is shown in Fig. 1, but the product in every instance is the corresponding, substantially pure, derivative of propylbenzene, except, perhaps, in the case of propionylresorcinol.

A catalyst, similarly prepared with platinum, was completely inactive toward propiophenone, although active toward isonitrosopropiophenone. This result is particularly interesting in connection with the recent report of Zelinsky, Packendorff and Leder-Packendorff,[4] who found it desirable, in the reduction of acetophenone and its derivatives to ethylbenzene, to activate platinized charcoal by the addition of palladium.

Experimental

The reduction procedure and the catalyst have been described.[1a] The solvent was alcohol, preferably anhydrous. The following ketones were used: propiophenone, *o*- and *p*-hydroxypropiophenone,[5] propionylresorcinol,[6] propionylcatechol, *m*-propionylphenol, *o*- and *p*-methoxypropiophenone[7] and *m*-methoxypropiophenone.[8] The reduction products are given in Table I.

TABLE I

Product	Boiling point, uncorr. °C.	Mm.	Ref.
Propylbenzene	163–165	...	9
p-Propylphenol	108	6	10
m-Propylphenol	100–102	6–7	11[a]
o-Propylphenol	112–115	18–20	12
Propylresorcinol	182–186	5–7	13[b]
Propylcatechol	136–139	4–5	14[c]
p-Propylanisole	125	45	15
m-Propylanisole	90–91	5	11
o-Propylanisole	95–98	9	16

[a] Aqueous solution gave slight brown color with ferric chloride; alcoholic solution remained colorless.

[b] Gave deep color with ferric chloride. Pure alkylresorcinols give practically no color.

[c] M. p. *ca.* 30°; described as melting at 56–60°.[14]

Summary

1. It was found that palladium on charcoal quickly and easily reduces propiophenone to propylbenzene. A platinum catalyst similarly prepared was inactive.

2. The substitution of hydroxyl or methoxyl groups in propiophenone influences the rate but not the extent of the reduction.

PHILADELPHIA, PA. RECEIVED AUGUST 22, 1933

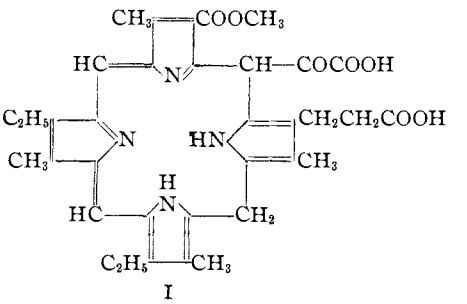
(4) Zelinsky, Packendorff and Leder-Packendorff, *Ber.*, **66**, 872 (1933).
(5) Miller and Hartung, "Organic Syntheses," Vol. XIII, 1933, p. 90.
(6) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).
(7) Hartung, Munch, Miller and Crossley, *ibid.*, **53**, 4154 (1931).
(8) *Cf.* Hiers and Hager, "Organic Syntheses," Vol. IX, 1929, p. 13.
(9) Beilstein, 4th ed., Vol. V, p. 390.
(10) Klages, *Ber.*, **32**, 1438 (1899).
(11) Ciamician and Silber, *ibid.*, **23**, 1162 (1890).
(12) Frankland and Turner, *J. Chem. Soc.*, **43**, 357 (1883).
(13) Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).
(14) Beilstein, 4th ed., Vol. VI, p. 920.
(15) Beilstein, 4th ed., Vol. VI, p. 500.
(16) Spica, *Gazz. chim. ital.*, **8**, 418 (1878).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Studies in the Chlorophyll Series. XII. The Phaeopurpurins[1]

BY EMMA M. DIETZ AND WILLIAM F. ROSS

In previous papers from this Laboratory we have reported the formation of two substances, phaeopurpurin 18 and phaeopurpurin 7[2] (a monomethyl ester) from the unstable chlorins. The latter compounds are formed by the "phase test hydrolysis" of the phaeophorbides and chlorin *e* trimethyl ester. The structure of phaeopurpurin 7, obtained in this way or by alkaline hydrolysis of dimethyl phaeopurpurin 7 (a trimethyl ester), has been established by a number of transformations as being that of an alpha ketonic acid with the carboxyl group of the pyrrol ring esterified[3] (Formula I).



