our previous observation[4] on the change of Raman spectrum on solidification, since the solid consists only of the molecules of the first form. Thus the Raman line observed at 865 cm.$^{-1}$ is assigned to the first form and that observed at 838 cm.$^{-1}$ to the second form or to the third. The intensity ratio of these two lines was obtained from the microphotometer tracings of the Raman spectra photographed at the two temperatures, and was found as

$$I(838)/I(865) = 1.21 \text{ at } 305°\text{K.}$$
$$= 0.77 \text{ at } 201°\text{K.}$$

Then the energy difference ΔE between the first form and another can at once be calculated from:[4a]

$$\frac{1.21}{0.77} = e^{-\frac{\Delta E}{R}\left(\frac{1}{305} - \frac{1}{201}\right)}$$

and we have

$$\Delta E = 0.53 \text{ kcal./mole}^{4b}$$

Similarly from a pair of lines at 865 and at 764 cm.$^{-1}$ we obtain a value of $\Delta E = 0.70$ kcal./mole which is somewhat larger than the preceding one. The difference may merely be due to the experimental error, but we cannot deny the possibility that the line at 764 cm.$^{-1}$ belongs to the rotational isomer different from what we stated above with regard to the line at 838 cm.$^{-1}$: *i. e.*, we may assign the line at 764 cm.$^{-1}$ to the third molecular form which is more unstable than the second one. We are not, however, sure whether this assignment is appropriate, since the number of lines seems to be too small to account for the coexistence of three molecular forms.[5]

TABLE I

OBSERVED INTENSITY RATIO OF PAIRS OF LINES AT ν AND 865 CM.$^{-1}$

ν	$I(\nu)/I(865)$ at 201° K.	at 305° K.	ΔE kcal./mole
764	0.27	0.49	0.70
838	.77	1.21	.53

We have not yet observed the temperature dependence of the intensity ratio in the gaseous state, the accurate determination of which would be considerably difficult, but we have reason to believe that the values of ΔE obtained above are not much different from that of a free molecule, since these values are of the magnitude which would be expected from the steric repulsion between the moving groups about the C–C bond as axis.[6]

In any case we are sure that on liquefaction the energy difference between the rotational isomers of *n*-pentane does not change so much as in the case of dichloroethane and it is, therefore, reasonable that we explained the difference in the spectral intensity between the gaseous and liquid dichloroethane mainly by the electrostatic interaction between polar molecules.

Summary

The relative intensity of the Raman lines of *n*-pentane was measured at 32° and at −72° and from this experimental result the energy difference between the rotational isomers was calculated as 0.5 kcal./mole.

(4) Mizushima and Simanouti, THIS JOURNAL, **71**, 1320 (1949).

(4a) See Langseth and Bernstein, *J. Chem. Phys.*, **8**, 410 (1940).

(4b) After the manuscript was submitted to the Editorial Board, Sheppard and Szasz (*J. Chem. Phys.*, **17**, 86 (1949)) reported the value of ΔE in excellent agreement with ours.

(5) The number of Raman lines observed for *n*-pentane is not larger than that observed for *n*-butane (see footnote (4)). It seems, therefore, probable to consider the coexistence of only two molecular forms for *n*-pentane as for *n*-butane. However, some Raman lines of *n*-pentane may escape detection because of their weak intensity and, therefore, we cannot deny the possibility of the coexistence of three molecular forms.

(6) The value of ΔE obtained by Pitzer (0.8 kcal./mole) in his calculation of entropies of *n*-butane and *n*-heptane is not much different from that obtained in the present experiment; see Pitzer, *Chem. Rev.*, **27**, 39 (1940), *J. Chem. Phys.*, **8**, 711 (1940).

