1923

Some condensation products of resorcinol and their relation to the phenomenon of fluorescence

Renzy Evert Flikkema
University of Massachusetts Amherst

Follow this and additional works at: http://scholarworks.umass.edu/theses

http://scholarworks.umass.edu/theses/1511

This thesis is brought to you for free and open access by the Dissertations and Theses at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Masters Theses 1911 - February 2014 by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.
Some Condensation Products
of Resorcinol and Their Relation to the Phenomenon of Fluorescence

RENZY EVERT FLIKKEMA

This thesis is not to be loaned outside the library building. For this purpose, use the copy in the department where the work of the thesis was done.
SOME CONDENSATION PRODUCTS

OF

RESORCINOL AND THEIR RELATION TO THE

PHENOMENON OF FLUORESCENCE

Thesis submitted for
the degree of
Master of Science

MASSACHUSETTS AGRICULTURAL COLLEGE
May 1923
PurposE oF tHe I.nvestigation

The purpose of the present investigation is to study the reaction which takes place when resorcinol and zinc chloride are fused at 150°; to isolate the fluorescent product and compare it with other fluorescent compounds in the light of the present theories of fluorescence. The problem is a continuation of the work started by R. B. French, and was suggested by Dr. Joseph S. Chamberlain, Professor of Organic Chemistry, Massachusetts Agricultural College.
INTRODUCTION

R. B. French\(^1\), during his investigation last year, noticed that when resorcinol or meta-dihydroxy benzene was heated in the presence of zinc chloride at \(150^\circ\) for five hours, and the resulting fused mass was extracted with sodium hydroxide and highly diluted, the result was a very fluorescent solution, and he suggested the further study of this reaction and its relation to the theories of fluorescence. The fluorescence resembled very closely the fluorescence produced by the sodium salt of fluorescein or uranine. Fluorescein is the product which results when one molecule of phthallic anhydride is heated with two molecules of resorcinol in the presence of zinc chloride. The reaction which takes place is as follows:\(^2\)

\[
\begin{align*}
\text{Phthallic anhydride} & \quad \text{Resorcinol} & \quad \text{Fluorescein} \\
\text{C}_6\text{H}_5\text{O} & \quad \text{C}_6\text{H}_4\text{O} & \quad \text{C}_6\text{H}_5\text{O} \\
\text{C}_6\text{H}_5\text{O} & \quad \text{C}_6\text{H}_4\text{OH} & \quad \text{C}_6\text{H}_4\text{OH} \\
\text{C}_6\text{H}_5\text{O} & \quad \text{C}_6\text{H}_4\text{OH} & \quad \text{C}_6\text{H}_5\text{O}
\end{align*}
\]

It is generally accepted, and so stated in most works on the constitution of dyes\(^3\) that fluorescein and its sodium salt uranine, may be represented by the following formulas:

\(^2\) Beil., II, 2060.
\(^3\) Fay. "Coal Tar Dyes.", p. 254.
In fluorescein we have the pyrone ring (A) while in uranine we have a tautomeric modification of the pyrone ring, and one of the normal benzene rings has taken the quinoid structure (B).

The phenomenon of fluorescence is very well known, but a description may not be out of place. When ordinary white light falls on a fluorescent substance it emits coloured light, so that for certain wave lengths the intensity of the reflected light is apparently greater than that of the incident light.

Three theories have been advanced to explain the relation between chemical constitution and fluorescence. The following is a resume of each:

1 Watson, F.R. "Color in Relation to Chemical Constitution", p. 156.
Hewitt's Theory. According to this theory fluorescence is due to a particular kind of tautomerism which Hewitt has termed double symmetrical tautomerism. The theory is almost identical in form with those which explain color or selective absorption as due to a vibration between different tautomeric forms, and according to Hewitt, if this vibration is symmetrical it will cause fluorescence. To explain what is meant by symmetrical vibration we may take as an example the very fluorescent compound fluorescein. Fluorescein may be considered to tautomerise from the quinoid form $A_1$ to the non quinoid form $B$, and then to the quinoid form $A_2$.

