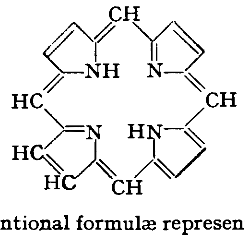
Chlorophyll and Related Substances. Part I. The Synthesis of Chlorin.

By Ulli Eisner and R. P. Linstead.

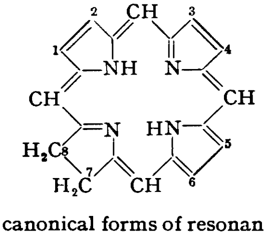
[Reprint Order No. 6389.]

Chlorin (II), the parent substance of chlorophyll, has been synthesised in one step from 2-dimethylaminomethylpyrrole (VI) in yields of up to 3·9%. Metal derivatives have been prepared. Light absorption data are given.

The porphyrins, the most important colouring matters in Nature, can be divided into two main structural groups. These are, broadly, the " red " and the " green " pigments typified by hæmin and chlorophyll, respectively. The respective parent compounds of the two series are porphin (I) and chlorin (II), about which, respectively, little and nothing has hitherto been known.



(I)



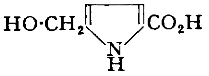
(II)

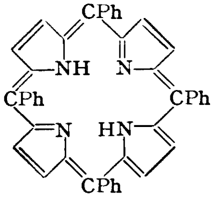
These conventional formulæ represent single possible canonical forms of resonance hybrids. There is no decisive evidence for the placing of the two " extra hydrogens " of chlorin on $C_{(7)}$ and $C_{(8)}$. This has been done in formula (II) following Hans Fischer's practice in analogous compounds. The general question of the place of the extra hydrogens will be the subject of a later communication.

Two syntheses of porphin have been reported (Fischer and Gleim, *Annalen*, **1936**, **521**, 157; Rothemund, *J. Amer. Chem. Soc.*, **1936**, **58**, 625) but the amounts of material obtained were so small that its properties were not described in detail. Moreover, certain anomalies exist which have not been satisfactorily explained. Chlorin has never been prepared.

We now describe a synthesis of chlorin and its quantitative conversion into porphin, which is most readily prepared by the new method.

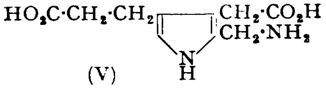
The methods described in the literature for the synthesis of porphyrins (Fischer and Orth, " Die Chemie des Pyrrols," Leipzig, 1937, Vol. II, p. 1) have in general been developed for compounds containing substituents on the β-carbon atoms of the pyrrolic intermediates. When these are unsubstituted, the methods fail either completely or almost so. Thus Siedel's method (*Annalen*, 1943, **554**, 162) breaks down and no porphin was obtained from the intermediate (III). Fischer and Gleim's synthesis of porphin consisted in treating pyrrole-2-aldehyde with boiling formic acid, whilst Rothemund heated pyrrole with methanolic formaldehyde. The reported yields were of the order of 0·1%. The preparation of *ms*-tetraphenylporphin (IV) by the reaction between pyrrole and benzaldehyde (Rothemund, *J. Amer. Chem. Soc.*, 1941, **63**, 267; Priesthoff and Banks, *ibid.*, 1954, **76**, 937, *et seq.*) is, however, more favourable. Yields of up to 18% of the zinc derivative of (IV) have been reported and we have found no difficulty in preparing the compound by this method. The phenyl group appears to exercise its beneficial effect by inhibiting side-reactions involving an attack on the β-carbon atoms.

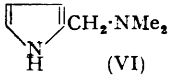

(III)


(IV)

Excluding the *meso*-substituted compounds, all known chlorins carry β-groups. They have been prepared either by mild degradation of chlorophyll derivatives (Fischer and Orth, *op. cit.*, p. 2) or by the reduction of porphyrins. The only direct synthesis has been the formation of *ms*-tetraphenylchlorin as a by-product in the preparation of the corresponding porphin (IV) from pyrrole and benzaldehyde (Aronoff and Calvin, *J. Org. Chem.*, 1943, **8**, 205; *J. Amer. Chem. Soc.*, 1943, **65**, 2259).