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[CONTRIBUTION FROM (a) THE WELLCOME RESEARCH LABORATORIES AND (b) CHEMICAL INSTITUTE, UNIVERSITY OF MUNICH, GERMANY]

The Synthesis of Pterorhodin (Rhodopterin)[1,1a]

BY PETER B. RUSSELL,[a] ROBERT PURRMANN,[b] WERNER SCHMITT[b] AND GEORGE H. HITCHINGS[a]

Pterorhodin is a violet-red substance which is formed during autoxidation of acid solutions of crude butterfly wing pigments,[2] and xanthopterin[3] and erythropterin[3] of natural origin. Both Schöpf[5] and Hopkins[3] suggested that it was formed from erythropterin, but the proportion of pterorhodin obtainable from this source diminishes with increasing purity of the erythropterin.[6] Moreover, xanthopterin is not the precursor since synthetic xanthopterin fails to yield the substance.[4,7]

A structural formula for pterorhodin (I) was suggested by Purrmann and Maas[4] primarily on the basis of degradative experiments in which leucopterin (II) and xanthopterin-7-carboxylic acid (III) were obtained as the products of oxida-

(1) Presented in part at the 115th meeting of the American Chemical Society at San Francisco, California, March 30, 1949.

(1a) Pterorhodin has been named first lepidoporphyrin,[2] then rhodopterin[3] by Hopkins, but Purrmann's proposal,[4] pterorhodin, is perhaps preferable since the substance is not a primary butterfly wing pigment.

(2) Hopkins, *Trans. Roy. Soc. (London)*, **B186**, 661 (1895).

(3) Hopkins, *Proc. Roy. Soc. (London)*, **B130**, 359 (1942).

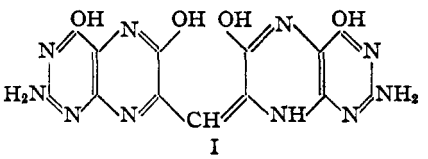
(4) Purrmann and Maas, *Ann.*, **556**, 186 (1944).

(5) Schöpf and Becker, *ibid.*, **507**, 266 (1933).

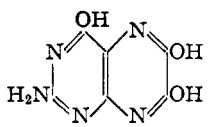
(6) Purrmann and Eulitz, *ibid.*, **559**, 169 (1948).

(7) A. R. Todd, personal communication.

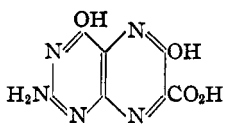
tion. This formulation is in agreement with the analytical data, the reversible reduction to a tetrahydro derivative by sodium amalgam, the cleavage by chlorine water to oxalylguanidine and other properties.[4] However, an alternative formulation (IV) could not be excluded by these properties and reactions.



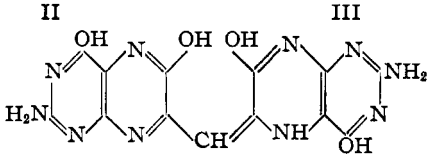
I



II

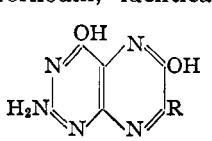


III

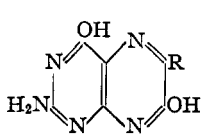


IV

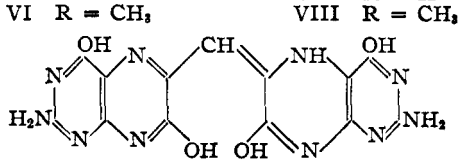
The formulations (I) or (IV) for pterorhodin suggested a possible synthetic approach to the problem if the reactivities of the pyrazine moiety and attached methyl groups were sufficiently great to permit the oxidative condensation of xanthopterin (V) or iso-xanthopterin (VII) with the respective methyl derivatives (VI) (VIII).[8] Condensation of xanthopterin (V) with 7-methylxanthopterin (VI) would be expected to yield (I). Compound (IV) could be formed either from xanthopterin (V) and 6-methyl*iso*xanthopterin (VIII) or from iso-xanthopterin (VII) and 7-methylxanthopterin (VI), while a third isomer (IX) would be expected from the condensation of iso-xanthopterin (VII) and methyl*iso*xanthopterin (VIII). Pterorhodin, identical with that from natural