It can tautomerise back from $A_2$, through $B$ to $A_1$, so that we have a cycle

According to this theory only symmetrical compounds should exhibit fluorescence, e.g.
The fluorescence of anthracene can be explained by a similar symmetrical vibration, although there is no movement of a labile hydrogen atom but only a rearrangement of valencies.

There are however many symmetrical compounds which are not fluorescent, e.g.

\[
\text{Di-nitro fluorescein (symmetrical)}
\]

Kauffmann prepared four derivatives\(^1\) of the di-methyl ether of hydroquinone which are fluorescent, and yet it is not very obvious how there can be any tautomerism of molecular rearrangement; and in any case their structure is asymmetrical. The following are the four derivatives of hydroquinone di-methyl ether.

\(^1\) Watson, p. 159.
Hewett's theory is therefore unsatisfactory in these cases just mentioned.

**Meyer's Fluorophore Theory.** According to this theory the fluorescence is due to the association of a fluorophore, with some other dense atomic complex. The groups recognized by Meyer as fluorophores are the following:

![Fluorophore structures](image)

The addition of a benzene nucleus at the sides of the fluorophore produces the requisite complexity and packing and we find fluorescence in anthracene, acridine, xanthone, etc.

![Fluorophore structures](image)

The theory does not explain the following facts; viz., (a) the introduction of certain groups or atoms, e.g., chlorine atoms, nitro groups, destroys the fluorescence; (b) the acetylation of the hydroxyl or the amino group has the same effect.
**Kauffmann's Theory.** A benzene nucleus in which the arrangement of the bonds is according to Dewar's formula, or approximate to this is the cause of luminescence.

![Dewar's formula.](image)

If salt-forming groups, e.g., hydroxyl, amino and substituted amino $(\text{NHCH}_3)$ and $\text{N(CH}_3)_2$, etc., are introduced into the benzene nucleus the tendency is for the double bonds to assume the Dewar arrangement and the luminescence is thereby increased. Such auxiliary groups influencing fluorescence are termed "auxochromes". A benzene nucleus together with the auxochrome is termed a "luminophore". A luminophore plus a new group termed a "fluorogen" gives a fluorescent substance. The following groups are classed as fluorogens; the carbonyl, the carboxyl, the cyanogen and the acrylic groups, a group containing an ethylene bond or a conjugated ethylene bond, the benzene ring, ortho and para quinoid rings, the azo methine group, $(\text{R-N=C=})$ and the conjugated azo-methine group.

We may notice a fundamental difference between Meyer's and Kauffmann's theories. For example, in fluorescein Meyer regards the $\gamma$-pyrone ring (A), the fluorophore, as the seat of fluorescence,

![Fluorescein](image)
The fluorescence is made manifest by attaching benzene nuclei to the sides of the pyrone ring and intensified by the auxochromes. Kauffmann regards the benzene nuclei as the luminophores, their luminescence being converted into fluorescence by the substituted \( \sqrt{\text{-pyrone ring}} \).

Due to the large number of modifications and variations Kauffmann's theory has become very complicated, and may be summarized as follows: Fluorescence is dependent on (1) the presence of a benzene nucleus (or similar); (2) its assuming approximately the arrangement of the bonds according to Dewar's formula which is determined by the total effect of all groups introduced into the nucleus, auxochromes, fluorogens and other groups; (3) the presence of a fluorogen; (4) a favorable arrangement of fluorogens with reference to the auxochromes and other groups present in the nucleus.

It is rather difficult to summarize the above theories and find any definite grouping to which fluorescence is due.

A list of a few dyes, with the same or similar grouping and arrangement of bonds, some of which are fluorescent while others are non-fluorescent, will show the peculiarity of the phenomenon of fluorescence.
Fluorescent

$\text{(CH}_3\text{)}_2\text{N} \quad \text{O} \quad \text{N(CH}_3\text{)}_2\text{Cl}$

Pyronine G - Fay - 249

Phenolphthalein, Fay, 251

Nonfluorescent

Fluorescein, Fay 254.

