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STRUCTURAL FEATURES OF HERQUEINONE, A RED PIGMENT FROM *PENICILLIUM HERQUEI*

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Isolation of a red pigment from *P. herquei* has been reported in an earlier paper (1). Further examination of this pigment and purification by adsorption chromatography has verified its homogeneity and the empirical formula $C_{20}H_{20}O_7$, although there remains the possibility of a slightly different ratio of hydrogen to carbon. Since the infrared spectrum of this pigment indicates the presence of at least one carbonyl group, and since Burton (2) has applied the name, herquein, to a yellow acid also isolated from *P. herquei*, the name herqueinone is proposed for the red pigment with a coppery lustre, which is the subject of the present study.

The infrared spectrum of herqueinone, Fig. 1, shows a band at 3.1 μ, characteristic of a hydrogen-bonded hydroxyl (3). For example, salicylaldehyde shows the band from the stretching vibration of the hydroxyl at 3.05 μ. The absence of absorption in the 5.5–6 μ region and occurrence of a strong band at 6.1 μ suggests carbonyl in an aromatic or quinonoid system which also contains hydroxyl. Among the few types of carbonyl compounds absorbing beyond 6 μ are hydroxyphenyl aldehydes (3) and ketones (4), and 2-hydroxy-1,4-naphthoquinones (5). Ettlinger (5) has noted that 2-hydroxy-1,4-naphthoquinones and their 3-alkyl derivatives are characterized by bands at 2.95–3.1 μ, 5.98–6.08 μ, and 6.23–6.3 μ. The spectrum of herqueinone exhibits bands in each of these three regions; however, all efforts to secure carbonyl derivatives of herqueinone have been unsuccessful. The 1,2-naphthoquinones (5) show a shorter wavelength band, below 6 μ, as do all types of γ- and δ-lactones. Further indication of absence of a 1,2-quinone system is furnished by failure of herqueinone to react with *o*-phenylenediamine under conditions which yield a quinoxaline with 1,2-naphthoquinone.

The ultraviolet spectrum of herqueinone, shown in Figs. 2 and 3, is quite characteristic, but yields little definitive information concerning structure other than the indication that an aromatic system is present. An interesting feature of the ultraviolet spectrum is its change with time when the compound is in 10^{-5} molar solution in alcohol. The spectrum in dioxane solution (Fig. 3) does not change with time. If the spectrum in dilute alcoholic solution is observed in the 270–275 mμ region immediately after solution, there is no inflection at 273 mμ, but an inflection appears in less than an hour. During the course of several days, the strong band at 273 mμ develops, and the original band at 313 mμ has decreased

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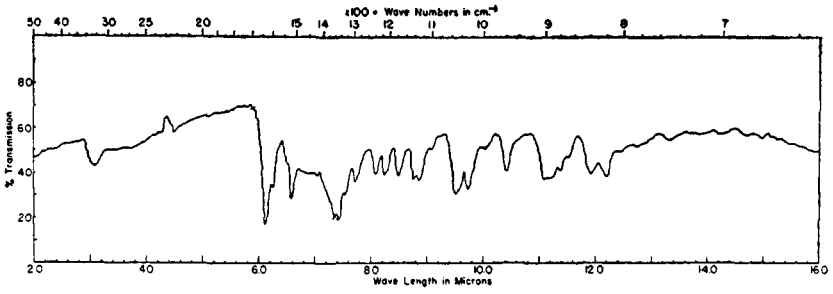

FIG. 1. INFRARED SPECTRUM OF HERQUEINONE TAKEN IN A NUJOL MULL.

to a shoulder. Several samples allowed to stand in 10^{-3} molar solution in alcohol did not show significant change in spectrum for periods up to 5 weeks, and no change was initiated by exposure to ultraviolet light or addition of traces of acid or alkali. These changes may be presumed to represent reaction with alcohol (possibly ring opening by solvation), but no definite correlation of these phenomena may be presented at this time. It is of interest that the spectrum of "aged" solutions of herqueinone bears a significant resemblance to those of 2-hydroxy-1,4-naphthoquinones (6). Lapachol (7) has maxima at 250, 280, 330 and 380 mμ. It may also be noted that the anion of herqueinone has a maximum near that which appears at 273 mμ when herqueinone solutions stand.