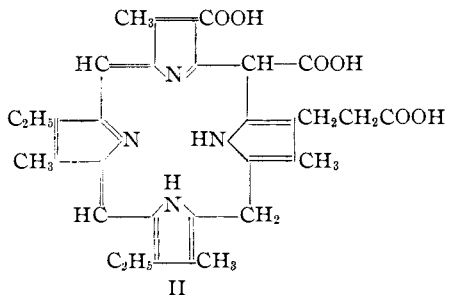
I

We have now been able to obtain further proof of the correctness of this formula since phaeopurpurin 7 can be oxidized to a monomethyl ester of a tribasic acid with loss of carbon dioxide. The parent tribasic acid is chlorin *a* prepared in this Laboratory in our earlier work (Paper III)

(1) The authors wish to acknowledge the direction and advice of Professor James B. Conant throughout the course of this research.
(2) Paper III, THIS JOURNAL, **52**, 3013 (1930).
(3) Paper IV, *ibid.*, **53**, 362 (1931); Paper XI, *ibid.*, **55**, 839 (1933).

but erroneously assigned an empirical formula with one too many carbon atoms. Fischer has shown that the compound has the same skeleton as rhodoporphyrin-γ-carboxylic acid and has designated it chlorin p_6.[4] We prefer the older name, and write the formula for it as shown below (II), since it can be transformed by saponification to chlorin *f*, which we have shown to be a dihydroporphyrin.

Fischer and his co-workers have recently investigated phaeopurpurin 18[4] and have come to the conclusion that it is the anhydride of a tribasic phaeopurpurin 18 (isolable only as the triester) comparable to the green anhydride of rhodoporphyrin-γ-carboxylic acid which they had previously studied.



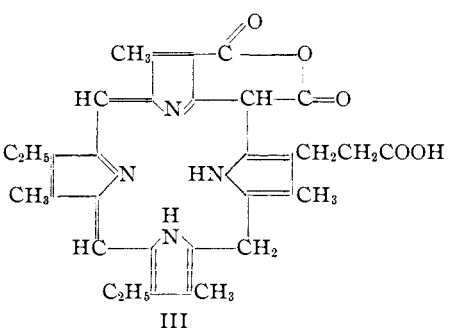
II

Chlorin *a* is believed to be an isomeric tribasic acid whose anhydride has thus far resisted isolation.[5] We have now continued our study of phaeopurpurin 18 and are in agreement with Fischer's anhydride formula except that in phaeopurpurin 18 as in chlorin *a* we feel certain that we are dealing with a partially hydrogenated porphyrin ring. We also prefer to regard phaeopurpurin 18 as the real anhydride of chlorin *a*, exactly paralleling the relation between the green rhodoporphyrin-γ-carboxylic anhydride and the free acid, since the same anhydride reagents bring about the transformation in both cases accompanied by the same marked drop in acid number and change in color and spectrum. It may be noted that Fischer reports a trimethyl ester of phaeopurpurin 18 which we have never been able to prepare.

We have found that both phaeopurpurin 18 and the green anhydride of rhodoporphyrin-γ-carboxylic acid react with hydroxylamine forming characteristic derivatives. The derivative from phaeopurpurin 18 was converted into that from rhodoporphyrin-γ-carboxylic acid by heating; in this reaction neither carbon monoxide nor carbon dioxide was lost; clearly a dehydrogenation of the partially hydrogenated porphyrin ring was involved. The two hydroxylamine derivatives were comparable to the well-known compounds formed from phthalic anhydride and hydroxylamine.[6] As compared with the oxime of rhodin *g* trimethyl ester, the hydroxylamine derivatives of the anhydrides were much more acidic, since they could be extracted from an ether solution with dilute alkali (the free carboxyl group having been previously esterified of course). They reacted very slowly with a molecule of diazomethane taking on one methoxyl group (in addition to the one already present in the propionic acid group) and then became insoluble in alkali.