V R = H
VI R = CH_3



VII R = H
VIII R = CH_3

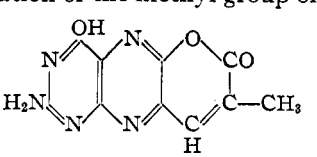


IX

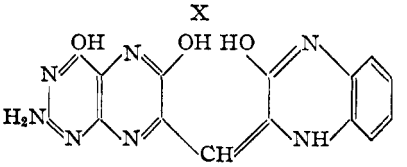
pterins of *C. argante* was in fact obtained by the condensation of xanthopterin with 7-methylxanthopterin. Moreover, iso-pterorhodin (IV) and *allo*-pterorhodin (IX) were obtained as predicted.

The formation of pterorhodin from xanthopterin may be carried out in a variety of ways. A mixture of xanthopterin and 7-methylxanthopterin in acid solution can be oxidized with air or with hydrogen peroxide, or 7-methylxanthopterin may be formed by the reaction of 2,4,5-triamino-6-hydroxypyrimidine with oxalacetic ester[9] and condensed with a further quantity of xanthopterin without isolation of the intermediate. Furthermore, appreciable quantities of pterorhodin are obtained when acid solutions of xanthopterin containing acetone or acetaldehyde are oxidized with hydrogen peroxide, and even during acetylation of xanthopterin with acetic anhydride.[10] Thus the methylene group of pterorhodin may have a variety of sources. However, in view of the close resemblance in properties of xanthopterin and 7-methylxanthopterin[8] it is highly probable that the latter is the precursor which is present in xanthopterin from natural sources.

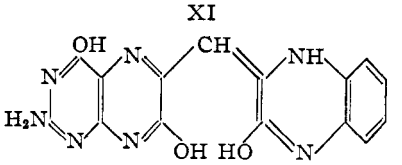
The reactivity of the methyl group which appears to be involved in these syntheses of pterorhodin (and its isomers) may be illustrated by other reactions of xanthopterin derivatives. In strongly acid solution, 2,4,5-triamino-6-hydroxypyrimidine and pyruvic acid give xanthopterin methacrylic acid lactone (X) which apparently arises through the condensation of the methyl group of 7-methyl-



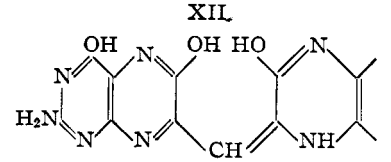
X



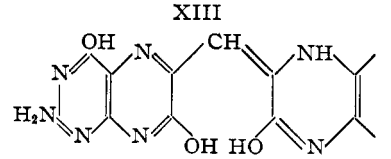
XI



XII



XIII



XIV

(8) Elion and Hitchings, THIS JOURNAL, 69, 2553 (1947).

(9) The condensation of ethyloxalacetate with 4,5-diaminopyrimidines gives almost exclusively 6-hydroxy-7-methylpteridines in strong acid and 7-hydroxy-6-methylpteridines in acetic acid solution. The yields are superior to those obtainable with pyruvic acid (Elion, Russell and Hitchings, to be published).

(10) Purrmann, unpublished observations.

xanthopterin with a second molecule of pyruvic acid. Xanthopterin and iso-xanthopterin both condense oxidatively with 2-hydroxy-3-methylquinoxaline to give substances, XI and XII, respectively, similar to the pterorhodins. It is interesting in this connection that the absorption spectrum of XI (Fig. 1) has the general characteristics of that of pterorhodin (I) (Fig. 1) which thus seems to be correlated with the grouping (XIII). The spectrum of XII resembles that of

