

Experimental

The vitamin E fraction from soybean oil was obtained by distillation in a centrifugal molecular still and further concentrated by redistillation. The resulting fraction (42.1% tocopherol by Emmerie-Engel assay) was cooled successively at -35 and -70° in ethyl formate solution (10%) to remove sterols. The recovered oil (55% tocopherol) was purified by chromatography and converted to the palmitate in the manner previously described.³ The γ -tocopherol palmitate, after three crystallizations from acetone, melted at $44-45^{\circ}$. This is the same value previously reported.² The ester was saponified and the free tocopherol distilled in a small pot still at 0.15-0.2 mm. pressure. Its extinction coefficient ($E_{1\text{cm}}^{1\%}$ (298 $m\mu$)) = 94.5 and that of the palmitate ($E_{1\text{cm}}^{1\%}$ (286 $m\mu$)) = 40.0 were slightly higher than those previously reported.

The γ -tocopherol so prepared was assayed in the Biological Department of this Laboratory, using the technique previously described.³ Its potency was only one-hundredth that of *d*, α -tocopherol, supporting the aforementioned hypothesis that pure γ -tocopherol has negligible activity in curing resorptive sterility.

Recently the vitamin A sparing activity of a specimen of natural γ -tocopherol from cottonseed oil was found to be fully equal to that of α - and β -tocopherols.⁵ It appears unlikely that the sparing activity of the more highly purified preparation just described will be significantly different but the point is being investigated.

(5) Hickman, Kaley and Harris, *J. Biol. Chem.*, **152**, 327 (1944).

CONTRIBUTION NO. 70 FROM THE
LABORATORIES OF DISTILLATION PRODUCTS, INC.
755 RIDGE ROAD WEST
ROCHESTER 13, NEW YORK RECEIVED APRIL 12, 1945

NEW COMPOUNDS

2-Phenyl-4-(4-quinolal)-5-oxazolone and 2-Phenyl-4-(4-quinolal)-5-glyoxalidone

In 1904 Erlenmeyer, Jr.,¹ suggested the general nature of the reaction between hippuric acid and benzaldehyde and the production of a glyoxalidone on treatment of the condensation product with alcoholic ammonia. Quinoline-4-aldehyde hydrate and hippuric acid condense in an analogous manner to yield 2-phenyl-4-(4-quinolal)-oxazolone-5. On treatment with ammonium hydroxide, the oxazolone yields 2-phenyl-4-(4-quinolal)-glyoxalidone-5.

2-Phenyl-4-(4-quinolal)-oxazolone-5.—A mixture of 5 g. (0.029 mole) of quinoline-4-aldehyde hydrate, 2.6 g. (0.29 mole) of fused potassium acetate, and 5.15 g. (0.29 mole) of hippuric acid was ground in a mortar and transferred to an Erlenmeyer flask. Twelve grams (0.18 mole) of acetic anhydride was added and the mixture allowed to stand for one hour. The temperature rose slowly to 70° when solution became almost complete. The mixture was cooled to room temperature, chilled in ice and filtered. The small amount of tarry matter was removed by washing with acetone. The portion of the product which dissolved in the acetone was recovered by evaporation under reduced pressure and again washed with acetone; total yield, 6.8 g. The product was purified by washing with hot water, drying and crystallization from 25 cc. of *s*-amyl alcohol. The yield consisted of fine greenish yellow

needles, m. p. $171-172^{\circ}$. The compound is soluble in hot *n*-amyl and *s*-amyl alcohol, insoluble in dilute hydrochloric acid and dilute sodium hydroxide. It is slightly soluble in cold acetone, methyl alcohol and ethyl alcohol.

Anal. Calcd. for $C_{19}H_{15}O_3N_2$: C, 75.98; H, 4.03; N, 9.33; mol. wt., 300. Found: C, 75.56, 75.86; H, 4.26, 4.07; N, 9.25, 9.38; mol. wt., 308.

2-Phenyl-4-(quinolal)-glyoxalidone-5.—A 2-g. portion of the oxazolone was suspended in 20 cc. of 95% alcohol in a 100-cc. flask. The mixture was heated to boiling under a reflux and treated with 10 cc. of concd. ammonium hydroxide. When the yellow compound dissolved 1 g. of potassium carbonate dissolved in a little water was added and the heating continued for one hour. Small amounts of ammonium hydroxide were added from time to time. Ten cc. of 25% sodium hydroxide solution was added to the orange colored solution and the heating continued for one-half hour. The solution was cooled and made slightly acid with acetic acid. The yellow precipitate was filtered, washed with water, dried, and crystallized from *s*-amyl alcohol, washed with ether and dried; yield 1.6 g., m. p. $304-305^{\circ}$ (dec.).