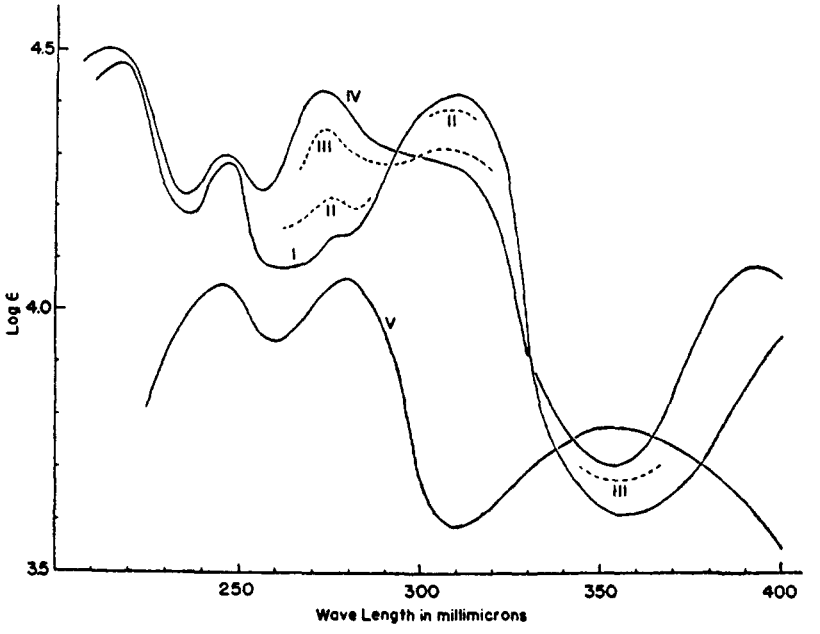

FIG. 2. ULTRAVIOLET ABSORPTION SPECTRA OF HERQUEINONE. Curve I, freshly prepared solution in 95% ethanol; curve II, same solution after 1 hr.; curve III, same solution after 1 day; curve IV, same solution after 1 month; curve V, solution in dilute aqueous sodium hydroxide.

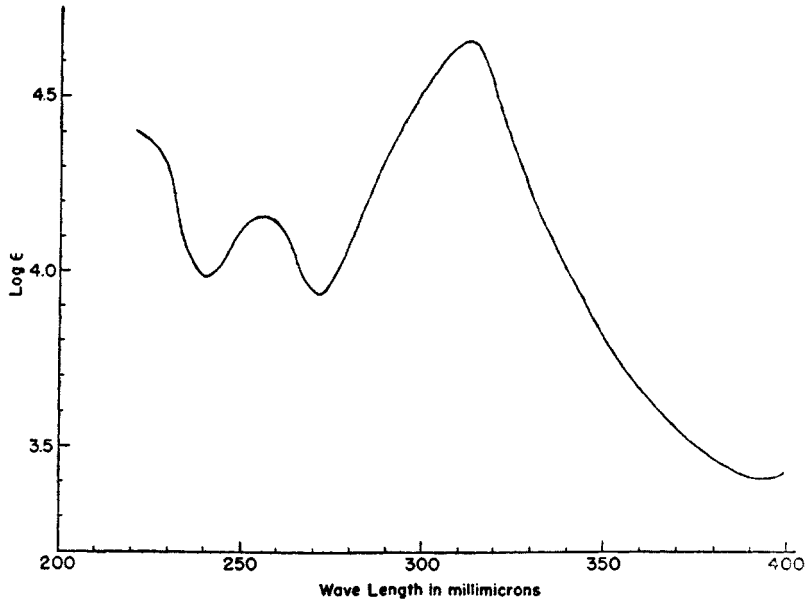

FIG. 3. ULTRAVIOLET ABSORPTION SPECTRUM OF HERQUEINONE IN DIOXANE.

Herqueinone is insoluble in alkali up to *p*H 11.5, but dissolves readily in dilute sodium hydroxide. When the *p*H of the sodium hydroxide solution is lowered, no precipitation occurs and material cannot be extracted into ether until the solution reaches about *p*H 4.9, at which point a yellow solid begins to separate. This yellow solid redissolves at about *p*H 8.5 if the *p*H is raised immediately.