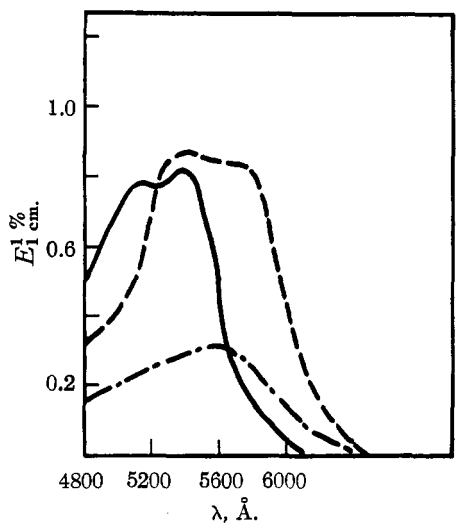


Fig. 1.—Absorption spectra of: isopterorhodin - - - - -; pterorhodin———; condensation product of xanthopterin and 3-methyl-2-quinoxalone —·—·— in concentrated sulfuric acid.

allo-pterorhodin (IX) (Fig. 2) and both substances contain the structure (XIV). Isopterorhodin (IV) which might be viewed as containing either or both of the structures XIII or XIV gives a spec-

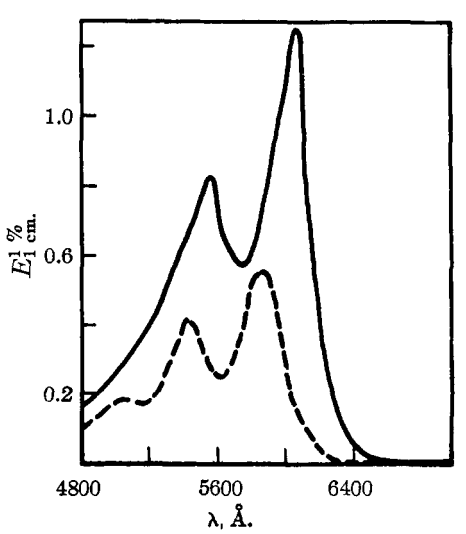
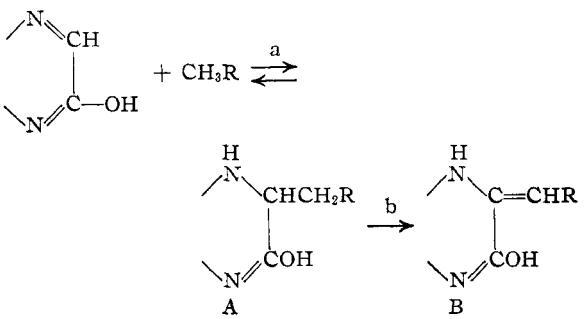


Fig. 2.—Absorption spectra of: *allo*-pterorhodin ——; the condensation product of iso-xanthopterin and 3-methyl-2-quinoxalone - - - - in concd. sulfuric acid.

trum more closely related to that of the pterorhodin series.

The oxidative condensations of the xanthopterin derivatives perhaps are best viewed as (a) an acid catalyzed reversible addition of the active 7 (or 6) methyl group to the 7,8 (or 5,6) double bond to give aldol-like intermediates (A) followed by (b) dehydrogenation in the side-chain to give the products B. In the formation of pterorhodin from xanthopterin and acetone or acetaldehyde an intermediate carboxylic acid would be postulated (A or B, R = CO_2H) as arising from the carbonyl group by oxidation. Decarboxylation then would result in 7-methylxanthopterin (B, R = H). Some evi-



dence for the formation of an intermediate of the postulated type was obtained. When xanthopterin and 7-methylxanthopterin are mixed in acid solution a rapid change in spectrum occurs after which an equilibrium state appears to be reached (Table I). At equilibrium the spectrum resembles that of a mixture of xanthopterin and dihydroxanthopterin and therefore approximates that which might be expected of a substance (A) containing isolated nuclei of this type.