Anal. Calcd. for $C_{19}H_{15}ON_3$: C, 76.24; H, 4.38; N, 14.04. Found: C, 76.07, 76.44; H, 4.01, 4.08; N, 14.20, 14.10. Melting point of picrate was $275-277^{\circ}$ (dec.).

The glyoxalidone treated with hydrochloric acid yielded a brilliant red compound, m. p. $308-309^{\circ}$ (dec.).

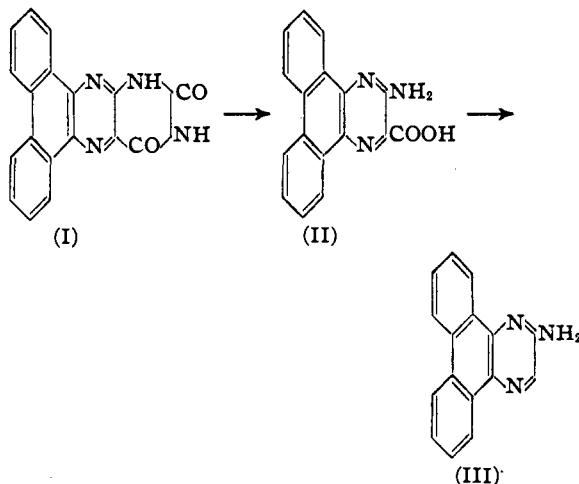
CHEMISTRY LABORATORY
UNIVERSITY OF COLORADO
BOULDER, COLORADO

DALE M. GRIFFIN
PAUL M. DEAN

RECEIVED APRIL 30, 1945

2-Amino-dibenzo[f,h]quinoxaline-3-carboxylic Acid, 2-Amino-dibenzo[f,h]quinoxaline and 2-Sulfanilamido-dibenzo[f,h]quinoxaline

By the hydrolysis of 9',10'-phenanthrolumazine, (dibenzo[f,h]pyrimido[4,5-b]quinoxaline-11,13(10,12)-dione)¹ (I), the amino acid, 2-amino-dibenzo[f,h]quinoxaline-3-carboxylic acid (II) was obtained which could be decarboxylated readily to 2-amino-dibenzo[f,h]quinoxaline (III). The parent substance, phenanthrapyrazine, has been reported by Mazon.²



2-Amino-dibenzo[f,h]quinoxaline-3-carboxylic Acid.—To a solution of 9 g. of sodium hydroxide in 75 cc. of water was added 9 g. of 9',10'-phenanthrolumazine, and the mixture was held in a steel bomb at $225-235^{\circ}$ for twenty hours. The reaction mixture was dissolved in 1000 cc. of boiling

(1) Kuhn and Cook, *Ber.*, **70**, 761 (1937).

(2) Mazon, *ibid.*, **19**, 112 (1886); *ibid.*, **20**, 268 (1887); *J. Chem. Soc.*, **55**, 97 (1889).

(1) Erlenmeyer, *Ann.*, **337**, 265 (1904).

water, the solution was treated with charcoal, filtered and acidulated with hydrochloric acid to a pH of 2. The bright-yellow precipitate was collected, washed with water and dried at 80°; yield 7.0 g., 85.3%; m. p. 219–221°. A sample was purified by dissolving in sodium bicarbonate solution and reprecipitating with hydrochloric acid; m. p. 220–222°.

Anal. Calcd. for $C_{17}H_{11}O_2N_3$: C, 70.57; H, 3.83. Found: C, 70.49; H, 3.97.

2-Amino-dibenzo[f,h]quinoxaline.—Eight grams of crude, melted 2-amino-dibenzo[f,h]quinoxaline-3-carboxylic acid was held at 250° until the frothing ceased. The mass was cooled, powdered, and extracted in a Soxhlet with acetone. The acetone was distilled and the residue triturated with ether; yield 4.28 g., 63.7%; m. p. 238–241°. A pure sample was prepared by agitating the crude with 10% sodium hydroxide and extracting with a mixture of two volumes of alcohol and eight volumes of ether, and concentrating the extracts *in vacuo* to a small volume, chilling, collecting the crystals, etc.; yield 85%, m. p. 249°.

