizing agent at temperatures of 168-180° (20). Bordeianu has suggested two methods for the iodination of phenols. The first method makes use of a solution of iodine in methyl alcohol, added to a solution of the phenol in methyl alcohol containing dry ammonia. The second method makes use of the acetoxymercuri derivative of the phenol dissolved in sodium hydroxide solution. The sodium hydroxide solution is added to dilute acetic acid containing iodine and potassium iodide. The reaction is instantaneous and quantitative, and the acetoxymercuri derivatives are said to be easy to prepare. Furthermore, the iodine enters the ring in the same position as that formerly occupied by the acetoxymercuri group (7).

Still another method of iodinating phenols makes use of

alcoholic iodine and silver nitrate. The phenol is iodinated quantitatively when the mixture contains at least 65 per cent alcohol with an optimum molecular ratio of silver nitrate and iodine equal to 1.5:1 (22). Block and Powell obtained 2,6-di-iodo-p-nitrophenol in 82-87 per cent yields by iodinating p-nitrophenol with iodine monochloride, ICl , in acetic acid (6). Weygand has suggested that the iodine monochloride first chlorinates the organic compounds and then changes them subsequently to iodine compounds. The reaction can be represented by the equation



Birchenbach and Gaubeau, investigating the action of silver perchlorate and iodine on organic compounds, concluded that iodine perchlorate was the active iodinating agent:



Undesirable side reactions caused by the anhydrous perchloric acid formed can be avoided by the addition of magnesium or calcium oxide (4). However, because of tar formation, the above method is generally unsatisfactory for iodinating aromatic compounds under normal conditions.

Other investigators have reported iodination of organic compounds by means of potassium iodide and chloroamides in a

neutral solution. Iodination takes place without the liberation of iodine. Intermediate products and iodoamides are formed which are hydrolyzed. The resulting HOI effects iodination. The investigators believed that no ICl was formed in the reaction, since chloroamides could be replaced by various oxidizers with the same results and the intermediate formation of HOI (35). On the other hand, Hunter and Budrow presented evidence that HOI is not necessarily the iodinating agent. The anhydrous sodium salt of phenol was prepared from phenol in dimethylbenzene with oxide-free sodium. This salt was iodinated rapidly, almost as fast as in the presence of water. There was no opportunity for the intermediate formation of HOI (31).

A generally satisfactory method of iodinating phenols involves the use of a solution of iodine in potassium iodide in the presence of concentrated ammonium hydroxide. Varma and Yashoda, using the above method, reported satisfactory yields in the iodination of several halogenated phenols (40). Colbert and co-workers, using the same method, obtained a crude yield of 91 per cent of 3-iodo-4-hydroxybiphenyl from the iodination of 4-hydroxybiphenyl (19). Choguill made use of this method while investigating the iodination of hydroxy derivatives of diphenyl ether and reported the active iodinating agent to be nitrogen triiodide (11).

The method of iodination chosen for this investigation was that of using a solution of iodine in potassium iodide in the presence of concentrated ammonium hydroxide. This method offered the advantages of being comparatively simple and easy to perform, the

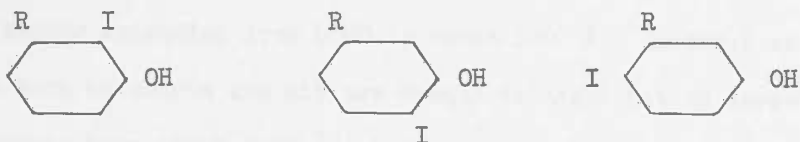
reagents were readily available and undesirable side reactions were not expected.

Substitution on the Benzene Ring

Substitution on the benzene ring generally takes place in such an orderly manner that certain rules of substitution have been proposed. Outstanding among these are the substitution rules given by Brewster, who has classified various groups according to their orienting powers when already present in the aromatic nucleus (9). Substitution on the benzene ring consists essentially of an oxidation-reduction process, whereby the incoming group, such as chlorine, bromine or iodine, is reduced by the benzene ring (10). Groups which are ortho-para orienting may be called electron donors, as, for example, $-\text{NH}_2$, $-\text{OH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CH}_3$, and others. Electron acceptors, such as $-\text{NO}_2$, $-\text{SO}_3\text{H}$, $-\text{CN}$, $-\text{COOH}$, and $-\text{CHO}$ are meta orienting groups. Brewster formulated the following rules of substitution:

1. The group already present on the benzene ring determines the position taken by the next entering group.
2. Electron donors direct a new group to the ortho or para position, and the rate of substitution is faster than it is in benzene.
3. Electron acceptors direct a new group to the meta position, and the rate of substitution is slower than it is in benzene.
4. Electron donors always take precedence over electron acceptors in benzene derivatives which contain a representative of each class. (9)

Using the rules of substitution given above, it is possible to predict the position to be taken by a group entering a molecule of a substituted phenol. The hydroxyl group is an electron donor and a strong ortho-para orienting group. As was suggested previously, an atom of iodine entering a molecule of a meta-substituted phenol could be expected to yield one of the following types of compounds



Proof of Structure

Proof of structure, seldom a simple process, often necessitates a transformation of the compound whose structure is to be determined into a new compound which may be identified by its physical and chemical properties. Thus, decarboxylation of diiodo-*m*-hydroxybenzoic acid should yield one of the diiodophenols, for which physical constants can be found in available literature. Determination of the relative positions of the substituted iodine atoms would permit assignment of a structural form to the diiodo-*m*-hydroxybenzoic acid. In the same manner, diazotization of diiodo-*m*-aminophenol and subsequent replacement of the diazonium group by hydrogen should yield a diiodophenol which could be identified from its physical constants. It is likely that, for each of the reactions suggested, protection of the -OH group would be necessary. By related chemical processes

it should be possible to identify each of the iodinated phenols being investigated.

Ultraviolet Absorption Spectra

Visible light consists of light having wavelengths from about 7500 to 4000 Angstrom Units, the Angstrom Unit being equal to 10^{-8} cm. and designated by the symbol Å. Ultraviolet light may have wavelengths extending from 4000 to about 100 Å. Inasmuch as substances such as quartz and air are opaque to light having wavelengths shorter than about 2000 Å, the working range for ultraviolet spectroscopy generally is limited to the region from 4000 to 2000 Å.

Spectra may be either of two general types: emission or absorption spectra. Emission spectra are caused by light emitted from a luminous source, such as a spark, a flame, or an electric arc, and consist of bright lines or bands against a dark background. Absorption spectra are produced by placing an absorbing medium between a light source and a spectroscope, and consist of dark lines or bands against a bright background (5), (41). The distinction between line and band spectra will be considered.

Absorption spectra of molecules can be attributed to transitions, upon the absorption of radiant energy such as ultraviolet light, from states of low energy-content to states of high energy-content. Differing from the sharp line spectra of atoms, molecular spectra are broad and spread over a comparatively wide range of wave-

lengths. This difference may be understood by a consideration of atomic and molecular energy levels. In atoms, separate levels are a result of different distributions of electrons. In molecules, in addition to energy levels corresponding to various electron distributions, there is also the possibility of vibrations among the atoms, accompanied by differences in energy. The combination of atomic rotational energies and vibrational energies creates complex energy level relationships differing by very small amounts. If the Bohr relation is used, the frequency ν of light absorbed is directly proportional to the difference in energy states, $E_2 - E_1$, as expressed by the relation

$$h\nu = E_2 - E_1$$

where h is Planck's constant. When spectra of molecules are examined, many lines in close proximity are observed and appear to be in the form of a band (34), (21).

When properties of light absorption are utilized for analytical purposes, certain laws of absorption must be considered. If a beam of monochromatic light is weakened by passage through an absorbing medium, the intensity is found to decrease exponentially with the thickness of the medium such that

$$I = I_0 e^{-kd}$$

where I is the intensity of the emerging beam, I_0 is the incident intensity, d is the thickness and k is an absorption coefficient

which is a constant for a given temperature and wavelength. This relationship is Lambert's Law.