The monomethyl ester of chlorin *a* prepared by the oxidation of phaeopurpurin 7, designated by us as the beta ester, loses methyl alcohol slowly in the solid state at room temperature, or on standing in pyridine or on gentle heating, and free phaeopurpurin 18 is formed. An isomeric monomethyl ester of chlorin *a* (alpha ester) was prepared by very mild alkaline hydrolysis of phaeopurpurin 18 ester. On gentle heating it lost water but retained the methyl group, reforming phaeopurpurin 18 ester. These facts are entirely in accord with the position of the methyl group in our formula for phaeopurpurin 7 (as explained above) and with Fischer's anhydride formula for phaeopurpurin 18 (III).

Two apparently isomeric dimethyl esters of chlorin *a* were prepared by suitable treatment of the triester with alcoholic potassium hydroxide but their complete structures were not definitely established.



III

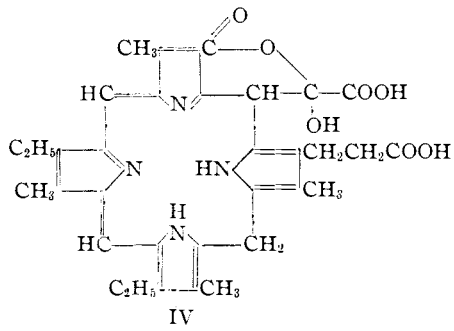
(4) Fischer, *Ann.*, **498**, 199 (1932).

(5) It is interesting that both chlorin *a* and phaeopurpurin 18 were prepared by Marchlewski some years ago and their relation to one another correctly interpreted. His beta-phyllotaonin appears to be identical with chlorin *a* and the anhydro-beta-phyllotaonin is certainly phaeopurpurin 18 [Malarski and Marchlewski, *Biochem. Z.*, **42**, 219 (1912)].

(6) Lassar Cohn, *Ann.*, **205**, 295 (1880); Orndorff and Pratt, *Am. Chem. J.*, **47**, 89 (1912); Brady and Baker, *J. Chem. Soc.*, 533 (1928).

Since phaeopurpurin 18 like chlorin *a* has one less carbon atom than the unstable chlorins or phaeopurpurin 7, somewhere in its preparation this atom is split off. Fischer and his co-workers[4] concluded that this loss occurred as formic acid in the original phase test hydrolysis. We have made a careful study of this problem and find that this is not the case. The mixture of unstable chlorins formed directly in the "phase test hydrolysis" still contains the full complement of carbon atoms. This is established by the fact that on treatment with diazomethane, an excellent yield of dimethyl phaeopurpurin 7 (a trimethyl ester) is obtained. The —CO—$COOCH_3$ grouping in this compound has been rigorously established as explained above. We have found that during the standing of the solution of the unstable chlorins in ether, oxidation occurs and the carbon atom is eliminated as carbon dioxide; the carbon dioxide was collected and weighed as explained in the experimental portion of this paper. The transformation occurs only with the methoxyl-free unstable chlorin from the a_1 series and not with the precursor of phaeopurpurin 7 which is derived from chlorophyll a_2 (Paper XI).[3]

A more convenient method of preparing phaeopurpurin 18 is to oxidize an alkaline solution of the unstable chlorins with potassium ferricyanide. The transformation is practically instantaneous but under these mild oxidizing conditions phaeopurpurin 7 (a monomethyl ester, Formula I) is not attacked. To explain this difference in the ease of oxidation of the tribasic keto acid and its monomethyl ester, we suggest that the former may be present largely in the form shown in Formula IV.



IV

Such a structure is not possible with the monomethyl ester (Formula I). A structure represented by Formula IV might well be expected to oxidize more readily than a simple keto acid since it is in effect an α-hydroxy acid. It should be emphasized that the distinction in the oxidation of the tribasic acid and its monomethyl ester is one of degree and not of kind since under suitable conditions both are oxidized to a chlorin *a* derivative.

We are greatly indebted to Miss G. M. Ware for carrying out the microanalyses reported in this paper.