The compounds which we have examined as intermediates for the synthesis of porphins and chlorins are the Mannich bases (such as VI) derived from pyrrole. They have not previously been used for this purpose, but possess certain attractive features. The α-methylene group can provide the methine link, and it is known that Mannich bases condense with compounds containing an active methylene with loss of primary or secondary amine. A particular instance is self-condensation, for example the formation of di-(1-methyl-2-indolyl)methane from *N*-methylgramine (Snyder and Eliel, *J. Amer. Chem. Soc.*, 1949, **71**, 663). Moreover, the recent work of Cookson and Rimington (*Nature*, 1953, **171**, 875; **172**, 292, 457; *Biochem. J.*, 1954, **57**, 476) provided favourable indications. They showed that the naturally occurring porphyrin precursor porphobilinogen (V), which is a substituted Mannich base, was converted into uroporphyrin under mild conditions.


(V)


(VI)

We accordingly prepared 2-dimethylaminomethylpyrrole (VI) following Herz, Dittmer, and Cristol * (*J. Amer. Chem. Soc.*, 1947, **69**, 1698). Preliminary experiments were carried out on the action of the following agents on the base (VI) or its methiodide: heat, boiling formic acid, dilute hydrochloric acid (cf. Cookson and Rimington, *loc. cit.*), sodamide, magnesium formate, zinc acetate, ferric or mercurous chlorides, sodium or magnesium hexyloxides (cf. Linstead and Whalley, *J.*, 1952, 4839). All failed to give a porphyrin-type pigment. Heating the base (VI) with cuprous chloride in boiling decalin, xylene, or toluene gave copper porphin in very low yield. This was purified by chromatography; the spectrum agreed well with that recorded by Stern (*Z. phys. Chem.*, 1936, **177**, *A*, 58) for

---

* The method gave erratic results with the occasional formation of much polymeric material.

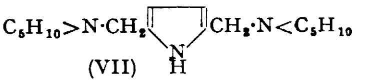
Fischer's material. Treatment of the base (VI) with a mixture of stannic and stannous chlorides in boiling xylene gave a purplish-blue pigment, with a porphyrin-type of light absorption, which was not obtained homogeneous.

As, however, our primary objective was the metal-free pigment, we concentrated on procedures involving a labile metal. Snyder, Eliel, and Carnahan (*J. Amer. Chem. Soc.*, 1951, **73**, 970) have investigated the reaction between the methiodide of (VI) and methylmagnesium iodide in boiling *n*-butyl ether with the object of determining whether alkylation of the pyrrole nucleus occurred. They detected no alkylation, nor did they record the formation of pigment.

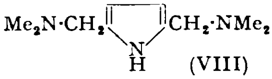
We found that when the free base (VI) was heated with one equivalent of ethylmagnesium bromide in boiling xylene it yielded magnesium chlorin as a greenish blue solution with an intense red fluorescence. The pigment rapidly decomposed in the presence of light and air and was therefore immediately converted into the stable metal-free compound by treatment with cold dilute hydrochloric acid. The overall yields of chlorin were fairly reproducible and of the order of 1%. (This and subsequent yields were determined spectroscopically by using data subsequently determined for pure chlorin.) The method of isolating the chlorin from the complex reaction mixture is described later.

A systematic study was made of variations in the preparative method with the object of improving the yield. These are summarised in the Experimental section. Salient points are that the use of the solid ethobromide in place of the free base (VI) reduced the yield of chlorin to 0·1%. Phenetole gave a yield of about 1·5% of a spectroscopically slightly different pigment, perhaps an oxychlorin formed by some process involving oxygen or peroxide (compare p. 3745). The best yield of chlorin (3·9%) was obtained by the action of the Grignard reagent on the free base in boiling *o*-dichlorobenzene.

The reaction was also varied by condensing a bifunctional Mannich base, 2 : 5-bispiperidinomethylpyrrole (VII; Bachman and Heisey, *J. Amer. Chem. Soc.*, 1946, **68**, 2496) with pyrrylmagnesium bromide in boiling xylene. Magnesium chlorin was again formed but not in improved yield. Attempts to prepare the unknown 2 : 5-bisdimethylaminomethylpyrrole (VIII) yielded an impure product from which the picrate of the desired base was isolated. The base itself was not obtained pure, or in useful amount.