Absorption is also a function of the concentration of the absorbing medium, from which Beer's Law is deduced:

$$I = I_0 e^{-kc}$$

If all factors considered are gathered into one relationship, there results an expression for the Beer-Lambert Law for monochromatic light:

$$I = I_0 e^{-k_m cd}$$

where c is the concentration in moles per liter, d is the thickness in centimeters and k_m is the molar absorption coefficient. Experimental results are often given in terms of the molar extinction coefficient, ϵ , which is defined by the expression

$$\log \frac{I}{I_0} = \epsilon cd \quad (41)$$

Much work has been done with ultraviolet absorption spectra. Stair, employing ultraviolet absorption, made a comparison of the spectra of several substituted benzenes to those of benzene and toluene (38). Jones has discussed the ultraviolet absorption spectra of aromatic hydrocarbons and condensed ring systems, emphasizing the importance of ultraviolet absorption in determining molecular structure (32). Benesi and Hildebrand, in studying the absorption

spectra of iodine in several aromatic compounds in the region from 270 to 700 m μ , discovered an intense absorption band in the ultraviolet region which was shown to be characteristic of a complex containing one iodine (I_2) and one aromatic hydrocarbon molecule (3).

Hodgson, investigating the absorption spectra of some m-substituted phenols, found maximum and minimum absorption bands of the compounds in neutral and acid solutions. The peak displacement of all the m-substituted phenols, with the exception of fluorophenol, relative to that of phenol, were toward longer wavelengths, giving a bathochromic shift. These results indicate a loosening of the electronic structure of the aromatic nucleus by the substituent groups, which included chloro-, iodo-, methyl- and methoxy- groups (30).

Ferguson, in a valuable review listing 312 references, discusses the relationship of absorption spectra to resonance and color, conjugation and insulation of chromophores, steric hindrance and other molecular properties (21). It has also been found that the larger the mass of a substituent group and the weaker its restraining forces, the more readily will it absorb electronic vibrational energy. Thus the fine structure of the benzene spectrum gradually lessens in passing over the spectra for fluorobenzene to iodobenzene (21). From the foregoing information, it is to be expected that spectra of the iodinated m-phenols would not show sharp changes in regions of maximum and minimum absorption.

Hall made an analysis of the ultraviolet absorption spectra of phenol, using the Hilger E-1 quartz spectrograph (27). He applied

theoretical considerations of vibrational energies to variations in absorption bands. Kiss and co-workers obtained absorption spectra of phenolic derivatives and found that displacement toward longer wavelengths was much larger for para compounds, where hindrance was least, than for ortho and meta compounds (33).

Coggeshall has performed outstanding work in the field of determining structure of organic compounds by molecular spectroscopy. He has proposed a chromophore theory which deals with ultraviolet absorption in terms of characteristic absorption of specific atomic groupings. He has assumed that the electric vector of electromagnetic radiation induces oscillations of valence electrons. The more loosely bound the electrons, the lower the frequency of absorption. Such a process is closely related to resonance. Thus resonating structures, such as benzene, possess characteristic ultraviolet absorption, whereas non-resonating compounds, such as the saturated aliphatic compounds, are transparent to ultraviolet radiation below 2000 Å (13).

Coggeshall suggests that ultraviolet absorption may be ascribed to types of atomic groupings known as chromophores, as the benzene molecule, which has a characteristic absorption band of about 250 to 280 m μ . Spectra are very similar for a homologous series, such as the alkylbenzenes, indicating that absorption is due to unsaturation and resonance effects and that alkyl groups have little effect (16).

Choice of satisfactory solvents is of major importance in

absorption spectrophotometry. Many compounds show a difference in displacement of absorption bands when dissolved in neutral and acid solutions (30). Coggeshall found a displacement of absorption bands caused by the ionization of substituted phenols in ethanol containing sodium hydroxide (12). Interaction of solvent and solute would be expected to cause a shift in the spectrum of a compound. Thus an examination of the absorption spectra of a substance in several solvents might yield information not otherwise obtainable. For example, a phenol in alcohol causes a shift toward the red in comparison to its behavior in a non-polar solvent. The shift is caused by interaction of the hydroxy groups of the solvent and solute molecules. When positions ortho and para to the phenolic group are filled the shift is almost eliminated. In such a condition the hydroxy group of the phenol is hindered from attaining close proximity with the solvent molecules (17). Distilled water, when it can be used, and the simple alcohols make satisfactory solvents because of their transparency to ultraviolet light. Solvents used for this purpose should be free of impurities. In some instances purification can be accomplished by selective adsorption (26).

Ultraviolet absorption is adapted to various types of determinations. The spectrum of an unknown material, when compared with that of known chromophores, may reveal what functional groups are present. Once an unknown has been classified according to chromophores, additional information may be obtained from shape, intensity and detailed location of the bands (15). There are, however,

certain disadvantages to be encountered in the use of ultraviolet absorption. It is not readily adapted for analysis of mixtures containing many components because materials of a given class have very similar spectra (14). Several exceptions have already been cited. Many compounds do not absorb ultraviolet light. Furthermore, the number of chromophores is small and there is much overlapping of the observed bands. For best results, ultraviolet absorption should be used in conjunction with infrared and Raman spectra (18).

The Beckman Model DU Photoelectric Quartz Spectrophotometer is an instrument well-suited for a laboratory investigation of absorption spectra and is the instrument which was used for this investigation. A hydrogen discharge lamp is used to supply a continuous source of ultraviolet radiation. When ultraviolet light is employed, absorption cells which are transparent to ultraviolet light must be used. This investigator used absorption cells of fused silica. The following is a schematic diagram of the instrument.

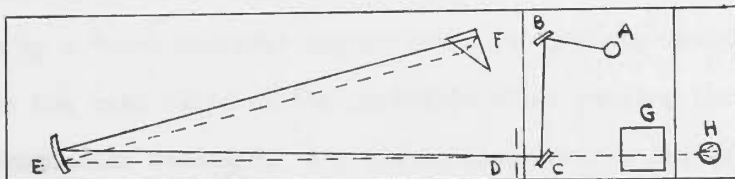


Figure 1. Beckman Model DU Quartz Spectrophotometer

Light from the light source A is focused on the slit D by means of a concave mirror B and the plane mirror C. The beam passes from the collimating mirror E to the reflecting surface F and returns along nearly the same path above the mirror C and through the sample at G. The intensity of the emergent beam is measured by the phototube H.

Either of two phototubes may be used at will. A "red sensitive" cesium oxide phototube is used in the range from 6200 to 12,000 Å. The other is a cesium-antimony phototube which is "blue sensitive" and is used below 6200 Å. With the hydrogen lamp, the range extends to about 2000 Å, using Corning 9740 glass where light must be transmitted.

The photometric scale is based on electrical rather than optical principles. The photoelectric current from the irradiated cell produces across the phototube load resistor a voltage drop which is balanced by a potentiometer. While this null setting is being made any imbalance is amplified electronically and is indicated by a milliammeter on the instrument. (24)

Usually three readings must be made to determine the transmission at any wavelength; the zero reading, in which the beam is blocked from the phototube and the galvanometer is brought to balance by a "dark current" adjustment; the 100-per cent reading, in which the beam falls on the phototube after passing through the transmission standard, and the milliammeter is brought to balance by adjusting the slit width or the "sensitivity" adjuster; and the transmission reading, in which the unknown or test sample is placed in the beam and the galvanometer is brought to

balance by turning the potentiometer dial. The switch is then set to "1" for the transmission reading (24).

EXPERIMENTAL

General

The method used in iodinating the meta-substituted phenols was similar to that used by Gill and Higgins (25), (29). The meta-substituted phenol was dissolved in a minimum amount of dilute sodium hydroxide, followed by an excess of ammonium hydroxide. The mixture was stirred by means of an electric stirrer while a solution of iodine in potassium iodide was added. To prepare the mono-iodo product of m-hydroxybenzoic acid, a corresponding equivalent amount of iodine was added. To prepare the diiodo products, a light excess of iodine beyond the amount required to produce the diiodo derivatives was added. When the reaction was complete, the excess iodine was destroyed by the addition of sodium bisulfite, the mixture was acidified and the product was collected on a Buchner filter. Recrystallization was effected from water-ethanol or water-acetone solutions.

Reagents

Phenols

The m-nitrophenol, m-hydroxybenzoic acid and m-chlorophenol were obtained from the Research Laboratory of Eastman Kodak Company. The m-cresol used was the redistilled product of Paragon Testing Laboratories. The m-aminophenol was purchased from The Matheson Company, Inc.

Ammonium Hydroxide

Ammonium hydroxide solutions were prepared from the chemically pure reagent, specific gravity 0.90, manufactured by the J. T. Baker Chemical Company.

Ethanol

The alcohol solutions used for purifying compounds by recrystallization were prepared from industrial grade, 95 per cent ethanol procured from U. S. Industrial Chemicals, Inc.

Hydrazine Sulfate

Reducing solutions of hydrazine sulfate were prepared from the chemically pure product manufactured by Fisher Scientific Company.

Iodine

The iodine used for iodination conformed to standards of the American Chemical Society and was manufactured by Merck and Company.

