

iodide we wish to draw attention to the fact that even a solution of the free alkaloid without any addition of acid is precipitated by potassium iodide. As there is no acid to combine with the potassium the question is, what becomes of the metal when the iodine of the potassium iodide is taken up by the berberine? That there is no potassium in the precipitated berberine hydriodide was proved by igniting the precipitate with sulphuric acid and ammonium nitrate, when no trace of residue was to be found. All the potassium must then pass into the filtrate and part of it must exist there as a salt of something acting as an acid, as there is no trace of alkalinity in the filtrate. No one of the indicators gives an alkaline reaction. We acidulated the filtrate with sulphuric acid, shook it up with ether, washed the ether till there was no reaction given for iodine by sodium nitrite and starch, nor for sulphates by barium chloride, and evaporated the ether to dryness; a very small amount of a crystalline substance was left, which would seem to indicate the presence of an organic acid, but the quantity was too small for a closer examination. We intend to take a larger quantity of pure berberine into operation and investigate the subject thoroughly in the near future.

UNIVERSITY OF MICHIGAN,  
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## UPON THE ACTION OF DIAZO COMPOUNDS ON THYMOLPARASULPHO ACID.

[SECOND PAPER.]

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**I**N my former paper<sup>1</sup> I described several azo compounds obtained by combining diazobenzene chloride, diazoparatoluene chloride, and diazoxylene chloride with thymolparasulpho acid.

Contrary to precedent, it was observed that the three compounds named, notwithstanding their increasing molecular weight, were all possessed of about the same yellow color, and were all three more or less unstable, being partially decomposed by boiling water.

It therefore seemed of interest to ascertain in what manner the

<sup>1</sup> This Journal, 3, 112.

sulpho acids of higher diazotized amines would behave towards thymolparasulpho acid. With this end in view, the following experiment was made:

ACTION OF NAPHTHIONIC ACID ON THYMOLPARASULPHO ACID.

One twenty-eighth mol. of eighty-three per cent. sodium naphthionate, or 10.4 grams, were dissolved in 200 cc. of water, and to it were added one twenty-eighth of two mols. of hydrochloric acid of 1.20 sp. gr., or six and four-tenths grams. Furthermore one twenty-eighth mol. of seventy-nine per cent. sodium sulphite ( $\text{NaNO}_2$ ) or two and nine-tenths grams were dissolved in fifty cc. of water, and the solution thus obtained was gradually stirred into the naphthionate solution.

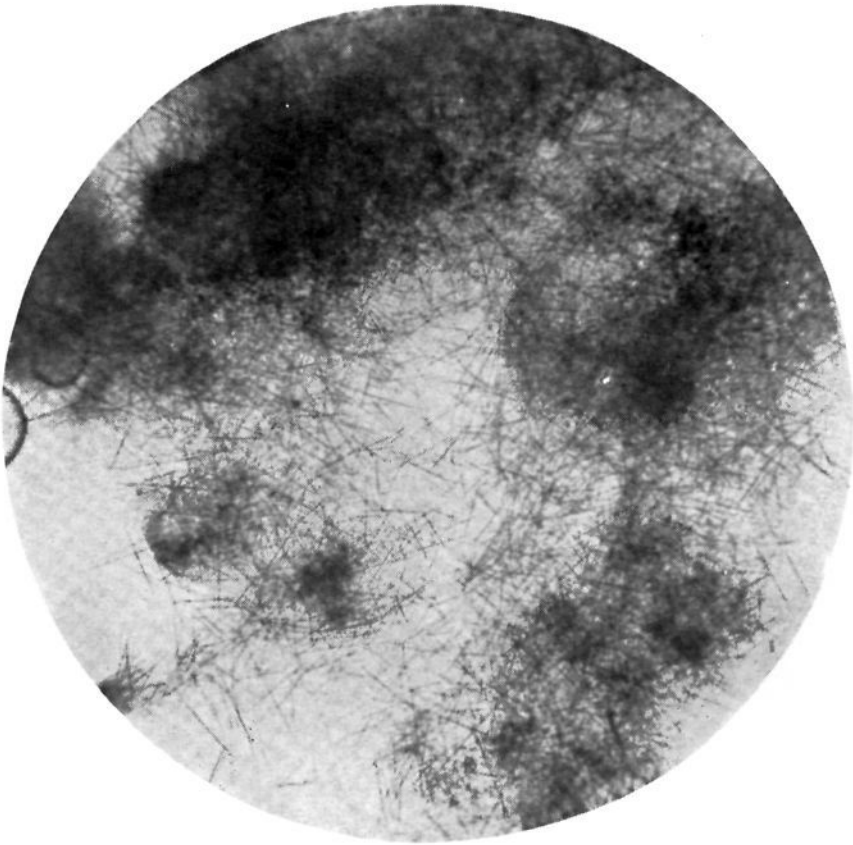
The diazonaphthionic acid thus formed, was then slowly run, under constant stirring, into a cooled solution of one-twenty-eighth mol. thymolparasulpho acid, or eight and two-tenths grams, dissolved in 100 cc. of water made alkaline with four and three-tenths grains of caustic soda.