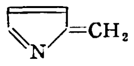
(VII)



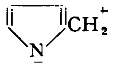
(VIII)

Attempts to use other sources of the linking methine group were uniformly discouraging. The action of gaseous formaldehyde on pyrrylmagnesium bromide in boiling xylene failed to give any macrocyclic pigment, which is not surprising as Taggart and Richter (*J. Amer. Chem. Soc.*, 1934, **56**, 1385) have shown that the primary product is 1-hydroxymethylpyrrole. Neither could any chlorin or porphin be obtained from 2-hydroxymethylpyrrole (Silverstein, Ryskiewicz, and Chaikin, *J. Amer. Chem. Soc.*, 1954, **76**, 4485), a compound which is extremely sensitive to acids. Its reaction with ethylmagnesium bromide in boiling xylene failed to give any macrocyclic pigment.

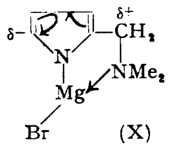
A few comments can be made on the mechanism of the production of chlorin from the Mannich bases, but these must be offered with reserve because of the low overall yield.



(IX*a*)



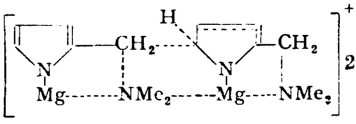
(IX*b*)



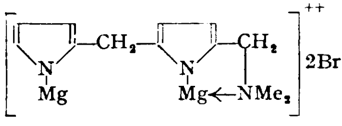
(X)

Hellmann (*Angew. Chem.*, 1953, **65**, 473) has suggested that the *C*-alkylation of a pyrrolic Mannich base can go through an unsaturated pyrrolenine form (IX*a*) which can then react with a compound containing an active hydrogen by Michael-type addition. Alternatively, the intermediate could be written in the extreme ionised form (IX*b*) in which case *C*-alkylation would proceed by reaction with a carbanion. Cookson and Rimington (*loc. cit.*) have used a similar mechanism to explain the formation of uroporphyrin from porphobilinogen (V).

For the self-condensation of a Grignard derivative of a Mannich base we suggest that the intermediate has the structure (X) and that *C*-alkylation and base elimination take place by a concerted process yielding the product (XII) through a transition state such as (XI):



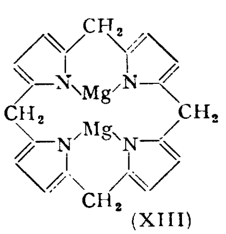
(XI)



(XII)

The product (XII) can react with another molecule of (X) to build up a linear tripyrryl intermediate and by a further step a linear polymer or a macrocycle, such as (XIII). The latter being at the unstable porphyrinogen reduction level would easily be dehydrogenated. The prevailing reaction conditions do not correspond to a very high oxidising potential and the process stops at the chlorin level, although, as is shown below, a little porphin is formed.

In connection with the proposed mechanism it is interesting that the Mannich base (VI) can also react with aluminium chloride to give a little chlorin. The aluminium chloride acts as a Lewis acid. Boron trifluoride, although it failed to give a macrocycle, gave highly coloured materials very possibly linear in structure.



(XIII)

Purification and Properties of Chlorin.—The product of the reaction between ethylmagnesium bromide and the base (VI) was a complex mixture containing at least four pigments. The solvent used in the reaction was first removed under reduced pressure and replaced by benzene, after which the complex was decomposed with 1% hydrochloric acid. Attempts to purify the metal-free chlorin at this stage by adsorption chromatography failed.

Counter-current distribution was found to be a much more satisfactory method. Chlorin could be obtained nearly pure, contaminated only with a little porphin, by successive distributions in a Craig machine (Weissberger, "Techniques of Organic Chemistry," Interscience, New York, 1950, Vol. III, Ch. 4), first between benzene and 3% hydrochloric acid, then between benzene and 10% hydrochloric acid. In the first series of operations, the chlorin remained in the benzene layer whilst the 3% acid retained a small amount of porphin and a brilliant red pigment.* At the second stage the chlorin passed into the 10% acid, whilst the benzene retained another pigment very similar to chlorin in spectrum and differing only in its lower basicity. We have not yet succeeded in obtaining this "pseudo-chlorin" pure. It may be an oxychlorin analogous to the compounds investigated by Pruckner (*Z. phys. Chem.*, 1941, **188**, *A*, 41). The application of counter-current distribution to the purification of chlorin has some analogy with the recent work of Granick and Bogorad (*J. Biol. Chem.*, 1953, **202**, 781) who separated mixtures of porphyrins between ether and dilute acid (compare also Treibs and Schmidt, *Annalen*, 1952, **577**, 105).