Nitric Acid

Dilute nitric acid solutions were prepared from the chemically pure concentrated nitric acid manufactured by Mallinckrodt.

Potassium Iodide

Potassium iodide used for preparing iodine solutions conformed to standards of the American Chemical Society and was manufactured by Merck and Company.

Potassium Thiocyanate

Potassium thiocyanate solution used for the quantitative determination of iodine was prepared from the chemically pure reagent, containing not more than 0.005 per cent chloride, made by the J. T. Baker Chemical Company.

Sodium Bisulfite

Reducing solutions of sodium bisulfite, containing negligible quantities of halogens, were prepared from the chemically pure reagent manufactured by Fisher Scientific Company.

Sodium Hydroxide

Dilute sodium hydroxide solutions were prepared from chemically pure pellets obtained from Fisher Scientific Company.

Sodium Peroxide

Sodium peroxide used in the Parr Bomb fusions was a special grade reagent prepared by the Parr Instrument Company.

Silver Nitrate

The silver nitrate solution used for the quantitative determination of iodine was prepared from chemically pure crystals made by Merck and Company.

Sucrose

Powdered sucrose used in the Parr Bomb fusions was prepared from high quality sucrose containing a negligible quantity of halogens as revealed by a blank test.

Sulfuric Acid

Dilute sulfuric acid solutions were prepared from the chemically pure reagent, specific gravity 1.84, manufactured by J. T. Baker Chemical Company.

Analysis

The prepared iodine compounds were analyzed for iodine by the Parr Bomb method, special conditions being observed with the iodinated m-chlorophenol, as described later. From 0.15 to 0.25 gram of the compound to be analyzed was mixed thoroughly with one gram of cane sugar and fifteen grams of sodium peroxide in a Parr Bomb. The bomb was then ignited and the contents were dissolved in nearly-boiling water. The solution was boiled to remove excess hydrogen peroxide and cooled. Iodates were reduced to iodides by the addition of an excess of hydrazine sulfate. The iodine was then determined as iodide by the Volhard method.

The iodinated m-chlorophenol was analyzed for iodine by first fusing a 0.2 gram sample in the Parr Bomb, using the method described above. After dissolving the contents of the bomb in water, the solution was made just acid to litmus with dilute nitric acid. Iodates were reduced to iodide by addition of a solution of sodium bisulfite. The halogens in solution were titrated with 0.1030 N silver nitrate solution, and the course of the reaction was followed potentiometrically with a Macbeth Titration-pH Meter, using calomel and silver electrodes. By plotting scale readings versus milliliters of silver nitrate solution, a significant break was found in the curve at the point where all of the iodide had been precipitated as silver iodide and precipitation of silver chloride began. A similar break occurred when precipitation of silver chloride

was complete. The relative positions of the breaks in the curve determined the equivalent amounts of iodine and chlorine present in the original compound.

Ultraviolet Absorption Spectra

Ultraviolet absorption spectra of the iodinated phenols were investigated by means of the Beckman Model DU Quartz Spectrophotometer, which was described previously. The instrument was equipped with an auxiliary constant voltage source and a hydrogen discharge tube. The absorption cells were of fused silica. Comparatively wide slit widths and rather high sensitivity were employed. It was necessary to determine experimentally the concentration of each phenol which gave the most satisfactory absorption curve. Absorption was investigated in the region of the spectrum from 220 to 350 millimicrons, which was the ultraviolet range of the instrument. All absorption curves were obtained using ethanol as the solvent. Ethanol is transparent to wavelengths in the near ultraviolet. Per cent transmission was plotted against wavelength.

Preparation of Diiodo-m-cresol from m-Cresol

Five grams of m-cresol were dissolved in a minimum amount of sodium hydroxide and an excess of ammonium hydroxide. A solution of iodine in potassium iodide was added slowly and with constant stirring until the iodine color remained in the solution. The excess iodine was reduced by the addition of sodium bisulfite. The

mixture was then acidified and the product was removed by filtration. Recrystallization was effected from a water-ethanol solution. The diiodo-*m*-cresol melted at 117° C. The reaction probably takes the form



Analysis for Iodine of the Product from the
Iodination of m-Cresol

SAMPLE I

Weight of sample	0.2023 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me. AgNO ₃	2.575
KCNS (0.0537 N)	26.94 ml.
me. KCNS	1.448
me Iodine	1.127
Per cent iodine found	70.69%

SAMPLE II

Weight of sample	0.2020 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me. AgNO ₃	2.575
KCNS (0.0537 N)	27.00 ml.
me KCNS	1.461
me Iodine	1.124
Per cent iodine found	70.61%
Iodine calculated for C ₇ H ₆ OI ₂	70.50%

TABLE I

ULTRAVIOLET ABSORPTION DATA FOR

DIIDO-m-CRESOL (1.2×10^{-3} M)

<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>	<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>
220	--	286	2.30
222	--	288	1.88
224	--	290	1.65
226	--	292	1.56
228	--	294	1.78
230	--	296	2.39
232	--	298	3.51
234	--	300	5.19
236	--	302	8.06
238	--	304	13.5
240	.02	306	23.2
242	.03	308	38.7
244	.03	310	60.9
246	.03	312	86.4
248	.03	314	--
250	.03	316	--
252	.11	318	--
254	.54	320	--
256	1.79	322	--
258	3.69	324	--
260	5.52	326	--
262	6.89	328	--
264	7.64	330	--
266	8.17	332	--
268	8.49	334	--
270	8.67	336	--
272	8.48	338	--
274	8.13	340	--
276	7.93	342	--
278	6.04	344	--
280	4.93	346	--
282	3.80	348	--
284	2.91	350	--

