sulfonating carvacrol and oxidizing the sulfonic acid by means of potassium bichromate. The quinone thus produced was reduced by means of sulfur dioxide. The yields were very poor and since this compound, from preliminary determination, shows no advantage over ordinary quinol, work along this line was not further prosecuted.

p-Aminothymol was also prepared, but this base did not seem to be so satisfactory a developer as the corresponding carvacrol derivative. One disadvantage is the relatively low solubility of the free base in water.

SUMMARY

p-Aminocarvacrol is a very satisfactory photographic developer, and its preparation and use for such a purpose would furnish a means of using a portion of the large amount of *p*-cymene which is not being utilized at present.

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A METHOD FOR THE PURIFICATION OF CERTAIN AZO DYES

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In the preparation of the direct cotton dyes of the benzidine group, the dye is usually precipitated from the solution by means of sodium chloride. The method is also used in the case of certain acid wool dyes. As a result of this procedure, commercial specimens of such dyes contain varying amounts of inert inorganic material. For certain pharmacological investigations it was desired to obtain a dye of this sort as free from salt as possible.

The method was originally developed for the purification of brilliant Congo R. In order to test the general applicability of the method, Congo red, brilliant orange R, cotton dyes, and azorubin, an acid wool color, were investigated.

Because of the simplicity of the method as developed and its possible use to those who wish to prepare dyes of this type free from inorganic and certain organic impurities, a brief description of the procedure used is given.

PURIFICATION OF DYES

Fifty grams of crude brilliant Congo R, No. 370,¹ are dissolved in 100 cc. of distilled water and filtered. The solution is heated to boiling and solid sodium acetate added until the dye is practically completely precipitated. This requires about 350 g. of the solid sodium acetate. The precipitate is sucked as dry as possible on a Büchner funnel, and then boiled with 250 cc. of 95 per cent alcohol. The suspended dye is then removed from the alcohol by filtration. The digestion with alcohol is repeated several times. A comparatively small amount of dye is dissolved by the alcohol.

One gram of crude dried material gave 32.7 per cent sulfated ash
One gram of purified dried material gave 25.9 per cent sulfated ash
Calculated as sodium, this corresponds to 8.4 per cent. Theory for sodium is 8.4 per cent

¹ The number refers to Schultz, "Farbstofftabellen," Weidmannsche Buchhandlung, 1914.

Azorubin and Congo red were also purified by this method, and the following figures are given to indicate the extent to which the impurities are removed.

AZORUBIN No. 163

One gram of crude dried dye gave 48.3 per cent sulfated ash
One gram of purified dried dye gave 26.8 per cent sodium sulfate
Sodium found, 8.8 per cent. Theory for sodium is 9.2 per cent

CONGO RED No. 307

One gram of crude dried material gave 50.6 per cent sulfated ash
One gram purified dried material gave 21.4 per cent sodium sulfate
Calculated as sodium, this corresponds to 6.9 per cent. Theory for sodium is 6.6 per cent

Besides removing inorganic impurities, the procedure described also removes certain organic impurities usually present in commercial dyes of this type. This fact is of special importance when the compound is to be used for pharmacological purposes.

For those dyes which cannot be purified by other simpler procedures, this method is of general application if the sodium salts can be precipitated from aqueous solution by sodium acetate and if they are relatively insoluble in hot 95 per cent alcohol. The amounts of sodium acetate and of alcohol to be used naturally vary with each dye.

In the case of those dyes which cannot be satisfactorily separated from the solution by filtration, centrifugalization should be of great assistance in securing a pure product.

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INTERMEDIATES USED IN THE PREPARATION OF PHOTSENSITIZING DYES. I—QUINOLINE BASES

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A recent article¹ from this laboratory outlined briefly the methods of preparation of a number of photosensitizing dyes and dye intermediates. Since then we have made a thorough study of the best conditions for the synthesis of intermediates required in the preparation of pinaverdol, pinacyanol and dicyanin, the three most important photosensitizing dyes. The methods of preparation are described in this and in the following paper.

The four bases required in the preparation of these dyes are quinoline, quinaldine, *p*-toluquinaldine, and 2,4-dimethylquinoline. All of these are well-known organic compounds, whose syntheses are recorded in the patent and chemical literature. The most important of these may be briefly reviewed. The Skraup synthesis of quinoline is so well known that it requires no further description. Hitherto the most satisfactory synthesis of quinaldine (or toluquinaldine) has been that of Döbner and Miller,² which depends upon the condensation of paraldehyde with aniline (or toluidine) hydrochloride, and which is quite similar to the process described in D. R. P. 24317 (1882). 2,4-Dimethylquinaldine is usually prepared by Beyers'³ method, in which ethylidene acetone (prepared from acetone, paraldehyde, and hydrogen

¹ Wise and Adams, THIS JOURNAL, 10 (1918), 801.

² Ber., 16 (1883), 2465.

³ J. prakt. Chem., [2] 33 (1886), 401.