TABLE I

CHANGES IN ULTRAVIOLET ABSORPTION SPECTRUM DURING REACTION OF XANTHOPTERIN WITH 7-METHYLXANTHOPTERIN

	Substance	Reference spectra $E_{1\text{ cm.}}^{1\%}$ 305 mμ / $E_{1\text{ cm.}}^{1\%}$ 390 mμ	Time, min.	Reaction mixture[a] $E_{1\text{ cm.}}^{1\%}$ 305 mμ / $E_{1\text{ cm.}}^{1\%}$ 390 mμ
A	Xanthopterin	0.20	0	0.20
B	7-Methylxanthopterin	0.12	15	.51
C	β-Dihydroxanthopterin	∞	30	.61
			45	.63
	A + C	0.70	60	.63
	B + C	1.20	105	.70

[a] Equimolecular quantities of xanthopterin and 7-methylxanthopterin were dissolved in 2 *N* hydrochloric acid and the solutions were mixed. The optical densities of the mixtures were determined at 305 and 390 mμ immediately and after the indicated period at 60°.

This reaction mechanism appears to be consistent with the observed reactions. The resemblance of the pyrazine —C=N— (7,8 or 5,6) linkage, in the xanthopterin-type compound, to a carbonyl group[11] is brought out in the condensations, and

(11) Wieland and Purrmann, *Ann.*, **544**, 163 (1940).

also in the decarboxylations which occur both in the formation of the methylxanthopterins *via* oxalacetic ester and in the formation of pterorhodin from xanthopterin and acetaldehyde or acetone. In this respect isoxanthopterin and xanthopterin (6 and 7) acetic acids resemble β-keto acids. A parallel reaction has been observed in the quinoxaline field.[12]

The discovery that a synthetic 7,8-dihydroxanthopterin is not identical with the reduction product of xanthopterin[13] may or may not be inconsistent with this view of the potentialities of the pteridine —C=N— linkage. The reduction of xanthopterin may follow a course differing from that of the condensations, in fact, 1,4-addition (*i. e.*, addition at the 5,8-position) of hydrogen would appear probable. In any case, the two isomeric dihydroxanthopterins probably should be regarded as "stable tautomers"[13] and the significance of their existence will depend on further work on the fine structure of the reduction isomer. The existence of stable isomeric dihydropteridines differing in the position of the double bond in the pyrazine ring has been reported.[14]

Since the preparation of this manuscript Karrer and Schwyzer[15] have reported the synthesis of "methylpterin red" by the reaction of 2,4,5-triamino-6-hydroxypyrimidine and glyceric aldehyde. The published spectrum of this substance is very similar, but not identical, to that found for natural and synthetic pterorhodin (Fig. 3). A direct comparison of these substances appears to be desirable.

Experimental

Pterorhodin from Xanthopterin and 7-Methylxanthopterin. (a) **With Air.**—One-half gram of xanthopterin[16] was mixed with 0.5 g. of 7-methylxanthopterin[8] and the mixture dissolved in 200 ml. of *N* hydrochloric acid; the solution was filtered from a small amount of insoluble matter, heated to 90° in a water-bath and a stream of air passed through at a rate of about 200 bubbles per minute. After about one-half hour the solution began to redden and shortly thereafter a dark purple, almost black, solid began to separate. After two and one-half hours the solid was filtered off, washed with hot *N* hydrochloric acid and hot water. The solid was a mass of minute dark purple needles (sample I). Its absorption spectrum in concentrated sulfuric acid differed only slightly from that of an authentic sample of pterorhodin in the same solvent (Fig. 3). It appears likely that one or both samples contain trace impurities, which would account for the observed differences.

(b) **With Hydrogen Peroxide.**—One hundred and twenty milligrams each of the two reactants were dissolved in 100 ml. of 3 *N* hydrochloric acid. The solution was filtered and 10 ml. of a 15% hydrogen peroxide solution was added. On standing at room temperature a dark solid separated. After three and one-half hours it was filtered off (100 mg.). It proved to be amorphous but was identical with the above product in every other respect.