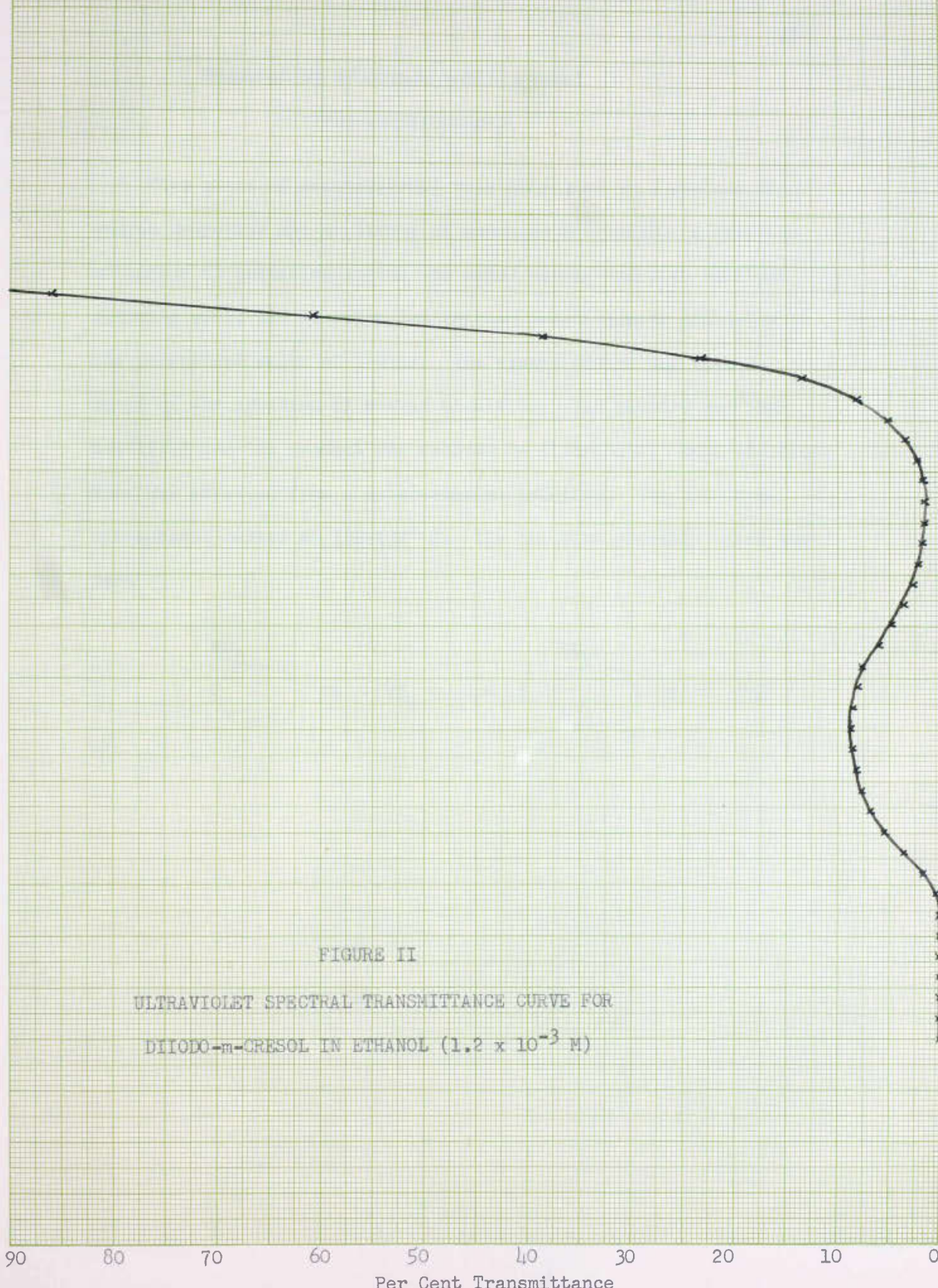


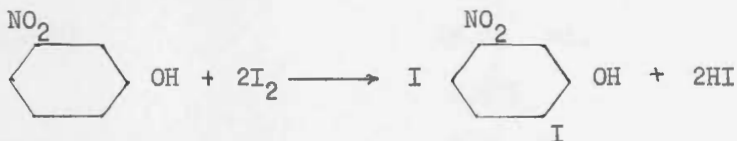
FIGURE II

ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
DIIDO-*m*-CRESOL IN ETHANOL (1.2×10^{-3} M)

90 80 70 60 50 40 30 20 10 0
Per Cent Transmittance

Preparation of Diiodo-m-nitrophenol
from m-Nitrophenol

Five grams of m-nitrophenol were dissolved in a minimum of sodium hydroxide and an excess of ammonium hydroxide. A solution of iodine in potassium iodide was added slowly and with constant stirring until the reaction had reached completion as indicated by the persistent color of iodine. The excess iodine was then reduced by the addition of sodium bisulfite. The mixture was then acidified and the product was removed by filtration. Recrystallization was effected from a water-ethanol solution. The diiodo-m-nitrophenol melted at 130-132° C. The reaction probably takes the form



Analysis for Iodine of the Product from the
Iodination of m-Nitrophenol

SAMPLE I

Weight of sample	.2228 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me AgNO ₃	2.575
KCNS (0.0537 N)	27.05 ml.
me. KCNS	1.454
me. Iodine	1.121
Per cent iodine found	63.85%

SAMPLE II

Weight of sample	0.2010 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me. AgNO ₃	2.575
KCNS (0.0537 N)	28.99 ml.
me. KCNS	1.558
me. Iodine	1.017
Per cent iodine found	64.21%
Iodine calculated for C ₆ H ₃ O ₃ NI ₂	64.93%

TABLE II

ULTRAVIOLET ABSORPTION DATA FOR
 DIIDO-m-NITROPHENOL (0.4×10^{-3} M)

<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>	<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>
220	--	286	4.05
222	.04	288	3.66
224	.05	290	3.39
226	.05	292	3.21
228	.05	294	3.12
230	.07	296	3.17
232	.09	298	3.32
234	.10	300	3.61
236	.11	302	4.00
238	.12	304	4.55
240	.12	306	5.27
242	.13	308	6.12
244	.15	310	7.18
246	.16	312	8.32
248	.20	314	9.69
250	.39	316	10.98
252	.81	318	12.3
254	1.62	320	13.6
256	3.20	322	14.8
258	5.02	324	15.8
260	6.49	326	16.5
262	7.82	328	17.6
264	9.04	330	18.7
266	9.64	332	20.2
268	9.64	334	21.7
270	9.36	336	23.8
272	8.89	338	26.0
274	8.22	340	29.2
276	7.46	342	33.1
278	6.64	344	37.7
280	5.85	346	43.8
282	5.16	348	50.9
284	4.52	350	59.5

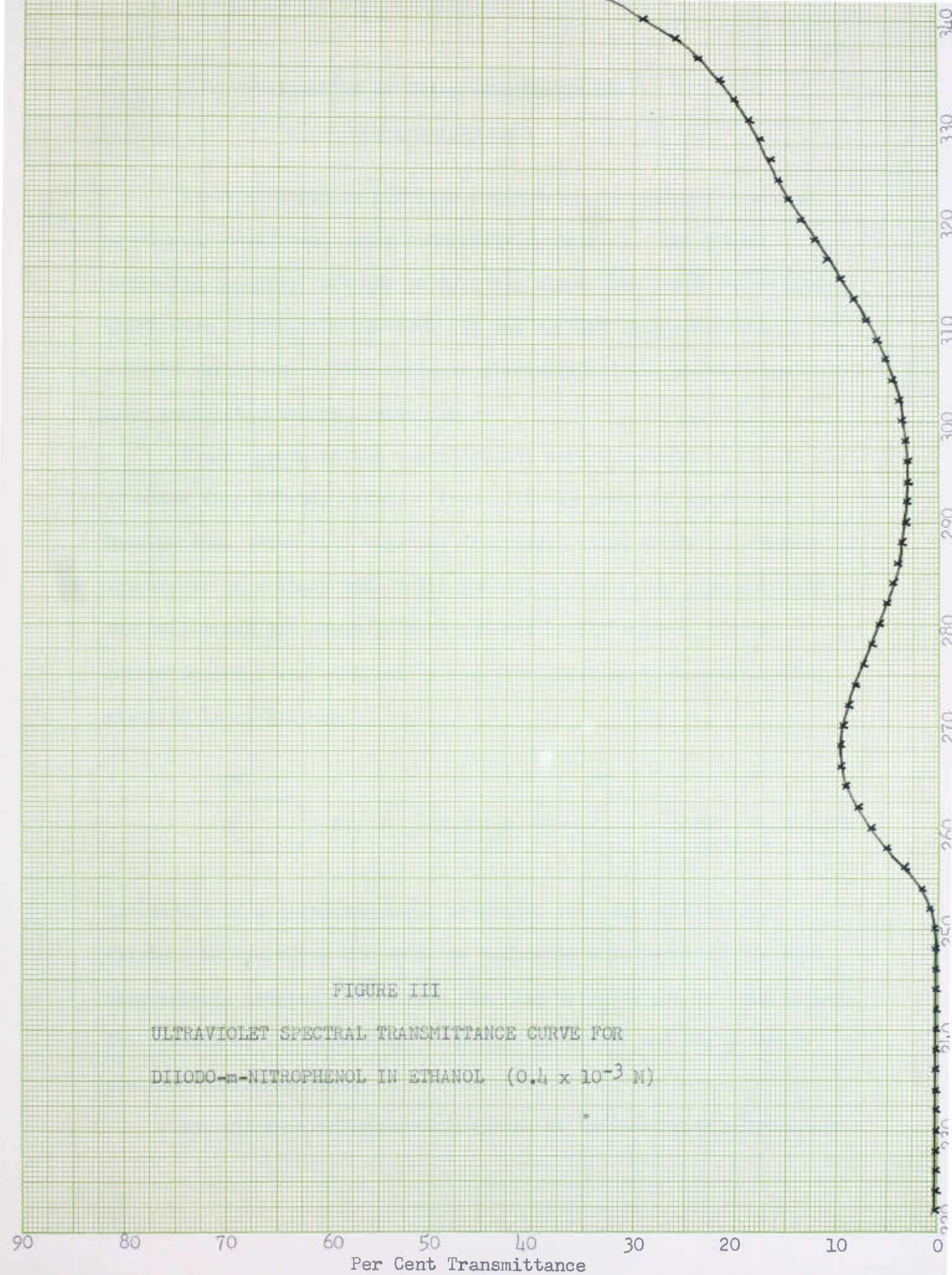


FIGURE III

ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
DIIDO-*m*-NITROPHENOL IN ETHANOL (0.4×10^{-3} M)

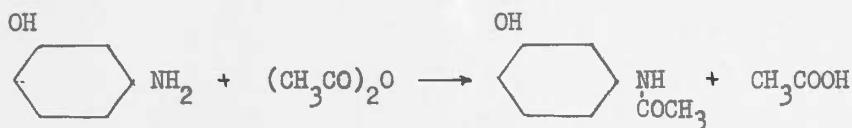
Per Cent Transmittance

Preparation of Diiodo-m-aminophenol

from m-Aminophenol

First attempts to iodinate m-aminophenol, using the method previously described, were moderately successful. The phenol iodinated readily, but the product was mixed with black impurities which were difficultly removed. It was decided that oxidation effects due to the iodine could be eliminated if the amino group were acetylated before iodination.