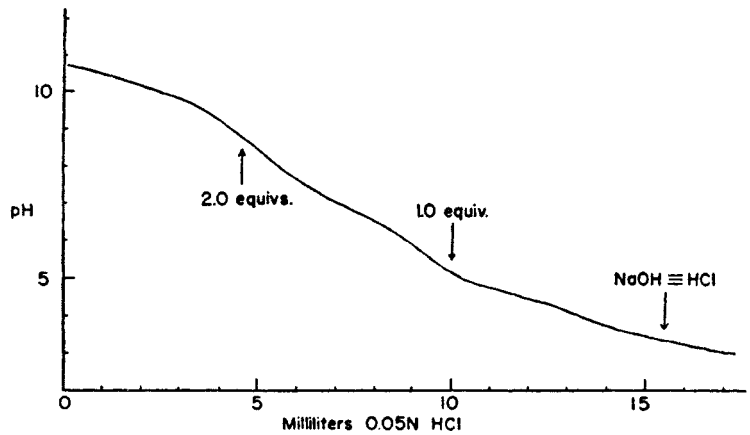

FIG. 4. BACK TITRATION OF HERQUEINONE IN ALKALINE SOLUTION. The deep red solution of 104 mg. (0.27 mole) of herqueinone in 15 ml. of 0.0510 *N* sodium hydroxide (3 equivs.) was titrated with 0.0495 *N* hydrochloric acid. The *p*H was followed with a Beckman *p*H meter. At about *p*H 4.9, a yellow solid began to precipitate and apparently interfered with the glass electrode; subsequent readings drifted badly. The yellow solid became red on standing, and 90 mg. of herqueinone was isolated.

When it is allowed to stand in contact with the acid solution, the yellow solid changes rapidly to herqueinone, identical in ultraviolet spectrum, melting point, and analysis with original samples. Attempts to separate rapidly the yellow solid and purify it by crystallization always yielded mixtures with herqueinone. Herqueinone was recovered quantitatively after the mixture had stood for 24 hours in 0.05 *N* aqueous sodium hydroxide solution, but after similar treatment in 0.1 *N* sodium hydroxide the recovery was only 65%. Back titration of an alkaline solution of herqueinone (Fig. 4) indicates presence of two acidic groups, one with a *p*K below 5, the other a much weaker acid.

The behavior of herqueinone in alkali is that of a lactone; however, the lack of absorption in the infrared at 5.5–6 μ is not consistent with such a structure. An alternate possible structure is that of a cyclic enol ether, and the behavior of herqueinone is similar to that reported by Hooker (8) and other authors (9) for compounds of the lapachone type. Furthermore, 2-hydroxy-1,4-naphthoquinones are comparable in acid strength to carboxylic acids; the *p*K of phthiocol (10) has been reported as 5.02.

Presence of the cyclic enol ether structure is further supported by the behavior of herqueinone on hydrogenation with platinum in ether or dioxane solution. Hydrogenation stops after consumption of about one mole of hydrogen, and the reaction product is an acid which contains one more terminal methyl group than does herqueinone and the same ratio of carbon to oxygen as herqueinone. This product, which is termed herqueinic acid, is rather unstable, but yields a stable methyl derivative on reaction with diazomethane. Ultraviolet spectra of herqueinic acid and methyl herqueinate are shown in Fig. 5. Titration of her-