Eosine, Fay, 255

Erythrosine, Fay, 258

Note relationship between the last two.

Eosine B.N. Fay, 259
Phloxine  Fay, 260  
Dyes without fluorescence.

Phloxine  T.A.  Fay, 261  
Slight dark green fluorescence

Cyclamine  Fay, 262  
Sulphur ether corresponding to Phloxine.

Rhodamine B.  Fay, 264.  
Very fluorescent in alcohol.
Fluorescence disappears when heated but returns when cooled.

Rhodamine 3B.  Fay, 266.  
Fluorescence lost on tannined cotton.
Examples of non fluorescent dyes with the N-ether linking prepared by the condensation of pyrogallol and phthalic anhydride.

![Pyrogallol](image)

**Galleine (Alizarine Violet)**  
Fay, 267

![Galleine - 2H₂O](image)

**Coeruleine (Alizarine Green)**  
Anthracene green. Fay, 269.

**Sulphonation products of the Rhodamines**

![Fast acid violet B.](image)

Violamine B.  
Cain & Thorpe, 104 (1)

![Fast acid blue R.](image)

Violamine 3 B. Fay, 273.
A Burhodine dye

\[(\text{CH}_3)_2\text{N} \quad \text{N} \quad \text{N} \quad \text{CH}_3 \quad \text{NH}_2 \cdot \text{HCl}\]

Neutral Red

Dissolves in alcohol with a magenta red shade that exhibits a slight brown fluorescence. Here we have a nitrogen ether and the o-quinoid structure. Fay, 297.

[Chemical structures of Neutral Red and Commercial Safranine]

Commercial Safranine

In alcohol it yields a yellowish red fluorescence. Fay, 308.

[Chemical structures of Formaldehydoxy tolufluoron and Trihydroxy fluoronedi-carboxylic acid]


Formula by H. v Liebig.
The fluorescent product obtained by French, and which was also obtained in this investigation, as described later on, seemed to result from a simple condensation of two or more molecules of resorcinol by loss of water, in the presence of zinc chloride, giving a resorcinol ether. In the formula for fluorescein and several other fluorescent compounds, this same grouping is also present, viz., a di-phenyl ether group with hydroxyls in each benzene ring meta to the ether linkage.

The association of these two facts led to the present investigation, the ultimate purpose of which was to see if the evidence could be obtained indicating that the di-phenyl ether meta-hydroxy grouping, rather than the pyrone ring, of which the ether is a part, is the essential grouping in fluorescent compounds. To this end two things were attempted and to a certain degree accomplished in the present study. (1) The isolation of the real fluorescent compound from the mixed product first obtained by French. (2) The preparation of other simple meta di-phenyl ether compounds to see if they also possessed fluorescent properties. Before taking up the work on these two lines, previous investigations on resorcinol ether and other condensation products of resorcinol, as cited in literature, were reviewed and repeated.

**Resorcinol Ether.** The description and methods of preparation of resorcinol ether as given by Beilstein are as follows:

(1) Beil., II, 917.
Resorcinol ether is prepared by heating with concentrated sulphuric acid in a sealed tube; by treating resorcinol with fuming sulphuric acid, or with carbonic acid and sodium. By heating resorcinol di-sulphonic acid with two molecules of resorcinol at 190; by heating phenanthrene di-sulphonic acid with resorcinol at 200. Also by heating resorcinol with concentrated hydrochloric acid in a sealed tube for one hour at 160.