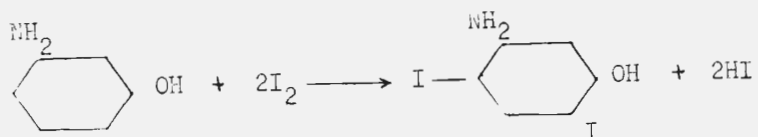
Eleven grams of the m-aminophenol were suspended in 30 ml. of water in a 250 ml. beaker. From 12 to 13 grams of acetic anhydride were added with vigorous stirring, after which the mixture was warmed on a steam bath until the solid dissolved. The solution was cooled and the crystals were removed by filtration. The m-acetaminophenol was purified by recrystallization from water. The reaction is as follows



Iodination of m-acetaminophenol proceeded very satisfactorily. Attempts to hydrolyze the amide by refluxing with hydrochloric acid unexpectedly removed iodine from the ring by oxidation to free iodine. The product of the hydrolysis contained no iodine and could not be purified and identified.

The diiodo-m-aminophenol prepared by iodination of m-aminophenol

was purified by successive decolorizations and crystallizations from water-alcohol and water-acetone solutions. The final product melted at $139-141^{\circ}$ C. The reaction probably takes the form



Analysis for Iodine of the Product from
the Iodination of m-Aminophenol

SAMPLE I

Weight of sample	0.2055 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me. AgNO ₃	2.575
KCNS (0.0537 N)	26.40 ml.
me. KCNS	1.419
me. iodine	1.156
Per cent iodine found	69.76%

SAMPLE II

Weight of sample	0.1896 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me. AgNO ₃	2.575
KCNS (0.0537 N)	28.22 ml.
me. KCNS	1.517
me. iodine	1.058
Per cent iodine found	70.81%
Iodine calculated for C ₆ H ₇ ONI ₂	70.30%

TABLE III

ULTRAVIOLET ABSORPTION DATA FOR
 DIIDO-m-AMINOPHENOL (0.8×10^{-3} M)

<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>	<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>
220	--	286	27.1
222	--	288	21.2
224	--	290	15.7
226	--	292	11.0
228	--	294	7.49
230	--	296	5.02
232	--	298	3.42
234	--	300	2.52
236	.02	302	1.97
238	.02	304	1.69
240	.02	306	1.63
242	.02	308	1.78
244	.02	310	2.27
246	.02	312	3.30
248	.02	314	5.57
250	.02	316	9.84
252	.02	318	19.2
254	.02	320	35.1
256	.02	322	58.2
258	.02	324	90.2
260	.03	326	--
262	.22	328	--
264	1.06	330	--
266	3.28	332	--
268	7.29	334	--
270	13.2	336	--
272	20.0	338	--
274	26.7	340	--
276	32.3	342	--
278	36.0	344	--
280	37.3	346	--
282	36.0	348	--
284	32.4	350	--

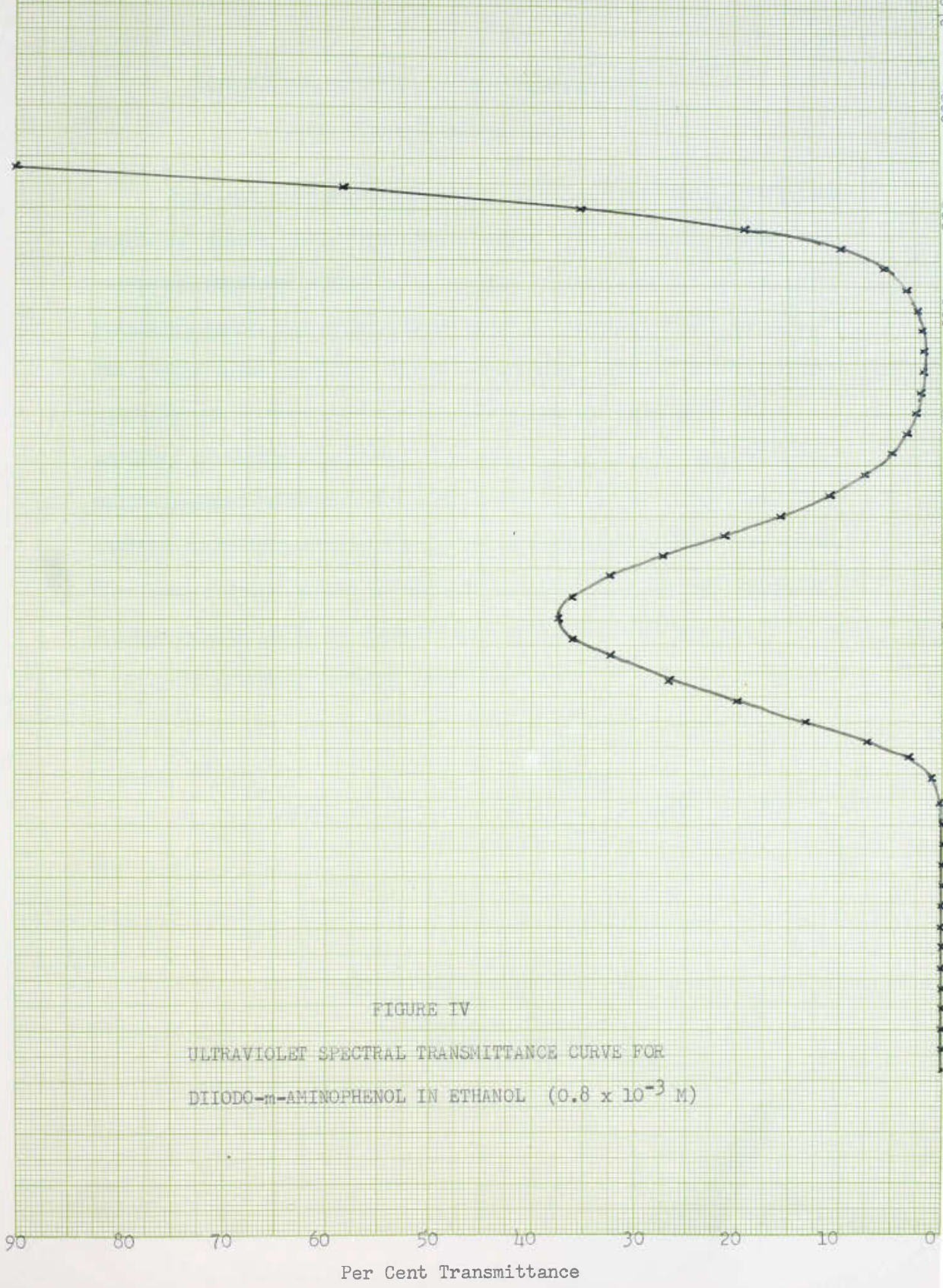


FIGURE IV

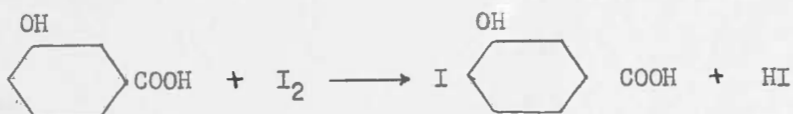
ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
 DIIDO-*m*-AMINOPHENOL IN ETHANOL (0.8×10^{-3} M)

Preparation of Iodo-m-hydroxybenzoic Acid

From m-Hydroxybenzoic Acid

Five grams of m-hydroxybenzoic acid were dissolved in a minimum amount of dilute sodium hydroxide, after which about 50 ml. of concentrated ammonium hydroxide were added. A solution of iodine in potassium iodide was added slowly and with constant stirring. When the iodine color persisted for a few minutes addition of the iodine solution was discontinued and excess iodine was reduced by the addition of sodium bisulfite. The mixture was then acidified with dilute sulfuric acid and the product was removed by filtration. The iodohydroxybenzoic acid was purified by recrystallization from water. The final product melted at 227° C. The melting point of 4-iodo-m-hydroxybenzoic acid, as reported in literature, is 226° C.