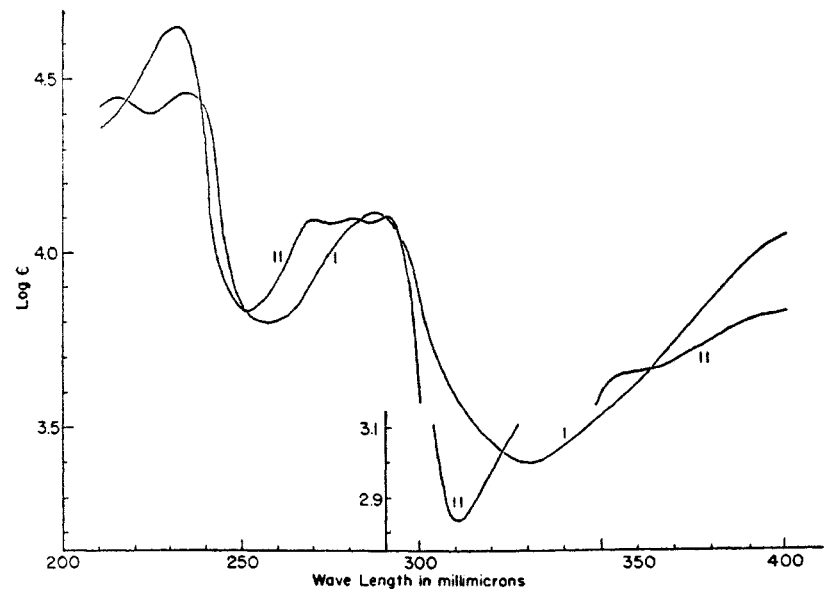

FIG. 5. ULTRAVIOLET ABSORPTION SPECTRA IN 95% ETHANOL. Curve I, Herqueinic acid; Curve II, Methyl herqueinate.

queinic acid (Fig. 6) shows it to be a considerably stronger acid than benzoic acid. Comparison of the titration curve with those of benzoic acid and *p*-hydroxybenzoic acid shows the presence in herqueinic acid of the phenolic group originally present in herqueinone. This phenolic group appears to be resistant to attack by diazomethane, for methyl herqueinate is soluble in cold dilute sodium hydroxide. Calculation of *p*K values from the curves in Fig. 6, determined in aqueous alcohol, gives for herqueinic acid 4.2, for benzoic acid 6.0, and for *p*-hydroxybenzoic acid 6.7. The alkaline solution of herqueinic acid is a deep olive-brown color; acidification precipitates the yellow herqueinic acid. The colored anion indicates some structure containing a highly mobile electron system rather than a simple carboxyl. Such behavior is characteristic of 2-hydroxy-3-alkyl-1,4-naphthoquinones; however, compounds of the lapachone type do not undergo ring-cleavage as the major reaction on hydrogenation (11).

Since considerable evidence, as cited above, is consistent with a naphthoquinone structure, various efforts have been made to secure a hydroquinone or derivatives thereof; however, presence of a quinone system has not been definitely established by these experiments. Hydrogenation with platinum in glacial acetic acid yields a nearly colorless solution which becomes colored red on exposure to air and is again decolorized by hydrogenation. Attempted isolation of the product of this reduction yielded only tarry materials. Only one of several methods examined for reductive acetylation yielded an isolable, reasonably homogeneous product, and this material is not the product of a simple reductive acetylation. The nature of the complex reaction has not yet been elucidated.

There is much evidence, in addition to the infrared spectrum, that the hydroxyl in herqueinone is highly hindered or chelated. All efforts to form an acyl derivative have been unsuccessful; even reaction with diazomethane is very slow, introduction of methoxyl being incomplete after three days' standing with excess of

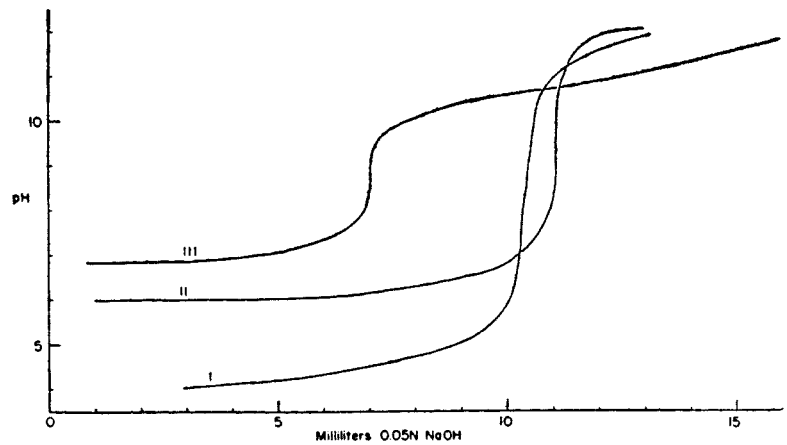

FIG. 6. POTENTIOMETRIC TITRATION CURVES IN AQUEOUS ETHANOL SOLUTION. Curve I, 214 mg. of herqueinic acid; Curve II, 68 mg. of benzoic acid; Curve III, 50 mg. of *p*-hydroxybenzoic acid. Each sample was dissolved in 10 ml. of neutral ethanol and titrated with aqueous base.

diazomethane. Insolubility of herqueinone at *p*H 11.5 has already been cited, as has resistance of the hydroxyl group in methyl herqueinate to methylation with diazomethane.