**Autocondensation of Resorcinol.** Two hundred and fifty grams of resorcinol were heated with 50 grams of zinc chloride for 30 hours at 160-180° in a flask fitted with a return condenser. The cooled mass was extracted with sodium hydroxide. This alkaline solution had a dark red color, which after diluting with a large quantity of water gave a greenish fluorescence, which quickly disappeared when neutralized with an acid. Upon the addition of a sufficient quantity of the acid a reddish yellow compound was precipitated which could easily be filtered off, washed and dried on a porous plate. This substance was boiled in a large amount of water, from which upon cooling a compound, C_{14}H_{18}O_{9}, separated as reddish brown needles. By frequent recrystallization from boiling water in the presence of animal charcoal we finally obtained fine colorless silk-like needles, which were slightly matted and which melted at 263°. They were easily soluble in alcohol, ether, acetone, acetic acid, ethyl acetate, and chloroform; soluble with difficulty in water and toluene. They were soluble in alkalies without fluorescence, but were reprecipitated with acids. The molecular weight was determined by the boiling point method in acetone, and was found to agree with the formula C_{14}H_{18}O_{9}.

1 Ber. 40; 1451, 1453.
The acetate was formed in the usual manner by boiling with acetic acid and sodium acetate. After pouring the resulting mixture in water the product quickly crystallized out. It was recrystallized from alcohol with animal charcoal, and fine white needles were obtained. They melted at 150-151°. They were soluble in benzene, ethyl acetate, chloroform, acetone, acetic acid and ether; soluble with difficulty in water and alkalies.

The benzoate was prepared according to the method of Schotten and Baumann1, that is, by treating with benzoic chloride and sodium hydroxide. The benzoate formed was purified by recrystallization from ethyl acetate and animal charcoal. Colorless short thick prisms were formed which melted at 180°. Soluble with difficulty in benzene, chloroform, and ethyl acetate, insoluble in alcohol, ether, ligroin and sodium hydroxide.

Meyer and Marx also tried another method by heating resorcinol alone in an oil bath with a condenser for 50 hours at 200-220°. The result was a large amount of a resin which melted at 263°; the greater part, however, was unchanged resorcinol. The structural formula of the product, C₁₄H₁₃O₃, which was isolated by these men was not definitely given, but they suggested a possible four, one of which may be correct.

The four suggested are the following:

\[ \text{I} \quad \text{II} \]
\[ \text{III} \quad \text{IV} \]

II might be changed even still more, e.g.,

1 Ber. 19; 5218.
Of these last two IV might be deserving of investigation. III would be a 3-6 dihydroxy methyl xanthin, the alkaline solution of which should be fluorescent.

Grimaux also fused resorcinol with zinc chloride at 140° and obtained a product which melted at 261°, to which he gave the formula C_{15}H_{10}O_{5}. It was insoluble in water, soluble at the boiling point in 20 parts of 50 per cent alcohol and 100 parts of toluene. He also claims to have received small quantities of another substance which he calls "umbelliferon".

Claus and Andre heated resorcinol with dehydrated oxal acid in sealed tubes for two or three hours at 200°. The product they obtained was soluble in alkalies with a green fluorescence, and was given the formula C_{20}H_{12}O_{6}. Claus subsequently altered this to C_{20}H_{14}O_{7} or C_{20}H_{12}O_{6}, the composition depending on whether it was dried at 100° or 150°.

Gukassianz effected the condensation by heating resorcinol with concentrated sulphuric acid at 120°. He gave the compound that he obtained the formula C_{14}H_{6}O_{5}.

Hewitt and A. E. Pitt examined the product prepared according to the directions of Gukassianz and altered the formula to C_{20}H_{14}O_{7}. The percentage of carbon and hydrogen being nearly identical.

Von Georgievicze condensed resorcinol with twice its weight of oxalic acid for three hours at 150°-160° without pressure or a condensing agent. The product was given the formula C_{16}H_{12}O_{6} and a provisional constitutional formula was assigned to it.

1 Beil., II, 516. 564
2 Ber., 10, 1305.
3 Ber., 14, 2563.
4 Ber., 11, 1164.
6 Hewitt, J.T., 236.
These last named investigators were endeavoring to form a fluorone compound.