The chlorin from the counter-current procedures still contained traces of porphin and minute amounts of the "pseudo-chlorin." Final purification was achieved by partition chromatography on cellulose, light petroleum–*n*-butanol–2N-hydrochloric acid being used as eluant. After crystallisation from benzene the chlorin was then spectroscopically and analytically pure and unchanged by further processing.

Chlorin is a deep bluish-green crystalline solid. It is soluble in benzene, ether, chloroform, and pyridine; insoluble in alcohol, acetone, and water. The solutions are green

---

* The identity of this material has not been established. We think it very possible that it is based on a pyrrole indigo type of structure, with two pyrrole rings directly joined by a double bond. It has a striking resemblance in light absorption to compounds of this type now under study in these laboratories (Elvidge, J. S. Fitt, and Linstead, unpublished).

with an intense red fluorescence. The solution in dilute hydrochloric acid is blue with an absorption band at 630 mμ. The acid number (Fischer and Kirstahler, *Z. physiol. Chem.*, 1931, **198**, 47) is about 5.

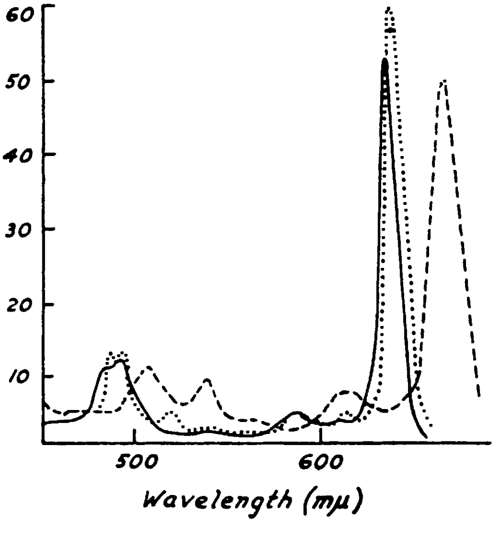
The light absorption of chlorin has been measured in benzene solution over the range 350—700 mμ. The results are given in detail in Table 1 and the typical five-banded spectrum is shown in the Figure.

TABLE 1. *Light-absorption data.*

Compound	$\lambda_{\max.}$ (mμ)	ε	Solvent	Ref.
Chlorin	388 *	128,000	Benzene	*a*
	484	10,600		
	493	12,400		
	540	1,300		
	588	3,600		
	610	2,700		
	637·5	50,000		
Magnesium chlorin	402 *	309,000	Benzene	*a*
	507·5	5,200		
	566	7,700		
	574·5	7,700		
	610	56,000		
Copper chlorin	396 *	195,000	Benzene	*a*
	490	5,300		
	560	8,200		
	602·5	48,900		
Copper porphin	393·5 *	329,000	Benzene	*a*
	517·5	13,000		
	552	9,800		
Copper porphin	518	14,100	Dioxan	*b*
	551·5	8,300		
Ætiochlorin	488	13,200	Dioxan	*c*
	494	13,400		
	519	4,200		
	522	4,100		
	542	1,800		
	564	1,200		
	586	4,000		
	613	4,100		
	642	59,400		

* Soret band.

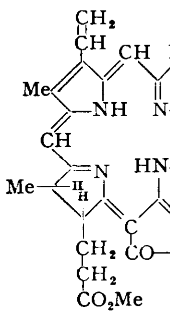
References: *a*, This work. *b*, Stern, *Z. phys. Chem.*, 1936, **177**, *A*, 58. *c*, Pruckner, *ibid.*, 1940, **187**, *A*, 257.



Absorption spectra of chlorins:
———— *chlorin.*
. . . . . . *ætiochlorin.*
– – – – – – *methyl pyrophæophorbide*-a.