Solution of herqueinone in cold concentrated sulfuric acid, followed by dilution with water and immediate distillation, gives rapid azeotropic distillation of a carbonyl compound which shows a negative aldehyde test. The easy purification of the 2,4-dinitrophenylhydrazone and other derivatives indicates a single carbonyl component. Identification as methyl isopropyl ketone was accomplished by direct comparison of three derivatives. Since alkaline cleavage of herqueinone (see below) yields a mixture containing aldehyde(s), acidic material, and no methyl isopropyl ketone, it seems probable that the ketone arose from a pinacol rearrangement of 2-methyl-2,3-butanediol. Ease of hydrolysis and absence of absorption in the infrared at 5.5–6 μ contraindicate a carboxylic ester of this glycol. Behavior of herqueinone on hydrogenation is not consistent with presence of an open chain enol ether or ester. Present evidence suggests that the glycol is combined as a cyclic acetal.

Kuhn-Roth analysis of herqueinone for terminal methyl shows presence of two such groups, and methyl isopropyl ketone yields the same value; therefore absence of other structures containing terminal methyl may be assumed. Generation of an additional terminal methyl on hydrogenation has been described.

The non-volatile fragment from acid cleavage of herqueinone has proved intractible, and no assurance has been obtained that it is a homogeneous substance. It is an acid soluble in sodium bicarbonate to give a deeply colored solution similar to that from herqueinic acid. The formula of $C_{15}H_{12}O_7$, indicated by analysis, contains all the oxygen present in herqueinone and the carbon remaining after cleavage of the C_5-residue.

Acetyl determination on herqueinone, using acid cleavage, yielded no volatile acid; but the procedure involving initial alkaline cleavage gave volatile acid amounting to 70% of one mole of acid per mole of herqueinone. This behavior suggests cleavage of a dicarbonyl system, and such a system is further indicated by distillation of a mixture of carbonyl components from the alkaline solution. The yield of volatile carbonyl components was less in alkaline cleavage than in acid cleavage, no methyl isopropyl ketone could be detected, and a positive test for aldehydes was obtained. Various chromatographic techniques failed to yield a homogeneous substance which could be characterized, and this line of investigation has proved so unpromising that it has been abandoned for the present.

Various efforts to secure definite information concerning the basic skeletal structure of herqueinone have been unfruitful thus far. Under present investigation is a methoxy ketone, $C_{10}H_{12}O_3$, obtained by oxidation of herqueinone with alkaline hydrogen peroxide.

EXPERIMENTAL[3]

Isolation and purification of herqueinone. A 50–75 g. quantity of dried mycelium grown as described previously (1), was covered with pure peroxide-free ether and allowed to

[3] All melting points are corrected. Microanalyses are by the Microanalytical Division, Dept. of Chemistry, Univ. of Calif. Ultraviolet spectra were recorded on a Beckman Model

stand at room temperature for at least one day, with occasional agitation. The deep red ether solution was decanted and replaced with another portion. This process was repeated (a total of 3–5 extractions) until the extract remained nearly colorless. The total extract was filtered and then extracted three times with 75-ml. portions of half-saturated sodium bicarbonate solution. Acidification of the bicarbonate extracts yielded 0.2–0.4 g. of yellow-orange solid which has not been further investigated. The ether extract was washed with water, dried over magnesium sulfate, and evaporated to dryness. The residue weighed 3.5–5.0 g. and had a powerful musty odor. One crystallization from benzene-hexane yielded orange-red needles with a characteristic coppery sheen. Various samples melted with decomposition in the range 215–224°. Further recrystallization effects little improvement in quality, and some samples prepared in this way could not be hydrogenated with a platinum catalyst.