The mixture at first turns bright red, but gradually increases in depth of color, as the diazo solution is run in, till at last the solution assumes a deep red-brown color, tinged with a suspicion of crimson, which latter color becomes all the more manifest if a drop of the solution be placed upon filter-paper. This phenomenon would suggest a mixture of two colors; *viz.*, a brown and a crimson color.

Some foam is formed during the operation, but whether this is due to an evolution of nitrogen, or to the presence of carbonates in the caustic soda used, I am at present unable to say. The reaction mixture was allowed to stand over night and was then heated to boiling, and saturated with dry sodium chloride.

A reddish brown precipitate A is thus thrown down, and was collected upon a filter and dried.

The filtrate B contains a crimson-red dye-stuff which is so exceedingly soluble in water that it was found next to impossible to precipitate it with salt. A small quantity, however, was obtained by saturating the filtrate at a boil with a large excess of salt, and filtering from the brownish red precipitate formed. Even after this treatment a considerable quantity of the coloring-matter remains in solution. It may, however, be precipitated



Ba-Salt Naphthionic Acid Azothymolparasulpho Acid.



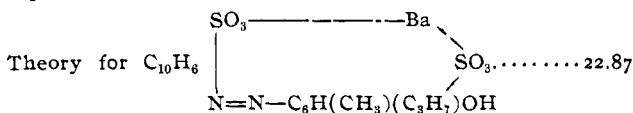
with barium chloride as a barium salt, but the yield was so small that an examination of the product had to be abandoned for the present.

*Brown Precipitate A.*—The brown product precipitated with salt, and alluded to above, was dissolved in water, filtered, and treated with an excess of barium chloride. A copious yellow-brown precipitate C of a barium salt was thrown down. This was collected upon a filter, and washed with cold water until free from all excess of barium chloride, and then dried. The filtrate from this barium salt contains a purplish red dye-stuff in solution, which seems to be identical in color with the dye-stuff contained in filtrate B. From this it would therefore seem, that two coloring-matters are formed by the action of diazonaphthionic acid on thymolparasulpho acid, one of which is brownish, and easily precipitable by sodium chloride or barium chloride, and the other purplish red to crimson, and so very soluble in water that it is only precipitated therefrom with great difficulty by either sodium chloride or barium chloride. The latter is, however, only formed in very small quantity, and its great solubility in water would indicate that it contains more than two sulpho groups. It is therefore possible that it owes its formation to the presence of a small quantity of thymoldisulpho acid, in the thymolparasulpho used.

The barium salt C, in a moist condition, is fairly soluble in boiling water, but once dried its solubility is greatly diminished. It is slightly soluble in boiling ninety-five per cent. alcohol, but readily soluble in proof spirit. It may be obtained in a crystalline form, by dissolving it in boiling water, and allowing it to cool slowly. It is thus obtained as a perfect network of orange-colored hair-fine needles. (See plate.)