Experimental

Hydroxylamine Derivative of Phaeopurpurin 18.—A solution of 150 mg. of phaeopurpurin 18 in 75 cc. of pyridine was heated for twenty minutes on a steam-bath with 1.5 g. each of hydroxylamine hydrochloride and anhydrous sodium carbonate. The product was transferred to 1500 cc. of ether and acid-fractionated. A small quantity of the hydroxylamine derivative of rhodoporphyrin-γ-carboxylic anhydride, of acid number 6, formed as a by-product. The yield of phaeopurpurin 18 derivative, of acid number 13, was 75 mg. Its color in ether is more red than that of phaeopurpurin 18; in acid it is green-blue. It forms an insoluble green potassium salt. For analysis it was crystallized from acetone–ligroin. The spectrum in ether (1 mg. in 30 cc. in a 5-cm. tube): I, 658–633; II, 560–535; III, 517–501; IV, 489–473. E. A., 444. Order: II, III or I, IV.

Anal. Calcd. for $C_{33}H_{35}N_5O_5$: C, 68.21; H, 6.07; N, 12.04. Found: C, 67.98, 68.11; H, 6.08, 5.97; N, 11.74, 11.78.

Hydroxylamine Derivative of Methyl Phaeopurpurin 18.—This compound was prepared from methyl phaeopurpurin 18 by the same procedure followed for the free acid above. It forms an insoluble green salt when an ether solution is shaken with 2% aqueous potassium hydroxide. The acid number is 15–16. Its spectrum is identical with that of the free acid.

Anal. Calcd. for $C_{34}H_{37}N_5O_5$: C, 68.60; H, 6.26; N, 11.75; OCH_3, 5.2. Found: C, 68.51; H, 6.90; N, 11.77; OCH_3, 5.5, 5.3.

Methyl Ether of the Hydroxylamine Derivative of Methyl Phaeopurpurin 18.—This compound may be prepared from either of the above hydroxylamine derivatives by treatment with excess diazomethane in ether solution. The methylation is not complete even after six hours as is shown by the low methoxyl values below. The color and spectrum in ether are identical with those of the derivatives of methyl and free phaeopurpurin 18. The acid number is 18 and the compound is not extracted by alkali.

Anal. Calcd. for $C_{35}H_{39}N_5O_5$: C, 69.00; H, 6.45; N, 11.51; OCH_3, 10.2. Found: C, 68.54, 68.67; H, 5.79, 6.11; N, 11.93, 11.58; OCH_3, 9.26, 9.42.

Methyl Ether of the Hydroxylamine Derivative of Methyl Rhodoporphyrin-γ-carboxylic Anhydride.—The anhydride itself was prepared from 1 g. of phaeopurpurin 18 by pyrolysis in 150 cc. of tetrachlorodiphenyl (Arochlor)[7] at 310° in an atmosphere of nitrogen. The color changed

(7) Arochlor is a viscous liquid, b. p. *ca.* 335°, marketed by the Swann Chemical Co., Birmingham, Alabama.

to green within one minute and the heat was removed.[8] The product was added to 14 liters of ether and fractionated. It was found to be homogeneous and the spectrum checked that reported by Fischer;[9] yield, 275 mg. The spectrum in pyridine–ether: I, 668–647; II, 614–582; III, ---558---542---(faint); IV, ---518---; E. A., 462. Order: I or II, III, IV.

This anhydride was treated with hydroxylamine as described above and the product transferred to ether and completely extracted with 6% acid. It was methylated in ether with an excess of diazomethane for four hours when a considerable fraction of alkali-soluble material, containing one methoxyl group by analysis, was still present. The alkali-insoluble fraction was recrystallized for analysis from acetone–ligroin, from which it separated as a crystalline powder with a green luster. The acid number of the hydroxylamine derivative of rhodoporphyrin-γ-carboxylic acid is 5, that of the methyl ester is about 7, and of the methyl ether of the methyl ester is 9. The color of these derivatives in ether is slightly more blue than that of the original anhydride. Their spectra in pyridine–ether are identical and as follows: I, 678–652; II, 623–592; III, ---552---(very faint); IV, ---526---(very faint); E. A., 466. Order: I, II, III, IV.

Anal. Calcd. for the dimethyl compound, $C_{35}H_{37}N_5O_5$: C, 69.0; H, 6.23; N, 11.53; OCH_3, 10.2. Found: C, 69.16; H, 6.62; N, 11.49, 11.58; OCH_3, 9.66.