For final purification, chromatographic separation on Magnesol-Celite mixtures, as used by Wolfrom (12), proved satisfactory. Magnesol (Industrial Regular SFS 13) was washed with 1 *N* hydrochloric acid, ten times with water, finally with acetone, then dried and sieved. Material passing a 100-mesh screen was mixed with an equal weight of Celite 521, and chromatography was carried out under a pressure of about 25 inches of mercury, in a column with a height to diameter ratio of about 5. Herqueinone was applied to the column in benzene, and development was with 2.5% acetone in benzene. The chromatogram consisted of a narrow leading zone colored blue-green, a principal zone of bright orange, a dull orange zone moving slowly behind the main zone, and a dark brown band remaining near the top of the column. From 340 mg. of once-crystallized herqueinone, there was obtained from the main zone 255 mg. of product of m.p. 218–220° (dec.), from the tailings of the main zone 42 mg. of m.p. 222–225° (dec.), and from the trailing dull orange zone a few mg. of material of m.p. 224–226°. One crystallization from benzene-hexane of the combined herqueinone fractions yielded 240 mg. (71% of pigment applied to the column), m.p. 221–223° (dec.). The mother liquors yielded an additional 55 mg. of the same appearance as the first crop (coppery needles), m.p. 222–224° (dec.). Slightly impure samples frequently melted somewhat above the purest samples, but less pure samples (such as those not hydrogenated) melted below 220°. Analysis of the highly purified material was in good agreement with the values previously reported (1), except that high methoxyl values were not encountered.

Anal. Calc'd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41; Methoxyl, 8.34.
Found: C, 64.62; H, 5.55; Methoxyl, 8.02, 7.91.

Kuhn-Roth oxidation yielded acetic acid equivalent to 92% of that calculated for two moles per mole of herqueinone. Parallel determinations on methyl isopropyl ketone yielded 86% of that calculated for two moles per mole of ketone.

Acetyl determination (13) by direct acid hydrolysis yielded no volatile acid. When hydrolysis was carried out in 1 *N* sodium hydroxide prior to acidification and distillation of volatile acid, there was obtained volatile acid equivalent to 70% of that calculated for one mole of acid per mole of herqueinone. This acid has not been identified.

In chloroform solution, herqueinone did not show mutarotation during 12 hrs., $[\alpha]_D^{23}$ +345°. In 0.1 *N* sodium hydroxide the rotation was $[\alpha]_D^{23}$ +5.5° with no change during 12 hrs; darkening of the solution prevented readings over a longer period.

Herqueinone is quite insoluble in dilute acids, but is soluble in concentrated (12 *N*) hydrochloric acid; dilution after brief standing yields herqueinone.

Herqueinic acid. A sample of 500 mg. of herqueinone in 75 ml. of absolute ether was hydrogenated over 25 mg. of commercial platinum oxide catalyst at 3 atmospheres pressure. Hydrogen uptake, which ceased after 5 hrs., amounted to 120% of that calculated for one mole. The initially red-orange solution became clear yellow. A similar hydrogenation in pure dioxane gave consumption of 115% of one mole of hydrogen.

DU ultraviolet spectrophotometer, with concentrations adjusted to give optical density readings between 0.2 and 1.5. The infrared spectrum was recorded on a Baird instrument.

Removal of ether from the hydrogenated solution left an amber solid, which was converted to a yellow solid by washing with two small portions of ether. This material was suitable for methylation with diazomethane. The substance was rather unstable, and attempted crystallization usually lead to a poorer product; one sample successfully recrystallized twice from acetone-hexane gave reasonably satisfactory analytical figures. All samples melted with decomposition in the range 230–250°. The substance dissolved readily in dilute sodium bicarbonate solution, and acidification appeared to precipitate the original material, although criteria for comparison were poor.

Anal. Calc'd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.95; Equiv. wt., 374.

Found: C, 64.04, 64.17; H, 5.86, 6.10; Equiv. wt., 411.

Equivalent weight was calculated from the titration curve shown in Fig. 6.

An attempt to prepare a *p*-bromophenacyl ester of herqueinic acid was unsuccessful.

Methyl herqueinate. A 200-mg. sample (0.54 mmole) of ether-washed herqueinic acid in 75 ml. of ether at 0° was treated with a cold methylene chloride solution of 1.3 mmoles of diazomethane. After the mixture had stood in an ice-bath for 5 hours., solvents were removed to leave 212 mg. of a yellow crystalline residue melting at 176–180°, after softening at 160°. One crystallization from hexane yielded 150 mg. of yellow needles, m.p. 177–180° (s. 165°). Two additional crystallizations gave material of m.p. 179–180° (s. 175°).