The reaction probably takes the form



Analysis for Iodine of the Product from the
Iodination of m-Hydroxybenzoic Acid

SAMPLE I

Weight of sample	0.2073 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me AgNO ₃	2.575
KCNS (0.0537 N)	33.89 ml.
me KCNS	1.821
me iodine	0.754
Per cent iodine found	47.23%

SAMPLE II

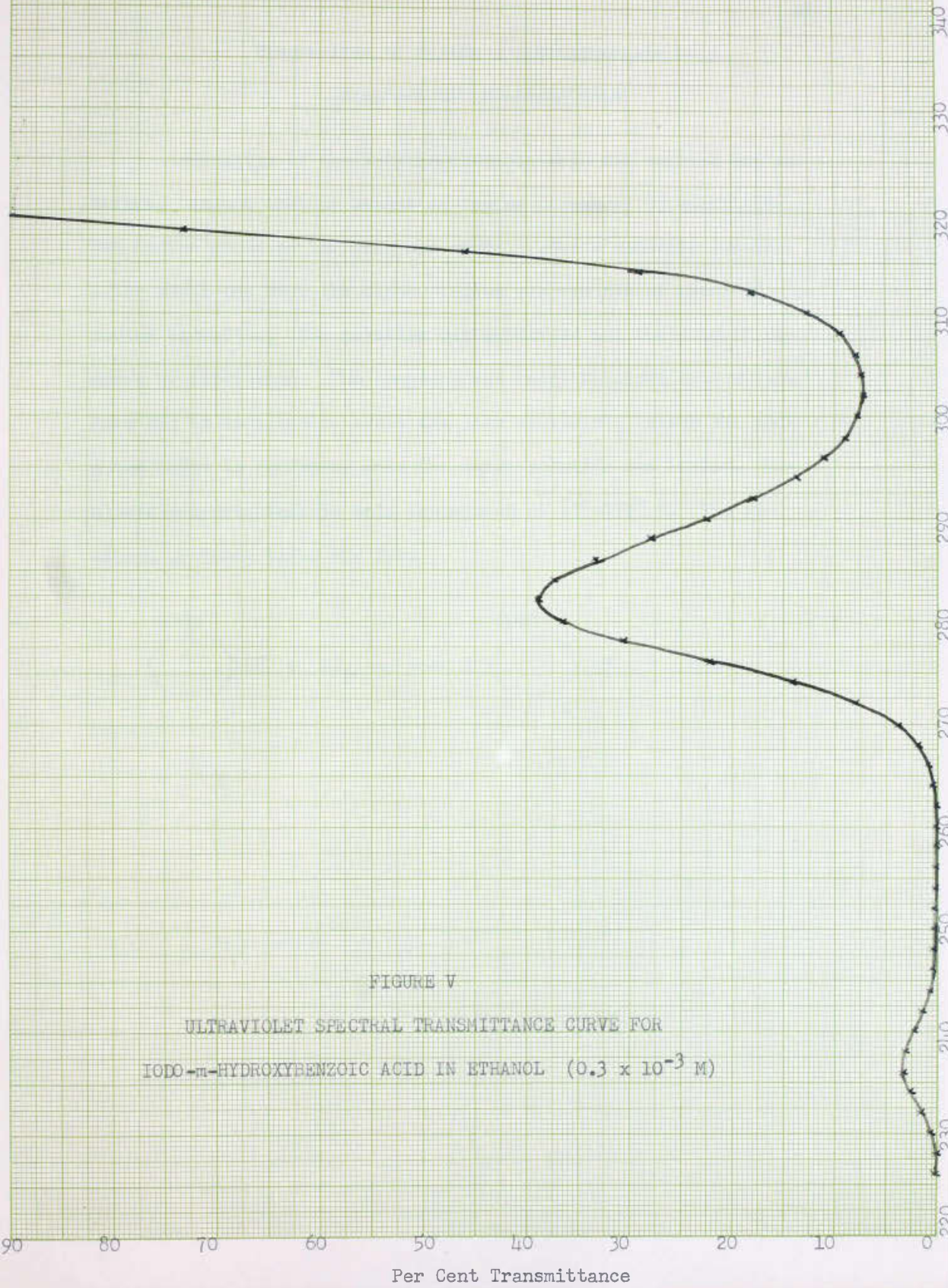
Weight of sample	0.2510 gram
AgNO ₃ (0.1036 N)	25.00 ml.
me AgNO ₃	2.575
KCNS (0.0537 N)	30.25 ml.
me KCNS	1.626
me iodine	0.949
Per cent iodine found	47.98%
Iodine calculated for C ₇ H ₅ O ₃ I	48.25%

TABLE IV

ULTRAVIOLET ABSORPTION DATA FOR
 IODO-m-HYDROXYBENZOIC ACID (0.3×10^{-3} M)

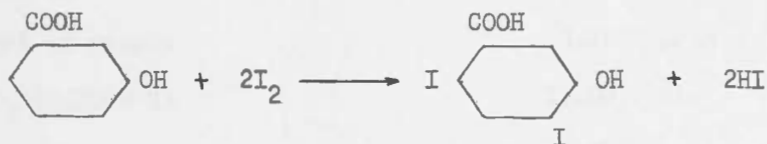
<u>Wavelength Millimicrons</u>	<u>Per Cent Transmission</u>	<u>Wavelength Millimicrons</u>	<u>Per Cent Transmission</u>
200	--	286	33.3
222	--	288	27.8
224	--	290	22.4
226	.01	292	17.7
228	.12	294	13.8
230	.55	296	11.0
232	1.50	298	8.97
234	2.68	300	7.80
236	3.38	302	7.25
238	3.15	304	7.37
240	2.39	306	8.07
242	1.55	308	9.59
244	.93	310	12.8
246	.53	312	18.2
248	.30	314	29.3
250	.17	316	46.1
252	.11	318	73.3
254	.09	320	100.0
256	.07	322	--
258	.08	324	--
260	.12	326	--
262	.22	328	--
264	.45	330	--
266	.94	332	--
268	1.96	334	--
270	4.08	336	--
272	7.95	338	--
274	14.2	340	--
276	22.3	342	--
278	30.8	344	--
280	36.6	346	--
282	38.8	348	--
284	37.3	350	--

FIGURE V
ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
IODO-*m*-HYDROXYBENZOIC ACID IN ETHANOL (0.3×10^{-3} M)



Preparation of Diiodo-m-hydroxybenzoic Acid
from m-Hydroxybenzoic Acid

Iodination of the m-hydroxybenzoic acid was carried out as before, except that an amount of iodine necessary to substitute two iodine atoms on the ring was added, plus a moderate excess. After about one hour the excess iodine was reduced by means of sodium bisulfite, the solution was acidified and the product removed by filtration. The compound was recrystallized from water. Care had to be taken to avoid the loss of iodine, since the compound began to decompose when the water solution was boiled. The diiodo-m-hydroxybenzoic acid decomposed at 172-174° C. The reaction probably takes the form



Analysis for Iodine of the Product from the
Iodination of *m*-Hydroxybenzoic Acid

SAMPLE I

Weight of sample	0.2014 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me AgNO ₃	2.575
KCNS (0.0537 N)	28.30 ml.
me KCNS	1.521
me iodine	1.054
Per cent iodine found	66.41%

SAMPLE II

Weight of sample	0.2201 gram
AgNO ₃ (0.1030 N)	25.00 ml.
me AgNO ₃	2.575
KCNS (0.0537 N)	26.53 ml.
me KCNS	1.426
me iodine	1.149
Per cent iodine found	66.25%
Iodine calculated for C ₇ H ₄ O ₃ I ₂	65.09%

TABLE V

ULTRAVIOLET ABSORPTION DATA FOR
 DIIDO-*m*-HYDROXYBENZOIC ACID (0.7×10^{-3} M)

<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>	<u>Wavelength</u> <u>Millimicrons</u>	<u>Per Cent</u> <u>Transmission</u>
220	--	286	20.3
222	--	288	17.3
224	--	290	14.9
226	.03	292	12.9
228	.04	294	11.6
230	.07	296	11.2
232	.10	298	11.8
234	.12	300	13.3
236	.15	302	15.4
238	.17	304	18.2
240	.18	306	22.2
242	.19	308	28.8
244	.19	310	38.8
246	.18	312	53.2
248	.16	314	73.5
250	.14	316	91.9
252	.13	318	--
254	.20	320	--
256	.62	322	--
258	1.81	324	--
260	3.98	326	--
262	7.32	328	--
264	11.3	330	--
266	15.9	332	--
268	20.5	334	--
270	24.8	336	--
272	28.3	338	--
274	30.8	340	--
276	31.9	342	--
278	31.7	344	--
280	29.8	346	--
282	26.8	348	--
284	23.5	350	--