Pyrolysis of Phaeopurpurin 18 Hydroxylamine Derivative.—A 132-mg. sample was pyrolyzed for five minutes at 325° in tetrachlorodiphenyl. Any carbon dioxide formed was swept out by a stream of nitrogen and collected in an ascarite tube. A dry-ice bath (−80°) and calcium chloride tube were interposed to remove vapors. Only 0.1 mole of carbon dioxide was formed in an hour although the color change to that of the green anhydride derivative was complete within one minute. No carbon monoxide was detected. The acid number and spectrum checked those of the hydroxylamine derivative of rhodoporphyrin-γ-carboxylic anhydride. The yield was very poor.

Oxime of Trimethyl Rhodin *g*.—This derivative was prepared for the purpose of comparing its acidic character and other properties with those of the above hydroxylamine derivatives. A solution of 100 mg. of trimethyl rhodin *g* in 50 cc. of pyridine was heated on a steam-bath for ten minutes with one gram each of hydroxylamine hydrochloride and anhydrous sodium carbonate. The dark green mixture was added to ether forming an olive-green solution with a red fluorescence. The oxime was the sole product and unlike the above hydroxylamine derivatives, it was insoluble in alkali. When recrystallized from chloroform-methyl alcohol it melted at 212° (in a tube). Its acid number is 13. The spectrum in ether: I, 684–645; II, 615---601(faint); III, ---544---(very faint); IV, 525–496; E. A., 447. Order: I or IV, II, III. This checks the spectrum recently reported by Fischer for the same compound.

Anal. Calcd. for $C_{37}H_{41}O_7N_5$: C, 66.5; H, 6.20; N, 10.5. Found: C, 65.89, 65.78; H, 6.10, 6.41; N, 10.72, 10.29.

(8) Fischer has accomplished this transformation with a variety of reagents [*Ann.*, **498**, 209–211 (1932)].

(9) Fischer, *ibid.*, **490**, 56 (1931).

Conversion of the Unstable Chlorins to Phaeopurpurin 18

Failure to Detect Formic Acid.—In a careful repetition of the procedure of Fischer[10] for the detection of formic acid in this reaction, it was found that traces were actually formed by the interaction of the alkali and ether during the phasing process. If these were removed by shaking the ethereal unstable chlorin solution with portions of 0.5 *M* sodium dihydrogen phosphate, no subsequent formation of formic acid during the five day standing period took place. The validity of the procedure was carefuly tested by an exactly parallel determination on a comparable known quantity of formic acid in ether.

Detection of Carbon Dioxide.—An ether solution of unstable chlorins prepared from methyl phaeophorbide *a* was freed of carbon dioxide and carbon monoxide and placed in an apparatus equipped to absorb these gases, if evolved during several days of standing. The procedure was as follows: a solution of 200 mg. of methyl phaeophorbide (0.33 m. mole) in 5 cc. of pyridine and 250 cc. of ether was shaken for thirty minutes with 25 cc. of 25% *n*-propyl alcoholic potassium hydroxide. Freshly boiled distilled water was added and the product transferred to 300 cc. of fresh ether. The chlorins were then completely extracted with 75 cc. of 20% hydrochloric acid and transferred to 300 cc. of ether which had been refluxed for an hour in a nitrogen stream.

The solution thus obtained was introduced into a liter flask fitted with ground glass joints and stopcocks and connected to an absorption train consisting of a cold trap for organic vapors, calcium chloride and ascarite tubes and a bubbler containing a dilute hemoglobin solution. The chlorin solution was refluxed for an hour in a stream of nitrogen during which time the color changed rapidly from green to red-purple, and 3.5 mg. of carbon dioxide (0.08 m. mole) was collected in the ascarite tube. The flask was then closed off by stopcocks and allowed to stand for two days. The refluxing and flushing with nitrogen was repeated. The ascarite tube gained 5.5 mg. (0.125 m. mole) but no carbon monoxide was detected. Fractionation showed the presence of some phaeopurpurin 7 and some unstable chlorin besides the phaeopurpurin 18 of which 0.1 mole was isolated.

In a total of three determinations comparable results were obtained. Also a blank experiment was performed repeating every detail of the above except that no methyl phaeophorbide was used. The ascarite tube gained 0.9 mg. during the refluxing period before standing and gained no weight after standing for two days.