## BARIUM ESTIMATION.

	Gram.
Substance taken .....	0.5379
Barium sulphate found .....	0.1939
	Per cent.
Equivalent to barium .....	24.43

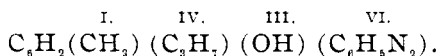


It is therefore probable that the compound under examination is represented by the above formula.

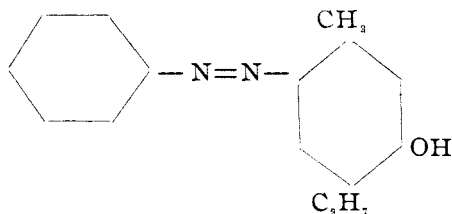
G. Mazzara and G. Posseto<sup>1</sup> on treating thymol in alkaline solution with diazobenzene chloride obtained a mixture of monophenylazo thymol,  $C_6H_5-N_2-C_6H_2(CH_3)(C_3H_7)-OH$  and monophenyldisazo thymol  $(C_6H_5N_2)_2C_6H(CH_3)(C_3H_7)(OH)$ .

The former of these two products on reduction with tin and hydrochloric acid, and then oxidation of the reduction product with ferric chloride, gave a thymoquinone melting at  $45^\circ$ , while the diazo product by the same treatment, gave an oxythymoquinone melting at  $167^\circ-169^\circ$ .

From this they conclude that the phenylazo thymol obtained has the following constitution:

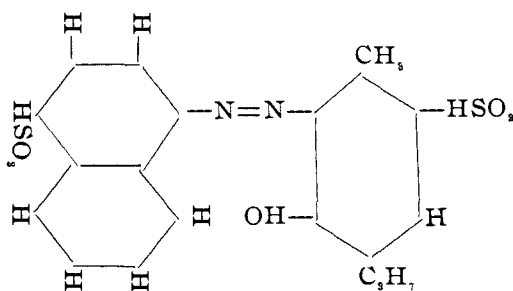


The above expressed graphically would give us the following:

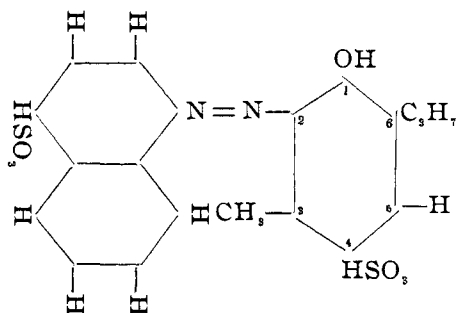


If we now consider the naphthionic acid azothymolparasulpho acid,  $C_{10}H_8N_2C_6H(CH_3)(C_3H_7)(OH)HSO_3$ , above alluded to, and produced by the action of diazonaphthionic acid, on thymolparasulpho acid, it will be seen that as the sulpho group in the thymol ring, occupies the para position with relation to the OH group, there are only two other positions for the diazo group to enter; *viz.*, the ortho and the meta positions, but from the general rules governing the formation of azo compounds, it is evident that the diazo group must enter the ortho position with relation to the OH group, and hence the constitution of this compound may probably be represented as follows:

<sup>1</sup> *Gazz. chim. ital.*, 15, 52.



Or using a somewhat less antiquated formula for thymolparasulpho acid, we would get



It will therefore be seen from the foregoing, that the union of thymolparasulpho acid with diazo compounds of the naphthalene series, produces brownish, to crimson coloring-matters, in contradistinction to those obtained with the diazo compounds of the benzene series.

A parallel test made with diazobetanaphthalenesulpho acid (Casella's acid), and sodium thymolparasulphonate has shown that here too a reddish brown coloring-matter is formed.

It was intended at the beginning of this investigation, to go into the matter more at length, but circumstances which I had not foreseen have forced me to suspend my work, and to present it in its present unfinished condition.