Anal. Calcd. for $C_{16}H_{11}N_3$: C, 78.35; H, 4.51; N, 17.14. Found: C, 78.20; H, 4.62; N, 17.39.

2-Sulfanilamido-dibenzo[f,h]quinoxaline.—2-Amino-dibenzo[f,h]quinoxaline (4.7 g.) was condensed with acetyl-sulfanilyl chloride (5.3 g.) in anhydrous pyridine. The reaction product was isolated, deacetylated and purified in the usual manner; yield 4.54 g., 59%; m. p. 258–260°.

Anal. Calcd. for $C_{22}H_{16}N_4O_2S$: C, 65.97; H, 4.03; N, 14.00. Found: C, 66.22; H, 4.38; N, 13.79.

2-N⁴-Acetylsulfanilamido-dibenzo[f,h]quinoxaline.—This was obtained in a pure form by acetylating 2-sulfanilamido-dibenzo[f,h]quinoxaline with acetic anhydride; m. p. 265–267°.

Anal. Calcd. for $C_{23}H_{18}N_4O_3S$: C, 65.12; H, 4.12; N, 12.67. Found: C, 64.69; H, 4.38; N, 12.55.

THE RESEARCH LABORATORIES
MERCK & Co., INC.
RAHWAY, N. J.

JOHN WEIJLARD
MAX TISHLER

RECEIVED MARCH 24, 1945

COMMUNICATIONS TO THE EDITOR

PARAMAGNETISM OF THE PHOSPHORESCENT STATE

Sir:

Lewis and Kasha¹ have shown that the phosphorescent state is the triplet state. Hence the phosphorescent state must be paramagnetic. We have undertaken to measure this paramagnetism, using an apparatus similar to that of Theorell,² except that the two suspending filaments (extremely fine glass threads, 140 cm. long) and the horizontal suspended bar (of very thin-walled glass tubing) were all contained in a framework of 2-cm. glass tubing, which guarded against draughts, and also permitted the apparatus to be filled with any gas at any pressure. The capillary tip of the horizontal bar which held the phosphorescent sample, centered in the magnetic field, was observed in a microscope which read the position to about 2 μ . With a total suspended weight of 0.14 g., a horizontal displacement of 1 μ is produced by a force of 0.1 microgram.

When the long thin phosphor was centered in the magnetic field the light from a high pressure mercury arc was thrown from below upon one-half of the sample. With no field, illumination produced no observable deflection.

In the magnetic field, the illuminated part, because of the triplet state molecules, should move inward. In our first experiments, while a small movement in the expected direction was observed at the moment when the illumination began, this was followed almost immediately by a

much larger deflection in the reverse direction. This remarkable phenomenon, which we are studying further, was found only when the gas surrounding the sample contained oxygen. When the surrounding gas was argon or carbon dioxide only a movement in the expected direction occurred.

Our phosphors were of fluorescein dissolved in boric acid glass, and of such concentration and thickness as to absorb practically all of the incoming light. Hence the number of paramagnetic molecules formed per cm.² of illuminated sample should depend only upon the intensity of the light. We used two long thin rectangular samples: one, a solid slab of the boric acid solution, the other of similar material coarsely ground and attached to a ribbon of cellophane by a thin coating of rubber cement.

The magnetic force at 20,000 gauss, per cm. width, was 4.1×10^{-3} mg. for the first sample, and 4.7×10^{-3} mg. for the second, each being a mean of 10 and 20 experiments, respectively; but neither of the two means is accurate to much better than 10%. The illumination was through a filter of concentrated aqueous copper sulfate. Experiments with screens showed that the displacement is proportional to the intensity of this blue light.

Assuming the magnetic moment of triplet state fluorescein to be that of O_2 , and from the curve (Fig. 6) of Lewis, Lipkin and Magel,³ showing the percentage of phosphorescent molecules as a function of light intensity, our numerical results correspond to those calculated for 20% of their

(1) Lewis and Kasha, *This Journal*, **66**, 2100 (1944); **67**, 994 (1945).

(2) Theorell, *Arkiv. Kemi, Mineral. Geol.*, **16A**, No. 1 (1943).

(3) Lewis, Magel and Lipkin, *This Journal*, **62**, 2073 (1940).