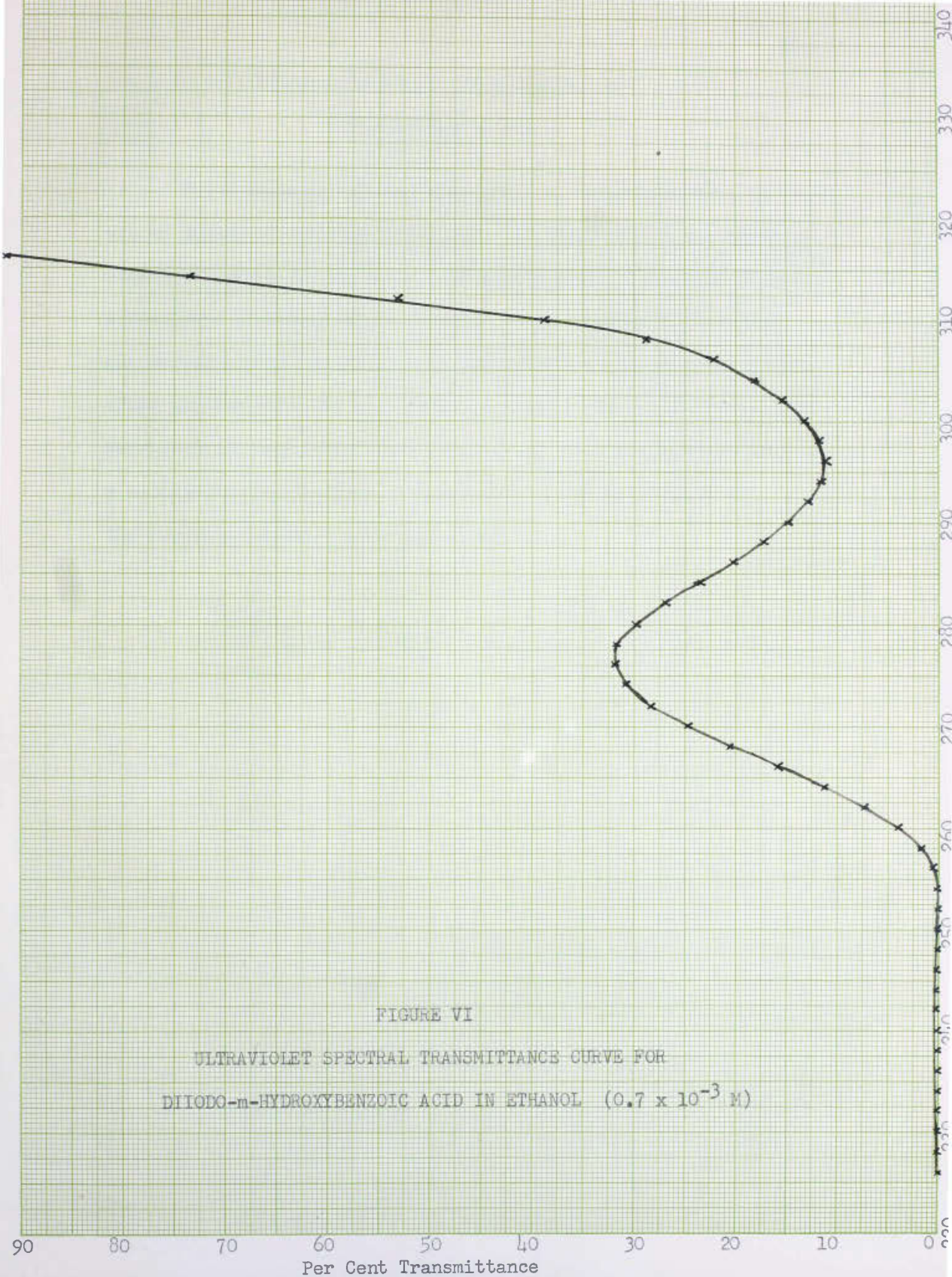


FIGURE VI

ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
DIIDO-*m*-HYDROXYBENZOIC ACID IN ETHANOL (0.7×10^{-3} M)

90 80 70 60 50 40 30 20 10 0
Per Cent Transmittance

Preparation of Diiodo-m-chlorophenol
from m-Chlorophenol

The m-chlorophenol was dissolved in sodium hydroxide solution and an excess of ammonium hydroxide. To the solution was added an amount of iodine in potassium iodide necessary to substitute two equivalents of iodine on the benzene ring, plus a small excess. Any excess iodine was reduced by the addition of sodium bisulfite after the reaction was considered complete. The solution was then acidified and the product was purified by recrystallization from a water-ethanol solution. The product melted at 120-122° C. The reaction probably takes the form



TABLE VI

TITRATION DATA FOR

m-CHLOROPHENOL

<u>Milliliters of AgNO₃ (0.1030N)</u>	<u>Scale Reading (MV)</u>
0	300
1.0	300
2.0	300
3.0	300
4.0	295
5.0	292
6.0	290
7.0	286
8.0	278
9.0	269
9.5	260
10.0	250
10.5	235
11.0	215
11.5	148
12.0	135
12.5	140
13.0	132
13.5	125
14.0	123
14.5	111
15.0	103
15.5	85
16.0	-72
16.5	-107
17.0	-121
18.0	-123

Ratio I:Cl - - 2:1

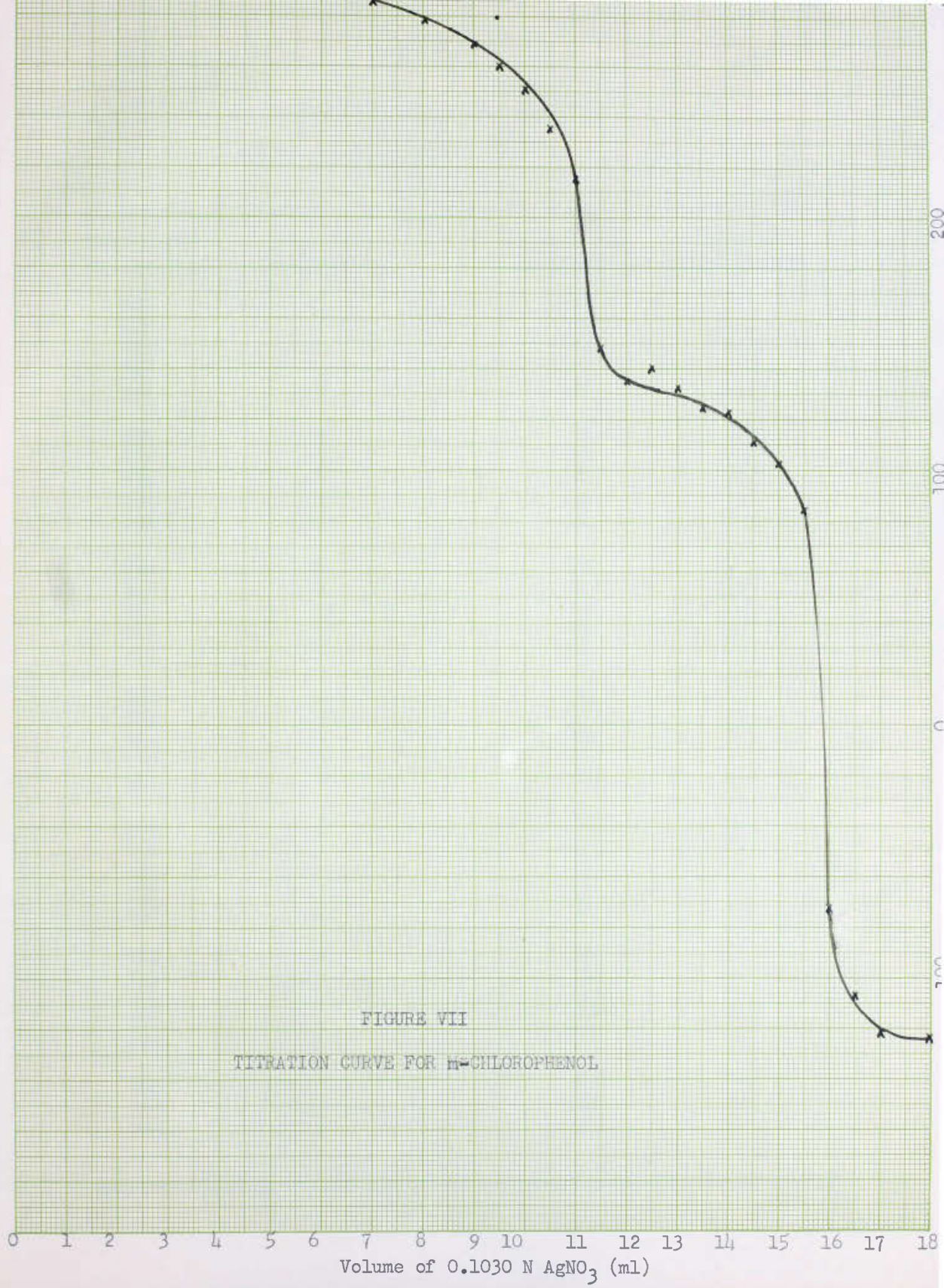


FIGURE VII

TITRATION CURVE FOR *m*-CHLOROPHENOL

Volume of 0.1030 N AgNO₃ (ml)

