A PURIFICATION OF MESO-TETRAPHENYLPORPHYRIN

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The ready availability of porphyrins and metalloporphyrins with phenyl substituents at the meso-positions stems from the work of Adler et al.\(^1\) whose methods allow for the preparation of gram quantities of porphyrins in a single step procedure.

Thus after refluxing benzaldehyde and pyrrole in propionic acid for only thirty minutes, yields of greater than 20% of crystalline meso-tetraphenyl porphyrin (TPP)\(^1\) are obtained. This crystalline material is, however, invariably contaminated with small amounts of meso-tetraphenylchlorin (TPC)\(^2\). We have shown that the chlorin

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arises from the \textit{in situ} reduction of the porphyrin, and is not an intermediate in the formation of the TPP.\textsuperscript{2} This observation is supported by the fact that TPC is not autoxodised under the conditions obtaining during TPP formation. Indeed TPC is relatively inert to aerial oxidation under a variety of conditions, and autoxidation does not provide a method for the removal of TPC.

It was recently reported\textsuperscript{3} that oxidation of a TPP/TPC mixture with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) followed by chromatography and crystallization yields chlorin-free TPP. We find however that this three step sequence is unnecessary, and on a large scale both irksome and expensive.

Thus when working with small amounts (\(< 1 \text{ g}\)) of TPP, chromatography on dry alumina suffices to remove the chlorin\textsuperscript{4}, but on a larger scale such chromatography becomes time-consuming and considerable volumes of solvent are required. Under these conditions the chlorin is best removed by oxidation with DDQ, but it is not then necessary to chromatograph the oxidised mixture since excess quinone and quinol are readily removed chemically, and pure (chlorin-free) TPP is obtained upon crystallisation. The purity of the product can be checked by its optical spectrum where traces of chlorin appear as an increased absorption at 656 nm due to the superposition of the 645 nm (\(\epsilon, 4.26 \times 10^3\)) band of TPP and the intense 651 nm band of TPC (\(\epsilon, 2.94 \times 10^4\)) Fig. 1. Chlorin free TPP has a ratio of 0.75 for 645:590 nm bands in methylene chloride (the ratio is 0.64 in toluene\textsuperscript{3}). This ratio increases as the chlorin content increases and the optical spectrum of a sample of TPP provides a suitable method of checking for chlorin impurity. However, care must be taken to ensure that the spectrum is run in neutral solution since the protonated porphyrin (TPPH\textsubscript{4}\textsuperscript{2+}) has an intense absorption at 653 nm (\(\epsilon, 4.61 \times 10^4\)) Fig. 1. The most convenient method of detecting TPC impurity in TPP involves the rapid chromatography (in CHCl\textsubscript{3}) of a small sample of TPP on a gram of dry basic alumina. After elution the red-purple TPP with CHCl\textsubscript{3}, a band of green at the top of the column shows that some chlorin was present.
EXPERIMENTAL

TTP (1 g) was dissolved in refluxing toluene (500 ml). DDQ (250 mg) was added in one portion. After half an hour the mixture was cooled to room temperature and extracted with 500 ml of a 1% sodium hydroxide solution which contained sodium dithionite (0.5 g). The organic layer was then washed with water (3 x 100 ml) and dried with sodium sulfate. The toluene was removed under reduced pressure and the product crystallised from methylene dichloride/methanol to give 890 mg of lustrous purple crystals.

Smaller amounts are more readily purified by the dry column method of Adler et al. Thus 0.5 g of TPP in the minimum volume of chloroform was chromatographed over 200 g of dry alumina and eluted with chloroform. The eluate was reduced in volume to 50 ml and
the product crystallised from chloroform/methanol.

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References

1. A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, 
5. Merck reagent grade aluminum oxide was used, but any chromatographic grade of neutral or basic alumina will suffice.