**EXPERIMENTAL**

In these investigations just reviewed the compound to which the formula of resorcinol ether was given was the fluorescent compound obtained by Barth and Wiedal\(^1\). The fluorescent condensation product termed "umbelliferon" was resinous character, and though different formulas were assigned to it no particular one has been well established. A study of the preceding literature will readily show that nearly all of the investigators who worked on this problem have given different formulas to their products. In the product obtained by French it is probable that the "umbelliferon" of Grimaux was also obtained, the indication being that they are the same. The experiments undertaken for the purpose of isolating the fluorescent product and determining as near as possible the cause of the fluorescence follow.
The first product was obtained by heating resorcinol and zinc chloride in a beaker in an oil bath at 150°-160° for five hours, which is practically following the procedure of both Grimaux and French. The resultant mass was extracted with sodium hydroxide and precipitated with hydrochloric acid.

The method used by Grimaux was also modified, by extracting with 95 per cent alcohol and reprecipitating with water. A red amorphous powder was thrown down as soon as an excess of water was added. As long as the neutral or acid solution was worked with there was no fluorescence, but alkaline solutions were intensely fluorescent. Also the filtrate from the alcoholic solution precipitated with water was fluorescent. If boiled or even placed on the water bath and concentrated all fluorescence seemed to have disappeared, and we obtained a small amount of precipitate which would not again become fluorescent even in alkaline solutions. The molecular weight of the red amorphous powder was determined by the freezing point method using phenol as a solvent, the result was, M.W. 218, corresponding to the formula \((C_{6}H_{12}OH)_{2}O\cdot H_{2}O\). This however did not agree with the results of Meyer and Marx, but did agree with the results of one of the products isolated by Barth and Weidal, who claim to have isolated two products from a like fused mass, one being a compound of the formula \(C_{12}H_{10}O_{6}\) and the other \(C_{6}H_{10}O_{8}\), the latter corresponding to a product isolated by Grimaux, when he fused resorcinol with zinc chloride for 6 hours at 135°-145°. The red amorphous powder was then boiled with a large amount of water and

1 Bail., II, 516.
2 Ber., 40, 1461-1453.
3 Ber., 10, 1466.
animal charcoal, and recrystallized from cold water. The product was identified by the melting point and other physical properties and found to be identical with the one isolated by Marx and Meyer\textsuperscript{1}, and to which they gave the formula $C_{14}H_{13}O_6$. This product was no longer fluorescent, but when the red amorphous powder was boiled in water, a black resinous mass separated from the rest of the compound, and upon cooling crumbled more or less to a black amorphous powder. This was still fluorescent in alkaline solution. The properties of this black amorphous powder seemed to be identical with the resinous mass which Grimaux and others isolated by the same or different methods, and which Grimaux\textsuperscript{2} termed "Embelliferon". The molecular weight of this resinous mass was determined by the freezing point method, using phenol as a solvent, and was found to agree with the formula $C_{24}H_{18}O_6$. Thus from this one fusion there was obtained a red amorphous powder which had a molecular weight of 216, agreeing with the molecular weight of the resorcinol ether that Barth and Weidal\textsuperscript{3} claim to have isolated. Also, the white matty crystalline compound to which Meyer and Marx\textsuperscript{4} gave the formula $C_{14}H_{13}O_6$, and the compound to which Grimaux\textsuperscript{5} gave the formula $C_{24}H_{18}O_6$, and to which Barth and Weidal gave the structural formula,

\[
\begin{align*}
&\text{HO} &\begin{array}{ccc}
&\text{O} &\text{O} &\text{O} &\text{OH}
&\end{array}
\end{align*}
\]

Not being able to find any more literature concerning the fluorescence of the products formed in the ways just mentioned attempts were made to prepare resorcinol ether by various methods,

\begin{itemize}
\item Ber., 40, 1451-1453.
\item Beil., II, 617.
\item Ber., 10, 1466.
\item Ber., 40, 1451.
\item Beil., II, 517.
\end{itemize}
some being original as far as known.