When a benzene solution of chlorin was heated with methanolic cupric acetate it yielded copper chlorin which separated from its blue solution in purple crystals. Light-absorption data are in Table 1. An attempted preparation in boiling acetic acid led to dehydrogenation and the formation of mainly copper porphin, which was characterised by analysis and light absorption (Table 1). Copper chlorin was also easily dehydrogenated to copper porphin in hot hydrochloric acid. Fischer, Platz, Helberger, and Niemer (*Annalen*, 1930, **479**, 27) attempted to prepare the copper derivative of ætiochlorin in acetic acid solution. The light absorption data recorded for their product indicate that it was a mixture containing largely copper ætioporphyrin, which is not surprising in view of our results on the parent compound. Ethylmagnesium bromide reacted with chlorin to yield a solution with an intense magenta fluorescence. The light-absorption data (Table 1) make it highly probable that this contained magnesium chlorin. The isolation of the pure magnesium pigment was not attempted.

The structure of chlorin (II) is indicated by the analytical data which correspond to $C_{20}H_{16}N_4$; the presence of two atoms of hydrogen in this molecule replaceable by bivalent metal to give $C_{20}H_{14}N_4M$; and the close resemblance to Fischer's chlorins, which is illustrated in the Figure. It will be seen there that the light-absorption curves for chlorin and ætiochlorin (Pruckner, *Z. phys. Chem.*, 1940, **187**, *A*, 257) in the visible region are almost identical in the main features. The weak doublets at about 520 and 564 mμ reported by Pruckner for ætiochlorin have no counterpart in the spectrum of our chlorin.


(XIV)

The Figure also includes the absorption curve for methyl pyro phæophorbide-*a* (Ficken, Johns, and Linstead, unpublished). The accepted formula for this compound is (XIV). (This is based on Fischer's work and neglects questions of fine structure.) This substance is a simplified phorbide derived from chlorophyll and retains the extra hydrogen atoms. There is a good agreement between the general features of the curves for methyl pyrophæophorbide-*a* and for chlorin. In the phorbide the maxima of the main bands are displaced about 25 mμ towards longer wavelengths, owing to the additional substitution.

The main evidence for the structure of chlorin lies in its ready and nearly quantitative dehydrogenation to porphin. This is dealt with in the following paper.

EXPERIMENTAL

Microanalyses are by Mr. Oliver of this Department.

Reaction of 2-Dimethylaminomethylpyrrole (VI) *with Cuprous Chloride.*—The base (VI) (1·2 g.) in xylene (15 c.c.) was added to cuprous chloride (1 g.) in boiling xylene (10 c.c.) during 3·5 hr. The solution was boiled for a further 2 hr., cooled, and filtered. The residual solid was continuously extracted (Soxhlet) with boiling benzene. The benzene extracts and the original filtrate were concentrated under reduced pressure and chromatographed on alumina (grade I). Benzene eluted a pink band which had absorption maxima at 395, 519, and 552 mμ. Evaporation of the benzene solution and crystallisation of the residual solid from chloroform–methanol furnished a red solid (0·5 mg.).

Reaction of (VI) *with Tin Chlorides.*—The base (VI) (1 g.) in xylene (15 c.c.) was treated with stannic chloride (0·4 c.c.) and stannous chloride (0·5 g.). The solution was heated for 18 hr. at 120—130°, cooled, and evaporated to dryness under reduced pressure. The residual solid was continuously extracted with chloroform, and the extracts concentrated and chromatographed on alumina (grade I). A purplish-blue band was eluted with benzene–chloroform (1 : 4), and three arbitrary fractions were collected, having the following absorption maxima : (i) *610*, 564, 506 mμ; (ii) *610*, 535, 565 mμ; (iii) *610*, 535, 568 mμ. Fraction (i) was evaporated to dryness; crystallisation of the residue from chloroform–light petroleum furnished a greenish blue solid (1·3 mg.).

Preparation of Chlorin.—To the base (VI) (1·24 g.) in xylene (50 c.c.) a solution of ethylmagnesium bromide [from magnesium (0·24 g., 1 mol.)] in ether (3 c.c.) was added. The solution was boiled with stirring in an atmosphere of oxygen-free nitrogen for 7 hr., cooled, and filtered. The residual solid was continuously extracted with boiling benzene in an atmosphere of nitrogen. The extracts were mixed with the xylene filtrate from which the xylene had been displaced by benzene, and shaken with cold 1% hydrochloric acid. The yield of chlorin, determined spectroscopically from the band at 637·5 mμ, was 6·7 mg. (0·85%).