TABLE VII

ULTRAVIOLET ABSORPTION DATA FOR
 DIIDO-m-CHLOROPHENOL (1.2×10^{-3} M)

<u>Wavelength Millimicrons</u>	<u>Per Cent Transmission</u>	<u>Wavelength Millimicrons</u>	<u>Per Cent Transmission</u>
200	--	286	15.0
222	--	288	11.8
224	--	290	9.94
226	--	292	8.50
228	.05	294	7.40
230	.09	296	6.84
232	.11	298	7.17
234	.15	300	8.57
236	.19	302	10.9
238	.21	304	14.2
240	.24	306	18.6
242	.24	308	25.4
244	.24	310	38.0
246	.24	312	51.8
248	.20	314	82.7
250	.18	316	--
252	.15	318	--
254	.14	320	--
256	.42	322	--
258	1.76	324	--
260	5.42	326	--
262	12.3	328	--
264	19.5	330	--
266	26.0	332	--
268	30.2	334	--
270	32.5	336	--
272	33.3	338	--
274	32.8	340	--
276	31.4	342	--
278	29.7	344	--
280	26.2	346	--
282	22.4	348	--
284	18.3	350	---

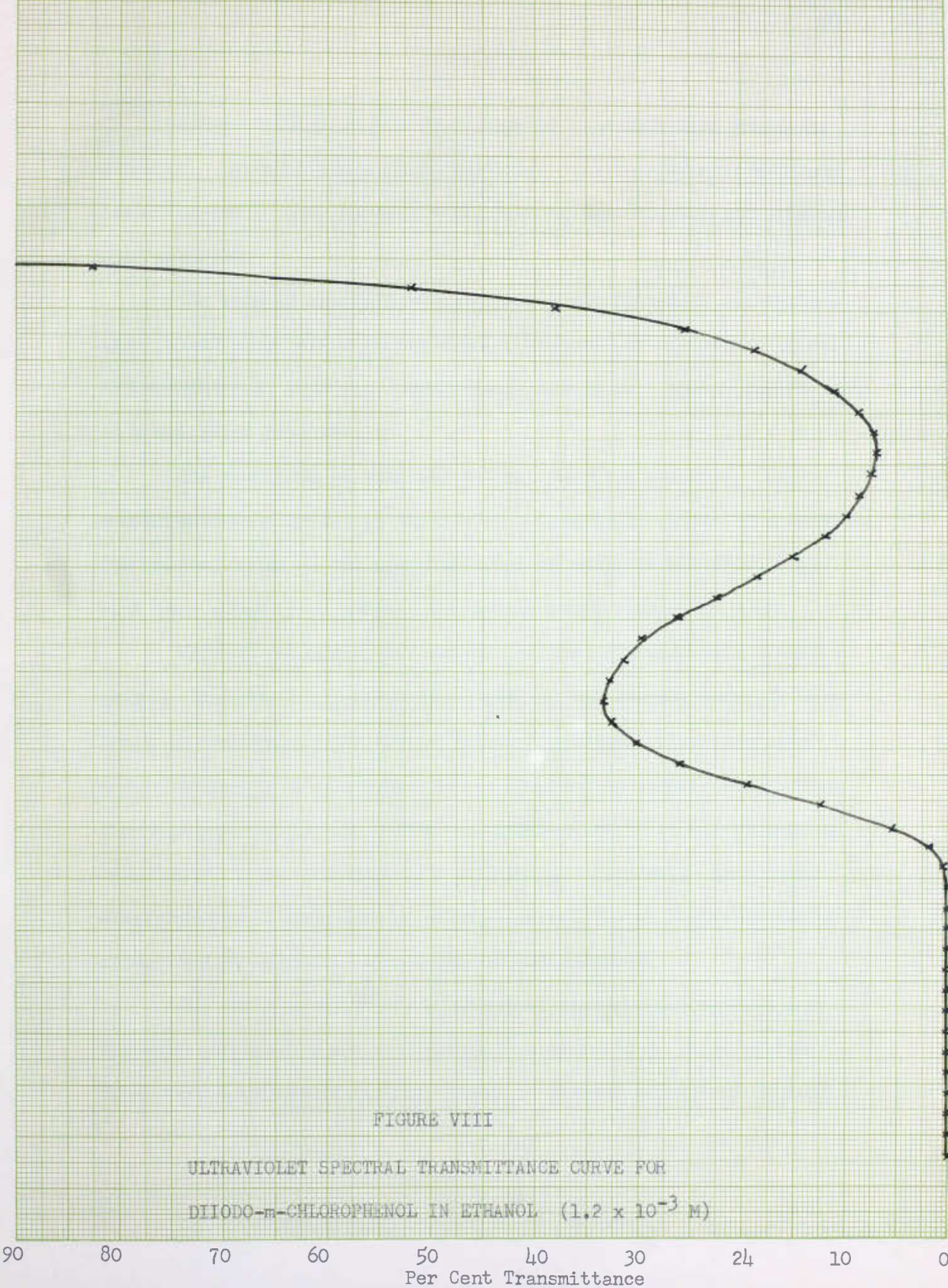


FIGURE VIII

ULTRAVIOLET SPECTRAL TRANSMITTANCE CURVE FOR
DIIDO-m-CHLOROPHENOL IN ETHANOL (1.2×10^{-3} M)

90 80 70 60 50 40 30 24 10 0
Per Cent Transmittance

CONCLUSION

Diiodo derivatives of the following compounds were prepared: m-cresol, m-nitrophenol, m-aminophenol, m-hydroxybenzoic acid and m-chlorophenol. The monoiodo derivative of m-hydroxybenzoic acid was also prepared.

The rate of reaction of iodine with m-nitrophenol was noticeably slower than that with the other compounds investigated. Diiodo-m-hydroxybenzoic acid was comparatively unstable, losing iodine even in a hot water solution.

The structure of only one of the compounds prepared, iodo-m-hydroxybenzoic acid, is known with a reasonable degree of certainty. The melting point of the prepared compound compares satisfactorily with that given in literature for 4-iodo-m-hydroxybenzoic acid.

Ultraviolet absorption spectra of the compounds were investigated. Characteristic absorption bands of the benzene molecule were found in the region from 290 to 310 millimicrons. There was some variation in the bathochromic shifts produced by substituent groups. The diiodo-m-aminophenol showed the greatest shift of the absorption band toward longer wavelengths. Following, in order, were iodo-m-hydroxybenzoic acid and the diiodo derivatives of m-hydroxybenzoic acid, m-chlorophenol, m-nitrophenol and m-cresol.

The bands of maximum absorption of diiodo-m-nitrophenol and diiodo-m-aminophenol were quite broad as compared to those of the other compounds in the series. Peaks of minimum absorption occurred

in the range from 270 to 280 millimicrons. A slight rise in the transmission curves was apparent in the region from 230 to 240 millimicrons for the diiodo derivatives of m-nitrophenol, m-hydroxybenzoic acid and m-chlorophenol, with iodo-m-hydroxybenzoic acid giving a decided rise at 236 millimicrons. With the exception of diiodo-m-nitrophenol, all of the compounds investigated displayed a sharp increase in per cent transmission at wavelengths above 310-315 millimicrons.

Absorption effects varied markedly as related to concentration. Diiodo-m-nitrophenol displayed the strongest absorptive powers at a given concentration, followed by the iodo-m-hydroxybenzoic acid. Diiodo-m-hydroxybenzoic acid required nearly twice the concentration used for the monoiodo compound to give a similar absorption effect. Diiodo-m-aminophenol exhibited absorption properties very similar to those of diiodo-m-hydroxybenzoic acid, giving maximum and minimum points at very nearly the same positions. The diiodo derivatives of m-chlorophenol and m-cresol displayed similar properties of ultraviolet absorption and were the weakest absorbers investigated.

Experimental evidence cited above indicates that, of the compounds investigated, the nitro group contributes most strongly to the resonance state of the benzene molecule, while the chloride and methyl groups contribute the least. Similarly, the monoiodo product of m-hydroxybenzoic acid is a much stronger absorber of ultraviolet light than is the diiodo product. This evidence confirms the

supposition that the former compound is a more freely resonating structure.

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