One sample of resorcinol was heated with phosphoric anhydride, another with zinc chloride, and still another with aluminium chloride. The procedure in each case was the same. The materials were mixed in an iron crucible and heated in an oil bath, the temperature being held at 180°-180° for 4 hours. In all cases the resulting product was fluorescent if dissolved in an alkaline solution. The fluorescence was greatest in the order named. This may have been due to the difference in the ability of the different dehydrating agents to remove water. The properties of the resulting masses were practically the same in all cases, and as explained under the first fusion. The reaction which probably takes place to form the resorcinol ether is

\[
\text{HO} \quad \text{OH} + \text{HO} \quad \text{OH} \quad \text{Minus 1 H}_2\text{O} \quad \text{HO} \quad \text{O} \quad \text{HO} \quad \text{OH}
\]

The reaction that takes place to form the compound C₁₄H₁₄O₅ has been given above in the review of the work of Meyer and Marx. The reaction that takes place to form the compound C₂₄H₂₀O₆ or a tetra-resorcinol ether is

\[
\text{HO} \quad \text{OH} \quad \text{HO} \quad \text{OH} \quad \text{HO} \quad \text{O} \quad \text{HO} \quad \text{OH} \quad \text{Minus 3 H}_2\text{O}
\]

\[
\text{HO} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{OH}
\]
Resorcinol and hydrochloric acid were also heated in a sealed tube at 180° for one hour. The same procedure was followed using sulphuric acid and as a result in both cases a resinous mass that was very fluorescent in alkaline solution was obtained. The resinous mass was washed and dried and then dissolved in 95 per cent alcohol. An alcoholic lead acetate solution precipitated the resorcinol ether\(^1\) while another substance \(C_{24}H_{18}O_5\) remained in solution. The lead salt of the ether was decomposed by dissolving in acetic acid, and reprecipitated with hydrochloric acid. Barth and Weidal claim that the product which they isolated was fluorescent. This was not true, however, in the present case for the product obtained was the same as that which was isolated from the fusion of resorcinol and zinc chloride. It appears as if Marx and Meyer also tried the method used by Barth and Weidal and also received the product to which they gave the formula \(C_{14}H_{12}O_2\).

The next step was to form a meta-hydroxy phenyl ether, or a resorcinol ether without using any resorcinol, and in this way, if possible, to avoid getting a mixture of any of the products just mentioned or those corresponding to the formulas \(C_{12}H_{10}O_2\), \(C_{14}H_{12}O_2\), \(C_{24}H_{18}O_5\). The following attempts were made to accomplish this result.

**Fusion of Diphenyl Ether with Sodium Hydroxide.** By fusing diphenyl ether \((C_6H_5)_2O\) with sodium hydroxide, which is analogous to the reaction by which resorcinol may be prepared by fusing phenol with sodium hydroxide\(^2\), it was thought that resorcinol ether would result. The diphenyl ether was prepared according to the method used

---

1 Ber., 10, 1468.
2 Ber., 12, 417–420.
by V. Marx and W. Weith\textsuperscript{1} which, in short, is as follows: Two parts of phenol and one part of aluminium chloride (by weight) were placed in a flask whereupon a great deal of heat was evolved. The mixture was then heated under a reflux condenser for one and one half hours until all the hydrochloric acid was evolved, and there remained, upon cooling, a pulverizable brown resinous substance. On heating the residue a volatile product was distilled over. The distillate was then shaken with an excess of sodium hydroxide solution to remove the phenol and redistilled in steam. This distillate was then further fractionated and the product distilling over at 250° - 253° was the phenyl ether M.P. 428. A mixture of sodium hydroxide and the diphenyl ether was heated for 5 hours under a reflux condenser at 253°, but there was no change. Due to the low boiling point of the phenyl ether, it was not possible to heat the mixture to the fusion point of the sodium hydroxide (M.P. 318). In the case of phenol and sodium hydroxide the sodium salt is probably first formed, and this in turn forms a sodium phenolate with a higher boiling point. The result was, therefore, that we could not form the product sought for in this manner.