The following experiments were done in boiling xylene, ethylmagnesium bromide being added to the base unless otherwise stated.

Expt.	Concn. of (VI) (mole/l.)	Mode of addition	Time of reaction (hr.)	Yield (%) of chlorin
1 *	0·1	All at once at 130°	8	0·8
2	0·04	During 1·5 hr. at reflux	5	1·0
3	0·16	Reverse at room temp.	6	1·0
4	0·07	During 4 hr. at reflux	9	0·86
5 †	0·14	All at once at room temp.	7	0·1

* In presence of excess of ethyl bromide. † Solid ethobromide.

The concentration of the base (VI) was kept at 0·2 mole/l. throughout the following experiments; the reactants were mixed at room temperature.

Expt.	Solvent	Temp.	Time (hr.)	Yield (%) of chlorin	Remarks
1	Xylene	140°	40	0·88	No red pigment
2	,,	,,	24	0·64	Red pigment
3	,,	(*a*) Room temp.	15	—	—
		(*b*) Same expt. continued at 140°	24	1·11	No red pigment
4	Mesitylene	(*a*) 165°	29	1·79	—
		(*b*) Same expt. continued	46	1·11	No red pigment
5	Decalin	190°	6	0	—
6	,,	(*a*) 190°	2·5	0·63	—
		(*b*) Same expt, continued	5	0·54	No red pigment
7	Phenetole	170°	7	1·24	Product had $\lambda_{\text{max.}}$ = 640 mμ
8	,, *	,,	29	1·43	Product had $\lambda_{\text{max.}}$ = 640 mμ
9	Bromobenzene	155°	23	1·82	Red pigment
10	*o*-Dichlorobenzene	180°	10·5	3·86	No red pigment

* Freshly distilled from sodium.

Reaction of (VI) *with Aluminium Chloride.*—Aluminium chloride (1 g.) in chlorobenzene (50 c.c.) was warmed to 70° with stirring under nitrogen. The base (VI) (1 g., 1 mol.) in chlorobenzene (10 c.c.) was added and the solution was boiled for 10 hr. The resulting dark brown solution had an intense green fluorescence; chlorin was detected spectroscopically but no attempt was made to isolate it. An essentially similar result was obtained in boiling xylene.

Reaction of (VI) *with Boron Trifluoride.*—The base (VI) (1 g.) and boron trifluoride–ether complex (1 c.c., 1 mol.) in xylene (50 c.c.) were boiled for 2·5 hr. in an atmosphere of nitrogen and set aside at room temperature overnight. The resulting deep red solution had a brilliant green fluorescence and showed a faint absorption band at 622 mμ.

2 : 5-*Bisdimethylaminomethylpyrrole* (VIII)—To a solution of dimethylamine hydrochloride (21·63 g., 2·3 mols.) in aqueous formaldehyde (20·11 g., 2·3 mols.), pyrrole (7·75 g., 1 mol.) was added dropwise with stirring at 0° in an inert atmosphere. The mixture was kept for 1 hr. at 0—5°, for 2 hr. at room temperature, and overnight at 0°. It was made alkaline with 20% sodium hydroxide solution and extracted with ether. The ethereal extracts were washed with water and dried ($MgSO_4$), and the solvent removed. Distillation of the residue afforded a forerun, b. p. 71—78°/0·1 mm., and a fraction, b. p. 76—80°/0·15 mm. (1·65 g.), the remainder being non-distillable polymeric material. The distillate partially solidified at 0° affording crystals, m. p. ~30°, which could not be further purified. It was converted into the *picrate* which crystallised from acetic acid in yellow needles, m. p. 202—205° (decomp.) (Found : C, 41·3; H, 4·0; N, 19·6. $C_{22}H_{25}O_{4}N_{9}$ requires C, 41·3; H, 3·9; N, 19·7%).

Isolation of Chlorin.—(a) *Attempted adsorption chromatography.* The following adsorbents were too weak to effect a useful separation : grade III alumina; calcium carbonate; calcium hydroxide; sucrose; tartaric acid. Talc, magnesium trisilicate, and grade I alumina all held chlorin too strongly for useful elution. Chlorin was partly decomposed on the last-named adsorbent. When chromatography was tried before demetallation, the magnesium was removed on all the adsorbents tried except sucrose and calcium carbonate; but even on these no satisfactory separation was achieved.