Anal. Calc'd for $C_{21}H_{24}O_7$: C, 64.94; H, 6.20; Methoxyl, 15.98.

Found: C, 65.16; H, 6.19; Methoxyl, 15.20.

Kuhn-Roth analysis for terminal methyl gave acetic acid equivalent to 86% of that calculated for three moles per mole of herqueinone.

Methyl herqueinate is soluble in 0.1 *N* sodium hydroxide, but not in sodium bicarbonate. When the *p*H of the alkaline solution is reduced, turbidity appears at *p*H 10, and precipitation is complete by *p*H 8. The recovered material was identified by mixture m.p. as methyl herqueinate.

Solutions of methyl herqueinate exhibit a brilliant yellow-green fluorescence, especially in ultraviolet light.

Cleavage of herqueinone in acid. A 100-mg. sample of herqueinone was dissolved in 4 ml. of concentrated sulfuric acid. This solution was diluted dropwise with 12 ml. of water, then steam distilled immediately. Six 10-ml. fractions of distillate were collected in receivers cooled in solid carbon dioxide and acetone. None of the fractions contained acidic material, and only the first gave a positive test for carbonyl. Fuchsin test for aldehydes was negative.

To the first fraction of distillate was added a filtered solution of 60 mg. of 2,4-dinitrophenylhydrazine in 12 ml. of 1.5 *N* hydrochloric acid. There rapidly separated 40 mg. of yellow-orange solid, m.p. 113–120°. After two crystallizations from ethanol, there was obtained 31 mg. of the *2,4-dinitrophenylhydrazone*, m.p. 121–122°.

Anal. Calc'd for $C_{11}H_{14}N_4O_4$: C, 49.63; H, 5.30; N, 21.04.

Found: C, 49.51; H, 5.15; N, 20.52.

The 2,4-dinitrophenylhydrazone from a sample of methyl isopropyl ketone had m.p. 122–123°, mixture m.p. with the sample from herqueinone, 121–123°.

The distillate from the acid cleavage of 100 mg. of herqueinone yielded 25 mg. of the *p-nitrophenylhydrazone*, m.p. 97–103°. After two crystallizations from 50% ethanol, the m.p. was 106.2–107.0°. A sample of this derivative from a known sample of methyl isopropyl ketone had m.p. 106.3–107.2°, and the melting point of the mixture showed no depression. These compounds were not analyzed, for both had decomposed to tarry material after standing for 48 hrs.

From the distillate from acid cleavage of 125 mg. of herqueinone, there was secured 84 mg. of *2,4-dinitrophenylsemicarbazone* (14). After crystallization from benzene, the derivative had m.p. 218–219.5° (dec.). The same derivative prepared from a sample of methyl isopropyl ketone had m.p. 218.5–219.5° (dec.), mixture m.p. no depression.

Anal. Calc'd for $C_{12}H_{15}N_5O_5$: N, 22.64. Found: N, 22.52.

The clear yellow-orange solution left after acid cleavage of herqueinone and steam-distillation was treated while still hot with Norit, filtered, and poured on 50 g. of ice. The

crude ether-washed material decomposed in the range 230–250°, and all samples secured decomposed in this range. Heating of this material with alkali, followed by distillation from acid solution, gave only a trace of volatile acid; so the original herqueinone skeleton had been modified. Chromatography of this material on Magnesol led to decomposition, but crystallization was finally accomplished from 50% aqueous alcohol. After two crystallizations, the material was clear yellow but indistinctly crystalline. It dissolves readily in aqueous sodium bicarbonate to give a dark greenish-brown solution.

Anal. Calc'd for $C_{15}H_{12}O_7$: C, 59.08; H, 3.97; Methoxyl, 10.18.

Found: C, 58.83, 58.07; H, 4.64, 4.29; Methoxyl, 9.69.

Cleavage of herqueinone in alkali. A solution of 200 mg. of herqueinone in 25 ml. of 1 *N* sodium hydroxide was steam-distilled with a slow stream of nitrogen passing through the system. After 10 ml. of distillate had been collected (see below for investigation), the alkaline solution was acidified with 6 *N* sulfuric acid and steam-distillation was continued. Traces of acid, but no carbonyl compounds were found in each of six 10–15 ml. portions of distillate.