\textit{Preparation from meta-Nitro Phenol.}\textsuperscript{2} The meta-nitro phenol was prepared by mixing meta-nitraniline and sufficient dilute sulphuric acid to form, on cooling, a thick paste of sulphate. To this was added, with cooling a solution of sodium nitrite until all was dissolved. To this dilute sulphuric acid was added (for 10 grams of meta-nitraniline one and one-half liters of 1:10 acid were used). The filtered solution was boiled, shaken with ether, the ether evaporated and the residue boiled with hydrochloric acid (1:1). The solution was allowed to cool at 40° or 50° and filtered. On recrystallizing from ether, thick sulphur-yellow

\textsuperscript{1} Ber., 14, 189.
\textsuperscript{2} Bell., II, 681.
crystals were obtained, M.P. 96°. This product was identified as meta-nitro phenol. The reactions that take place are as follows:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NO}_2 (1) & \quad \xrightarrow{\text{diazotization and}} \quad \text{C}_6\text{H}_5\text{NO}_2 (1) \\
\text{C}_6\text{H}_5\text{NH}_2 (3) & \quad \xrightarrow{\text{decomposed with } H_2O} \quad \text{C}_6\text{H}_5\text{OH} (3)
\end{align*}
\]

meta-Nitraniline \hspace{2cm} meta-Nitro phenol

An attempt was made to fuse equal parts of the sample of meta-nitro phenol and zinc chloride, but when the temperature was raised to 160° the mass exploded. There remained only carbon and zinc chloride in the flask. It was thought that the ether of the meta-nitro phenol could be prepared, and if so it was our intention to then reduce and diazotize the ether. The action of zinc chloride should theoretically have been

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{OH} \\
\text{meta-Nitro phenol} & \quad \text{Eth} \text{er of meta-Nitro phenol}
\end{align*}
\]

As soon as it was determined that this reaction could not be carried out, the meta-nitro phenol was reduced to meta amino phenol with iron filings and hydrochloric acid.¹

\[
\begin{align*}
\text{C}_6\text{H}_4\leq \text{NO}_2 (1) & \quad \xrightarrow{\text{Iron + HCl}} \quad \text{C}_6\text{H}_4\leq \text{NH}_2 \\
\text{C}_6\text{H}_4\leq \text{OH} (3) & \quad \xrightarrow{+ H} \quad \text{C}_6\text{H}_4\leq \text{OH}
\end{align*}
\]

meta-Nitro phenol \hspace{2cm} meta-Amino Phenol

¹ Beil., II, 714.
Also some stock meta- amino phenol was used.

Upon fusing meta- amino phenol with either zinc chloride or aluminium chloride at 150° for five hours, and then diazotizing the resultant mass, a non- fluorescent product was obtained. As far as could be determined there has not been isolated a product such as we expected to get with this fusion. The product should be the ether of meta- amino phenol, or

\[
\text{NH}_2 \quad \text{O} \quad \text{NH}_2
\]

and if our theory that fluorescence is due to a meta ether grouping the product expected should be fluorescent.

Another portion of the meta- amino phenol was fused with zinc chloride at 180° for 10 hours. After extracting with alcohol and precipitating with water, a fluorescent product was obtained. This product was not further investigated.

A final attempt was made to prepare the resorcinol ether by starting with meta- benzene di- sulphonic acid. The steps and methods used were as follows:

**Preparation from meta- Benzene Di- sulphonic Acid.** One hundred cubic centimeters of benzene were heated with 100 cc. of sulphuric acid until they formed one solution, then 200 cc. more of fuming sulphuric acid were added and heated under a reflux condenser while white fumes evolved. The mixture was cooled and neutralized with calcium oxide, filtered and an excess of potassium carbonate added to precipitate the calcium. By repeated evaporation and filtration the excess potassium carbonate was removed, the solution being finally evaporated to dryness. The residue was extracted with absolute alcohol, the alcohol extract evaporated again to dryness and the final residue identified as the meta- disulphonic acid.