A portion was purified by solution in concentrated sulfuric acid and precipitated with water. It was dried at 150° *in vacuo* for analysis (sample IV). Several repetitions of the hydrogen peroxide oxidation, with or without added seeds, failed to produce pterorhodin in crystalline form.

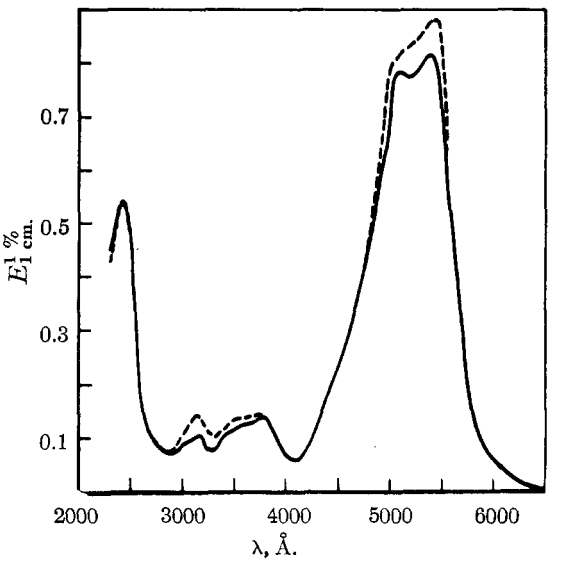


Fig. 3.—Absorption spectrum of pterorhodin in concd. sulfuric acid: natural - - - -; synthetic ——.

On standing, the mother liquors from the above oxidation deposited some bright red needles. These could be recrystallized from 3 *N* hydrochloric acid but too little was obtained to allow further examination.

Pterorhodin by Oxidation of the Condensation Product of 2,4,5-Triamino-6-hydroxypyrimidine and Ethyl Oxalacetate with Xanthopterin.—A solution obtained by treating 2 g. of 2,4,5-triamino-6-hydroxypyrimidine with 4 g. of sodium ethyl oxalacetate in 200 ml. of boiling 2 *N* sulfuric acid for one and one-half hours followed by filtration was treated with 1.5 g. of xanthopterin in 8 l. of 0.1 *N* hydrochloric acid. The solution was warmed and allowed to stand for three days after which time 1.35 g. of fine violet needles was collected (47%). After purification by precipitation from concentrated sulfuric acid with water and drying at 150° *in vacuo* the substance was analyzed (sample II).

In another experiment the original sulfuric acid solution was diluted to 1 l., the xanthopterin added and the solution heated on a water-bath while air was drawn through. The yield of violet-black needles was 1.15 g. (40%). This was analyzed (sample III) after drying at 150° *in vacuo*.

Anal. Calcd. for $C_{13}H_{10}O_4N_{10}$: C, 42.2; H, 2.7; N, 37.8. Found: Sample I: C, 41.5; H, 3.1; N, 37.4. Sample II: C, 42.4; H, 3.0; N, 34.4. Sample III: C, 42.2; H, 2.5; N, 37.2. Sample IV: N, 37.3.

Pterorhodin by Oxidation of Xanthopterin with Acetaldehyde or Acetone.—Three hundred milligrams of xanthopterin was dissolved in 20 ml. of warm *N* sulfuric acid and the solution filtered. To this solution was added 0.04 ml. of acetaldehyde in 4 ml. of water followed by 0.3 ml. of a 30% solution of hydrogen peroxide. The mixture was warmed for five minutes in a boiling water-bath and set aside for twelve hours. At the end of this time 56 mg. of purple material had separated. This was shown to be identical with pterorhodin after purification by precipitation from sulfuric acid with water.

When a solution of xanthopterin in 3 *N* hydrochloric acid was treated with acetone and hydrogen peroxide in a similar manner pterorhodin was obtained in about 20–30% yield.