With Potassium Molybdicyanide.—The oxidation in pyridine–acetone occurred with a rapid evolution of carbon dioxide. Its course was followed by electrometric titration of the oxidizing agent and by collection of the carbon dioxide as barium carbonate according to methods previously described. An ether solution of unstable chlorins was prepared from 150 mg. of methyl phaeophorbide as described above and taken to dryness *in vacuo*. It was then dissolved in 15 cc. of pyridine and added to the filtered oxidizing mixture previously prepared as follows: 500 mg. of potassium molybdocyanide in 10 cc. of water and 3 cc. of glacial acetic acid, oxidized with permanganate and diluted to 100 cc. with molar pyridine in

(10) Fischer, *ibid.*, **498**, 208 (1932).

acetone. Titration showed that 80% of two equivalents of molybdicyanide was destroyed in thirty minutes and 94% in ninety minutes. After three hours 56 mg. of barium carbonate had formed (110% of theoretical). The yield of phaeopurpurin 18 was 36%.

With Potassium Ferricyanide.—For preparative purposes a more convenient method is oxidation by potassium ferricyanide in dilute ammonia solution. The ether solution of phaeophytin is phased with alkali, water is added and the product is transferred to fresh ether. It is then extracted with dilute ammonia and treated with four equivalents of ferricyanide for fifteen minutes. It is then retransferred to ether, washed and fractionated; yield, 110 mg. from 500 of phaeophytin. Difficulty encountered in the ammonia extraction is probably due to incomplete removal of the propyl alcohol and may be overcome by the addition of acetone.

Iodine or quinone added to the ether solution of the unstable chlorins also greatly increases the rate of oxidation, but in qualitative experiments much chlorophyll material appeared to be destroyed.

Oxidation of Phaeopurpurin 7 to Beta-Monomethyl Chlorin *a* and Carbon Dioxide.—The phaeopurpurin 7 was prepared by two methods: (1) by fractionating the mixture of phaeopurin 7 and 18 resulting from the unstable chlorins from phaeophytin, (2) by alkaline saponification of dimethyl phaeopurpurin 7. Results were the same with both samples (a further proof of their identity). The reaction was carried out with potassium molybdicyanide in pyridine–acetone, under conditions similar to those given above for phaeopurpurin 18. Carbon dioxide was evolved less rapidly than in the case of chlorin *e* but the evolution seemed complete after one hour, although it was continued for two hours more. The reaction mixture was filtered and the product transferred to ether and fractionated. The main product, monomethyl chlorin *a*, was removed by 6–9% acid. The residue was phaeopurpurin 18 formed from the former in the oxidizing medium. Its yield doubled when the oxidation was continued overnight.

This instability of monomethyl chlorin *a* necessitated concentrating its ether solution *in vacuo* and also drying the isolated sample for analysis at room temperature. A sample dried at 60° gave carbon values close to those of phaeopurpurin 18 and on examination was found to contain a high percentage of the latter compound. The solid loses methyl alcohol slowly even on standing at room temperature. The yield of chlorin was 40%, and 33 mg. of barium carbonate was collected (70%). The color and spectrum check those of chlorin *a*. The acid number is 7.

Anal. Calcd. for $C_{34}H_{38}N_4O_6$: C, 68.23; H, 6.3; N, 9.36; OCH_3, 5.17. Found: (from phaeopurpurin 7 from source (1)) C, 68.58, 68.54; H, 6.63, 6.78; OCH_3, 4.6; (from phaeopurpurin 7 from source (2)) C, 67.91; 67.89; H, 6.57, 6.26; N, 9.47, 9.52; OCH_3, 5.3, 5.4.

Chlorin *a* monomethyl ester was converted to the triester by treatment with diazomethane in ether. Large black plates were obtained. The acid number is 10.

Anal. Calcd. for $C_{36}H_{42}N_4O_6$: C, 69.01; H, 6.75; OCH_3, 14.8. Found: C, 69.16, 69.27; H, 6.90, 6.67; OCH_3, 14.3, 13.7.