1 Beil., II, 116.
To prove that meta-benzene di-sulphonic acid was obtained 22 gms. of the product were fused with 66 gms. of potassium hydroxide at 170°-180° for about 10 hours, the resulting mass gave a violet coloration with ferric chloride which is a characteristic test for a phenol. A small portion of this product was fused with potassium hydroxide above 250°, and a characteristic test for resorcinol was obtained by fusing a small portion with an excess of phthalic anhydride with the formation of fluorescein.

The meta-benzene disulphonic acid was then converted into meta-phenol sulphonic acid as follows: - 66 grams of potassium hydroxide were heated with 33 grams of the benzene di-sulphonic acid at 190°-230° for 8 to 10 hours, or until a thick pasty mass remained. This was neutralized with as little sulphuric acid as possible, filtered and evaporated to dryness, and then extracted with absolute alcohol.

Preparation of the ether of phenol sulphonic acid. Five grams of the phenol di-sulphonic acid were fused with 3 grams of zinc chloride at about 180°-250° for 8 hours. The crude product formed by this fusion gave a distinct fluorescence in alkaline solution.

Preparation of the resorcinol ether. Five grams of the ether of phenol sulphonic acid were fused with 3 grams of potassium hydroxide for 8 hours at 200°. The alkaline solution of the resulting mass was fluorescent. This product was not further investigated, but according to our methods of procedure and to the description of the ether given, the product is the same.
The reactions involved in these changes are as follows:

\[
\text{Benzene} + H_2SO_4 \rightarrow HOO_S SO_2OH
\]

meta-Benzene disulphonic acid

\[
HOO_S SO_2OH + KOH \xrightarrow{\text{fusion}} HO SO_2OK
\]

meta-Benzene disulphonic acid K salt of meta-phenol sulphonylic acid

\[
HO SO_2OH + ZnO \xrightarrow{\text{fusion}} KOO_S SO_2OK
\]

K salt of meta-phenol sulphonie acid Ether of meta-phenol sulphonylic acid (K salt)

\[
KOOS SO_2OK + KOH \xrightarrow{\text{fusion}} HO SO_2OK
\]

Ether of meta-phenol sulphonylic acid (K salt) Resorcinol ether
SUMMARY

When resorcinol was fused with zinc chloride, three products were obtained. (a) First a product whose molecular weight was 318, and to which the formula $C_{16}H_{10}O_3$ had been given. (b) Second, upon boiling this product, another $C_{24}H_{18}O_6$ separated out as a resinous mass, which Grimaux called "umbelliform". (c) After the resinous mass had been removed from the boiling solution, another product $C_{14}H_{12}O_3$ crystallized out when the aqueous solution cooled. The latter product was crystallized out when the aqueous solution cooled. The latter product was identical with the one isolated by Marx and Meyer. The first two products were fluorescent, and as far as could be determined were ethers, the ether linking being meta to the hydroxyl and the other ether linkings.

From the fused mass extracted after heating resorcinol and hydrochloric acid, and resorcinol and sulphuric acid, two products $C_{16}H_{12}O_3$ and $C_{24}H_{18}O_6$, which were identical with the above, were isolated, the last one only being fluorescent.

The resultah mass after the fusion of meta-amine phenol and zinc chloride, yielded a fluorescent product, which was not further investigated.

The ether formed by dehydrating meta-phenol sulphonie acid was also fluorescent.

In the case of the ethers that have been prepared, fluorescent products were obtained. These compounds did not contain either the pyrone ring or the quinoid ring. The indication is, therefore, that fluorescence is not due entirely to either of these ring structures, but that it may be due to the meta ether linking.
Acknowledgements

Acknowledgements are due, especially to Dr. Joseph S. Chamberlain, under whose direct supervision this investigation has been carried on; to Dr. J. B. Lindsey, Dr. C. A. Peters, Dr. Charles Wellington and Professor Paul Berek for their kind and helpful suggestions; to Miss Chase for her cooperation, and to others for the interest that they have shown.