The first distillate from alkaline solution, which gave a positive fuchsin test for aldehydes, was treated with a filtered solution of 90 mg. of 2,4-dinitrophenylhydrazine in 22 ml. of 1.5 *N* hydrochloric acid. There precipitated 40 mg. of hydrazone, m.p. 130–138°. Chromatography on a 3 x 30 cm. column of silicic acid-Supercel, according to Roberts and Green (15), gave traces of material in three minor zones and a broad main zone yielding 35 mg. of m.p. 130–147°.

Crystallization of the main fraction from 3 ml. of ethanol gave a mixture of hair-like yellow needles and rectangular orange plates. Warming dissolved the yellow needles rapidly and left the orange plates. Recrystallization of the orange plates gave almost entirely the yellow needles, m.p. 145–150°; so the substance appears polymorphic.[4] For analysis, the combined material was crystallized from ethanol.

Anal. Calc'd for $C_8H_8N_4O_4$: C, 42.86; H, 3.59; N, 24.99.

Found: C, 43.40; H, 3.61; N, 24.70.

This analysis is in reasonably good agreement with that for acetaldehyde 2,4-dinitrophenylhydrazone,[4] as is the m.p.; and the derivatives from the natural product and a sample of acetaldehyde were not separated on a column of silicic acid-Supercel. However, the following experiments indicate that the volatile material from alkaline degradation is not acetaldehyde.

(a) The derivative from degradation could not be eluted from a Bentonite-Supercel column with 10% ether in hexane; whereas White (16) reports satisfactory elution of the acetaldehyde derivative under these conditions.

(b) A sample of acetaldehyde 2,4-dinitrophenylhydrazone, after chromatography on silicic acid-Supercel, had m.p. 146–147.5°.

(c) From another alkaline hydrolysis of herqueinone, there was obtained by chromatography on silicic acid-Supercel a hydrazone of m.p. 150–151.5°, which gave the analysis C, 44.26; H, 3.89.

(d) An additional chromatographic separation of 10 mg. of the material yielding the analysis agreeing with the acetaldehyde derivative gave two zones. The smaller zone gave material of m.p. 116–120° (large depression on admixture with the derivative of methyl isopropyl ketone), and the larger zone yielded 8 mg. of material of m.p. 145–146° (analysis C, 45.08; H, 3.79).

The 2,4-dinitrophenylhydrazone of γ-hydroxybutyraldehyde has been reported as melting at 104° (17), 120° (18), and 116° (19). There appears to be no mention of a di-hydrazine derivative of this hydroxyaldehyde. Investigation of alkaline cleavage of methyl herquei-

[4] Acetaldehyde 2,4-dinitrophenylhydrazone has been the subject of much discussion in the literature (20–22). Although the m.p. is usually reported as about 147°, and this form has always been obtained in this laboratory, there has also been reported (21) a form of m.p. 168°. A crystallographic study (22) seems to have established that the 2,4-dinitrophenylhydrazones of acetaldehyde, as well as several other aldehydes, are polymorphic.

nate appears preferable to further investigation of the mixture or intractable substance from herqueinone.

SUMMARY

The red pigment from *P. herquei*, termed herqueinone in the present work, has been investigated, and several structural features have been established or indicated.

1. A highly hindered or chelated phenolic hydroxyl is present.

2. There is present a carbonyl structure which absorbs beyond 6 μ in the infrared.

3. Hydrogenation in ether, with platinum catalyst, gives absorption of one mole of hydrogen with generation of a structure containing terminal methyl and an acidic group of acid strength comparable with that of salicylic acid.

4. There is probably present a cyclic ether of a highly acidic enol.

5. Although there is some evidence which suggests presence of a 2-hydroxy-1,4-naphthoquinone structure, no proof of such a structure has been secured.

6. Acid cleavage yields methyl isopropyl ketone. This probably arises from cleavage of a cyclic acetal of 2-methyl-2,3-butanediol.

7. Alkaline cleavage generates less than a mole of volatile acid and yields a mixture of volatile carbonyl components consisting in part, at least, of aldehyde(s). Methyl isopropyl ketone is absent.

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