Pyrolysis of Beta Monomethyl Chlorin *a*.—In diphenyl at 200° the pyrolysis to phaeopurpurin 18 is complete in a few minutes. The product was alkali-soluble and on analysis was found to be methoxyl-free. It was identified as phaeopurpurin 18 by color, spectrum and acid number.

Alpha-Monomethyl Chlorin *a* from Methyl Phaeopurpurin 18.—To a solution of 150 mg. of phaeopurpurin 18 ester in 50 cc. of pyridine was added 10 cc. of 0.15 *N* potassium hydroxide. The color changed to green immediately and after three minutes the product was transferred to ether. It proved to be a chlorin of acid number 6 and identical in spectrum with chlorin *a*. It still contained one methoxyl group.

Anal. Calcd. for $C_{34}H_{38}N_4O_6$: OCH_3, 5.17. Found: OCH_3, 5.6, 5.6.

Pyrolysis of Alpha-Monomethyl Chlorin *a*.—Pyrolysis of the above chlorin in diphenyl at 200° for three minutes resulted in conversion to phaeopurpurin 18 monomethyl ester. This was alkali-insoluble and identified by spectrum and acid number.

Hot Saponification of Trimethyl Chlorin *a*.—A 400-mg. sample of trimethyl chlorin *a* was added to 100 cc. of 25% methyl alcoholic potassium hydroxide at the boiling point and refluxed seventy minutes. The ether solution of the product proved to contain on fractionation some isorhodoporphyrin and a larger proportion of chlorin *f*. Both were identified by color, spectrum and acid number; the latter was further verified by conversion to isorhodoporphyrin with alkaline potassium ferricyanide.[11]

The aqueous layer obtained above after transfer of the saponified chlorin *a* ester was tested for oxalic acid as previously described.[12] The result was negative.

Metallic Derivatives of Trimethyl Chlorin *a*.—The copper and zinc derivatives were prepared according to the method of Treibs and Wiedemann.[13] To a solution of 100 mg. of the ester in 5 cc. of chloroform was added a solution of 30 mg. of the metal acetate in methyl alcohol. The mixture was evaporated to dryness and the product dissolved in acetone and added to ether. It was thoroughly washed with water and then concentrated.

Copper Derivative.—After two recrystallizations this formed fine black crystals melting at 235°. The color of its ether solution is blue-green. The spectrum in ether: I, 675–617---583---, II, 506–490; E. A., 433. Order: I, II.

Anal. Calcd. for $C_{36}H_{40}N_4O_6Cu$: C, 62.75; H, 5.86; OCH_3, 13.5; Cu, 9.25. Found: C, 62.90, 63.21; H, 6.36, 5.98; OCH_3, 13.5, 14.2; Cu, 9.25, 8.62, 9.18.

Zinc Derivative.---The zinc derivative formed fine greenish-black crystals melting at 242°. Its solution in ether is blue-green with a red fluorescence. The spectrum in ether: I, 680–625; II, 611---592; III, ---562---(very faint); IV, ---530---(faint); E. A., 435. Order: I, II, IV, III.

Dimethyl Chlorin *a*.—300 mg. of trimethyl chlorin *a* dissolved in pyridine was added to 25% potassium hydroxide in methyl alcohol. After the solution had stood thirty minutes the chlorin was transferred to ether and the alkali-soluble material isolated; yield, 275 mg. On re-

(11) Paper IX, THIS JOURNAL, **55**, 798 (1933).
(12) Paper IV, *ibid.*, **53**, 371 (1931).
(13) Treibs and Wiedemann, *Ann.*, **471**, 171 (1929).

crystallizing from acetone–ligroin it separated in blue iridescent crystals melting at 241–242°. The spectrum and color were identical with those of chlorin *a*.

Anal. Calcd. for $C_{35}H_{40}N_4O_6$: C, 68.62; H, 6.58; N, 9.15; OCH_3, 10.15. Found: C, 68.90, 68.61; H, 6.68, 6.46; N, 9.77, 10.14; OCH_3, 10.1, 10.3.

A dimethyl ester was also obtained when 200 mg. of trimethyl chlorin *a* was refluxed for thirty minutes in 1% methyl alcoholic potassium hydroxide. Only half of the product was alkali-soluble. On recrystallization from acetone–ligroin, minute greenish-black crystals separated, m. p. 208°.