Pterorhodin Sulfate.—Synthetic pterorhodin (100 mg., sample I) was converted to the sulfate by the method of Purrmann and Maas.[4] The sulfate (66 mg.) formed red

(12) Ruhemann and Stapleton, *J. Chem. Soc.*, **77**, 239 (1900).
(13) Hitchings and Elion, THIS JOURNAL, **71**, 467 (1949).
(14) Pesson, *Bull. soc. chim.*, [5] **15**, 963 (1948).
(15) Karrer and Schwyzer, *Helv. Chim. Acta*, **32**, 423 (1949).
(16) Elion, Light and Hitchings, THIS JOURNAL, **71**, 741 (1949).

plates identical in appearance to a sample prepared from authentic pterorhodin. It was dried at 120° *in vacuo*.

Anal. Calcd. for $C_{13}H_{10}O_4N_{10}\cdot 2H_2SO_4$: C, 27.6; H, 2.5; N, 24.7. Found: C, 27.8; H, 2.6; N, 24.3.

Tetrahydropterorhodin Perchlorate.—Synthetic pterorhodin (sample I) was reduced with sodium amalgam following Purrmann and Maas.[4] The colorless hydrochloride was converted to the perchlorate which separated from the solution in rhombic prisms. It was dried at 150° for analysis.

Anal. Calcd. for $C_{13}H_{14}O_4N_{10}\cdot 2HClO_4$: C, 27.1; H, 2.8. Found: C, 27.6; H, 2.6.

The solid perchlorate began to turn purple rapidly on exposure to air. The mother liquors of the hydrochloride and perchlorate on dilution and oxidation with air gave pterorhodin.

Isopterorhodin.—One hundred milligrams each of 7-methylxanthopterin and isoxanthopterin[17] were treated with 30 ml. of 5 *N* hydrochloric acid. The isoxanthopterin did not dissolve completely. Air was drawn through the solution as previously described. After six hours the red micro-crystalline powder was filtered (75 mg.). It was visibly contaminated with some white material. Seventy milligrams of the red powder was dissolved in 1 ml. of concentrated sulfuric acid, the deep purplish-red solution was filtered through a sintered glass plate and 3 ml. of water added cautiously. The almost black crystalline precipitate (50 mg.) was collected by centrifugation, washed twice with 40% sulfuric acid, six times with acetic acid and finally several times with ether. It was dried at 150° *in vacuo*.

Anal. Calcd. for $C_{13}H_{10}O_4N_{10}\cdot H_2SO_4\cdot H_2O$: C, 32.1; H, 2.9; N, 28.8. Found: C, 32.1; H, 3.1; N, 28.5.

When the above preparation was carried out with xanthopterin and 6-methylisoxanthopterin[8] the same product was obtained.

Allopterorhodin.—One hundred milligrams each of isoxanthopterin and 6-methylisoxanthopterin were suspended in 30 ml. of 5 *N* hydrochloric acid and the suspension oxidized as previously described. The oxidation was continued for two days and the product filtered off at the end of this time (103 mg.). It was converted to the sulfate by solution in 4 ml. of concentrated sulfuric acid and dilution with 6 ml. of water. The purple sulfate separated as a crystalline powder. It was centrifuged off, washed with dilute sulfuric acid, acetic acid and ether. It was dried at 150° *in vacuo*.

Anal. Calcd. for $C_{13}H_{10}O_4N_{10}\cdot H_2SO_4$: C, 33.4; H, 2.6; N, 30.0. Found: C, 33.9; H, 2.8; N, 30.3.

Ethyl 2-Quinoxalone-3-acetate.—To a solution of *o*-phenylenediamine (5 g.) in 300 ml. of 2 *N* acetic acid was added 10 g. of sodium ethyl oxalacetate. Almost at once a yellow solid separated. The solution was heated for two hours on a steam-bath and then cooled and filtered. The yellow solid (9.0 g., 85%) was recrystallized from ethanol. It formed yellow needles, m. p. 210° (after softening from 205°). Ruhemann and Stapleton[12] described this compound, obtained by the condensation of *o*-phenylenediamine and ethyl acetylenedicarboxylate, as melting at 210° with previous softening.