(b) *Counter-current distribution.* The apparatus used in this work was that described by Craig (*Analyt. Chem.*, 1949, **21**, 500). During the early part of this work an apparatus consisting of 12 tubes with a working capacity of 160 c.c. each was used; later we employed an apparatus with 50 tubes, holding 80 c.c. each. In a typical experiment, the mixed pigments (containing about 50 mg. of crude chlorin in 40 c.c. of benzene) were shaken in the Craig machine with 3% hydrochloric acid. After 15 transfers, tubes 3—8 contained the red pigment ($\lambda_{\text{max.}}$ 577, 540 mμ) whilst the chlorin was found in tubes 12—15. The contents of the latter tubes were mixed and made alkaline with ammonia, and the chlorin was extracted with benzene. The benzene solution was concentrated under reduced pressure and the counter-current distribution was repeated with benzene–10% hydrochloric acid. Ten transfers sufficed to separate chlorin (in tubes 1—3) from " oxychlorin " (tubes 8—10). The latter had absorption maxima at 642, 588, and 496 mμ. The general shape of its light-absorption curve was almost identical with that of chlorin.

(c) *Partition chromatography*. The purified chlorin obtained as above was dissolved in a solution obtained by taking the upper phase of an equilibrated mixture of light petroleum (b. p. 100—120°)–*n*-butanol–2N-hydrochloric acid (1 : 2 : 3) and chromatographed on cellulose powder. Elution with the same mixture of solvents effected separation into an upper pink band (porphin) and a lower purple band (chlorin) with a narrow green edge (" oxychlorin "). The purple band was eluted separately and immediately neutralised by a solution of light petroleum–*n*-butanol saturated with ammonia. The resulting solution was washed with water and evaporated to dryness.

After two crystallisations from benzene, *chlorin* was obtained as deep greenish-blue crystals (Found : C, 76·9, 77·2; H, 5·5, 5·5; N, 17·5%; C/H, 14·05, 14·0. $C_{20}H_{16}N_4$ requires C, 76·9; H, 5·2; N, 17·9%; C/H, 14·9).

Copper Chlorin.—Chlorin (10 mg.) in hot benzene (25 c.c.) was treated with cupric acetate (30 mg.) in methanol. The solution was boiled in an atmosphere of nitrogen for 2 min., cooled, diluted with benzene, and washed five times with water. Concentration of the solution afforded *copper chlorin* as small purple crystals which were recrystallised from benzene (Found : C, 64·2; H, 4·15; Cu, 16·1. $C_{20}H_{14}N_4Cu$ requires C, 64·3; H, 3·8; Cu, 17·0%). Chromatography of a small portion on heavy magnesium oxide revealed the absence of copper porphin.

Copper Porphin.—Chlorin (12 mg.) and excess of cupric acetate were boiled in acetic acid (50 c.c.) for 1 hr., no more copper chlorin being then detected in the solution. After removal of the solvent under reduced pressure, the residue was repeatedly extracted with boiling benzene, and the mixed solutions washed with aqueous ammonia and water, and concentrated to small bulk. Chromatography on alumina (grade I) with benzene as eluant afforded *copper porphin* as red microcrystals which were recrystallised from benzene (Found : C, 63·5, 63·95; H, 3·4, 3·9; Cu, 16·3, 16·7. $C_{20}H_{12}N_4Cu$ requires C, 64·6; H, 3·25; Cu, 17·1%).

Magnesium Chlorin.—A solution of chlorin ($\sim 10^{-4}$M; 10 c.c.) in benzene was treated with excess of ethereal ethylmagnesium bromide, and the solution washed with M-ammonium chloride solution (3 times) and water (3 times). It was concentrated to half its volume under reduced pressure and made up to 25 c.c., and the light absorption determined immediately (see Table 1). Aliquots were then converted into chlorin with 1% hydrochloric acid in order to determine its concentration spectroscopically. All operations were carried out with the exclusion of light and air. Solutions of magnesium chlorin were blue with an intense red fluorescence.

We are indebted to Dr. G. E. Ficken for the light-absorption data on methyl pyrophæophorbide-*a* and to Dr. L. M. Jackman for helpful discussions. The work has been made possible by financial support from the Rockefeller Foundation to whom our thanks are due.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7. [*Received, May 4th,* 1955.]