Anal. Calcd. for $C_{35}H_{40}N_4O_6$: C, 68.62; H, 6.58; OCH_3, 10.15. Found: C, 68.05, 68.26; H, 6.43, 6.19; OCH_3, 10.8, 11.4.

Pyrolysis of each of these two dimethyl esters of chlorin *a* gave apparently different porphyrins in small yields but these were not positively identified.

An Unstable Chlorin *a*.[14]—A solution of 250 mg. of phaeopurpurin 18 in 15 cc. of pyridine was added to 1500 cc. of ether, the pyridine was removed with dilute acid and the phaeopurpurin was extracted into 500 cc. of 20% hydrochloric acid. After drawing air through this solution for forty hours the products obtained were a chlorin of acid number 3 and spectrum similar to that of chlorin *a*, and also a small amount of chlorin *a*. Methylation of the new chlorin gave a trimethyl ester of acid number 11 whose color and spectrum were identical with those of chlorin *a*. Dark blue iridescent crystals were obtained by recrystallizing from acetone–ligroin. These melted at 227–228° and gave no depression with known trimethyl chlorin *a*, melting at 228°.

Anal. Calcd. for $C_{36}H_{42}N_4O_6$: C, 69.01; H, 6.75; OCH_3, 14.8. Found: C, 69.16, 69.20; H, 6.54, 6.45; OCH_3, 14.8.

(14) Compare Fischer's pseudo chlorin p. 6, *Ann.*, **498**, 222 (1932).

Summary

1. The transformation of the "unstable chlorins" to phaeopurpurin 18 has been shown to be an oxidation accompanied by loss of carbon dioxide.

2. Hydroxylamine derivatives characteristically formed by anhydrides have been obtained from phaeopurpurin 18 and rhodoporphyrin-γ-carboxylic anhydride. These facts substantiate the anhydride structure of phaeopurpurin 18.

3. Phaeopurpurin 7 is oxidized by potassium molybdicyanide to a monomethyl ester of chlorin *a* and carbon dioxide. This agrees with the α-ketonic acid structure previously postulated for this compound.

CAMBRIDGE, MASS. RECEIVED AUGUST 22, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Preparation of 2-Iodophenanthrenequinone

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As a part of an investigation carried on in this Laboratory of some derivatives of phenanthrenequinone it was observed that the literature does not record any iodine derivatives. This paper describes the preparation of the 2-iodo derivative and work is in progress on the preparation of the 4-iodo compound.

Since iodine is not easily introduced by direct methods, the course of procedure that suggested itself was through the usual diazo reaction. Starting with phenanthrene, the synthesis involved the dichromate oxidation to the quinone, nitration of the quinone, and reduction of the 2-nitro compound to the amino quinone. The diazotized amine was then treated with potassium iodide. The phenanthrenequinone was prepared by the method of Anschütz and Schultz[1] and purified through the sodium bisulfite addition compound and subsequent crystallization from glacial acetic acid.

(1) Anschütz and Schultz, *Ann.*, **196**, 38 (1879).

No method is described in the literature by which the 2- and 4-nitrophenanthrenequinones can be prepared separately by controlled nitration. We found the method of Schmidt and Austin[2] for the preparation of these compounds to be very unsatisfactory due apparently to the short time designated for the nitration. Also, we could not obtain the 2,7-dinitro derivative reported by them. Werner's[3] method, as given in detail by Schmidt and Spoun,[4] was finally used in a general way for the preparation and separation of the 2- and 4-nitro quinones. In the preparation of the amine our results differ somewhat from those described in the literature, particularly those of Brass and Ferber.[5]

Experimental

Preparation of 2-Aminophenanthrenequinone.—To 5 g. of the 2-nitro compound in 250 cc. of a 6% solution of

(2) Schmidt and Austin, *Ber.*, **36**, 3731 (1903).
(3) Werner, *Ann.*, **321**, 336 (1902); *Ber.*, **37**, 3086 (1904).
(4) Schmidt and Spoun, *ibid.*, **55**, 1194 (1922).
(5) Brass and Ferber, *ibid.*, **55**, 541 (1922).