3-Methyl-2-quinoxalone.—This compound was obtained in 80% yield by hydrolysis of the above ester with potassium hydroxide.[12] The acid decarboxylated spontaneously on acidification. The quinoxalone melted at 247–248° (dec.).[12,18]

Oxidative Condensation of 3-Methyl-2-quinoxalone with Xanthopterin.—Two hundred milligrams of each of the components was dissolved in 50 ml. of 3 *N* hydrochloric acid. Solution took place at once with the formation of a red color. The solution was warmed to 90° and air passed through as before. After about one hour the purple solid began to separate; at the end of four hours 125 mg. was collected. The product was converted to its sulfate by solution in 2.5 ml. of concentrated sulfuric acid and dilution with 2.5 ml. of water. The sulfate was separated by centrifugation, washed ten times with acetic acid and finally with ether. The red microcrystalline product was dried at 150°.

Anal. Calcd. for $C_{15}H_{10}O_3N_7\cdot H_2SO_4$: N, 22.7. Found: N, 22.9.

The sulfuric acid mother liquors deposited more amorphous material on dilution with water.

Oxidative Condensation of 3-Methyl-2-quinoxalone with Isoxanthopterin.—The reaction was carried out as above with isoxanthopterin and 3-methyl-2-quinoxalone. Isoxanthopterin was not soluble to any great extent and as a consequence the reaction mixture appeared as a suspension which on oxidation changed from gray to a reddish-brown. After four hours the brown solid was filtered off and washed with hot dilute hydrochloric acid and with hot water. The condensation product gave a greenish-red solution in concentrated sulfuric acid, the color changing to violet on addition of only a drop of water. Further dilution gave a precipitate of the violet sulfate which, on standing or on further addition of water, changed to the brownish-red free base. For analysis the process was repeated twice and the product dried at 150°.

Anal. Calcd. for $C_{15}H_{10}O_3N_7$: N, 29.0. Found: N, 29.3.

Xanthopterin Methacrylic Acid Lactone.—Five hundred milligrams of 2,4,5-triamino-6-hydroxypyrimidine bisulfite was treated with 30 drops of concentrated sulfuric acid and then warmed with 6 ml. of pyruvic acid for twenty minutes on the water-bath. On cooling the crystalline material (370 mg., 55%) was filtered, washed with acetic acid and crystallized twice from 5 ml. of concentrated sulfuric acid by addition of 5 ml. of water.

Anal. Calcd. for $C_{10}H_7O_3N_5\cdot H_2SO_4$: C, 35.0; H, 2.6; N, 20.5; SO_4, 28.0. Found: C, 35.3; H, 2.5; N, 18.6; SO_4, 30.3.

The free lactone was prepared by heating the sulfate with water. The precipitate was filtered and washed with water.

Anal. Calcd. for $C_{10}H_7O_3N_5$: C, 49.0; H, 2.8; N, 28.6. Found: C, 49.0; H, 2.8; N, 29.0.

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Summary

1. Pterorhodin (rhodopterin) has been synthesized by the oxidative condensation of xanthopterin and 7-methylxanthopterin. This suggests the presence of 7-methylxanthopterin as an hitherto undetected constituent of the pterins of butterfly wings.

2. Two isomeric substances, isopterorhodin and *allo*-pterorhodin have been prepared by similar means. Isopterorhodin has been synthesized from xanthopterin and 6-methylisoxanthopterin and from isoxanthopterin and 7-methylxanthopterin. *Allo*-pterorhodin was obtained by the condensation of the two isoxanthopterin derivatives.

3. Studies on the reactivity of the 7-position of xanthopterin (6-position of isoxanthopterin) and of the methyl groups attached to these positions are reported.

(17) Purrmann, *Ann.*, **548**, 290 (1941).

(18) Hinsberg, *ibid.*, **292**, 249 (1896).

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