Pyridine-2-sulfonic acid, trigonelline, 6-methyl-nicotinic acid, nipecotic acid, isonicotinic acid, β-acetylpyridine, β-picoline, and pyridine were completely devoid of growth-promoting activity. The following substances showed 3+ growth (comparable to veal infusion broth) in the dilutions indicated: nicotinic acid, nicotinamide, methyl nicotinate $M \times 10^{-7}$, trigonelline amide, ethyl nicotinate, nicotinuric acid, ethyl nicotino-acetate $M \times 10^{-6}$, nicotinic acid N-methyl amide $M \times 10^{-5}$, nicotinonitrile $M \times 10^{-4}$. Picolinic acid and quinolinic acid showed activity at a dilution of $M \times 10^{-4}$ but there is some possibility that these two preparations may be contaminated with traces of nicotinic acid. They are being synthesized by reactions which will exclude the possibility of any contamination and the results of tests of their growth-promoting activity will be reported later.

We are grateful to Dr. Frank M. Strong for samples of a number of compounds tested.

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DEPARTMENT OF BIOCHEMISTRY   ALBERT DORFMAN
AND DEPARTMENT OF BACTERIOLOGY   STEWART A. KOSER
AND PARASITOLOGY   FELIX SAUNDERS
UNIVERSITY OF CHICAGO
CHICAGO, ILL.
          RECEIVED JULY 15, 1938

THE CHEMILUMINESCENCE OF THE CHLORO-PHYLLS, AND OF SOME OTHER PORPHYRIN METAL COMPLEX SALTS

Sir:

Recently, Helberger [Naturwiss., 26, 316 (1938)] reported a case of chemiluminescence, found in experimenting with the complex magnesium salt of phthalocyanin, and of substances with related chemical structure.

It is of considerable interest to study the chemiluminescence of porphin and of meso tetrasubstituted porphins, which are now synthetically accessible [Rothemund, THIS JOURNAL, 57, 2010 (1935); 58, 625 (1936)], and of the chlorophylls, especially with regard to the problem of photosynthesis.

We found that upon adding pure chlorophyll a to tetrahydronaphthalene ("Tetralin"), heated to about 125°, the red chemiluminescence is just perceptible. The intensity of the phenomenon increases with increasing temperature, exhibiting a beautiful red glow between 160 and 190°, di-

minishes then, and disappears, when the solution is boiled for a few minutes. Addition of more chlorophyll a to the hot solution causes the chemiluminescence to reappear. Chlorophyll b shows the same behavior. The magnesium and the zinc complex salts of porphin as well as of α,β, γ,δ-tetraphenylporphin react in the same manner, and with the same color of luminescence. The free porphyrins, porphin, and $\alpha,\beta,\gamma,\delta$-tetraphenyl-porphin, or their hemins, copper, nickel, cobalt, or silver complex salts react negative. When one adds, however, magnesium filings to a solution of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin in tetralin, and allows the mixture to stand for some time, the chemiluminescence can be observed upon heating. No change of color or intensity of the glow takes place, if one bubbles oxygen or carbon dioxide through the hot solution. The following substances show the phenomenon, when used as solvents for porphyrin magnesium or zinc complex salts: tetrahydronaphthalene, xylene, p-cymene, and bromocyclohexane.

After the reaction, the solution differs spectroscopically from the unheated solution; the investigation of the reaction products from the above mentioned substances in the different solvents is in progress.

C. F. KETTERING FOUNDATION   PAUL ROTHEMUND
FOR THE STUDY OF CHLOROPHYLL
AND PHOTOSYNTHESIS
ANTIOCH COLLEGE
YELLOW SPRINGS, OHIO
          RECEIVED JULY 16, 1938

THE STRUCTURE OF THE INSULIN MOLECULE

Sir:

On the basis of the Cyclol hypothesis, a structure C_2 was proposed for the insulin molecule.[1] C_2 is a cage structure consisting of a fabric carrying side chains, bent over a truncated tetrahedral framework. The only metrical parameter, a (a mean between C-C and C-N bond lengths), taken as 1.5 Å., defines the dimensions of C_2. C_2 molecules with axes parallel fit the rhombohedral cell of the insulin lattice given by an x-ray analysis. They can be arranged with any orientation α in the corresponding hexagonal cell, and α was necessarily left undetermined.[1] Further data, namely, Patterson–Harker diagrams, have now become available.[2]

It has been stated that these diagrams are in-

(1) Wrinch, Trans. Faraday Soc., 33, 1368 (1937).
(2) Crowfoot, Proc. Roy. Soc., (London) 164A, 580 (1938).

compatible with the structure I proposed for insulin.[2] I have therefore made a study of the Patterson–Harker diagrams given by C_2. The skeleton of C_2 is a truncated tetrahedron with six slits whose centers give an octahedron of side $l = 8\sqrt{6}a$. All the vectors between points on its framework lie on or within a truncated octahedron of side $2l = 16\sqrt{6}a = 33.9$ Å. Postulating concentrations of atoms near these six octahedral points of the C_2 we obtain Patterson–Harker peaks for a molecule at O which lie at the corners and midpoints of the sides of the octahedron $2l$ with center at O. The figure shows the projection on the c-plane of these 18 peaks giving a hexagon with center at O, with side length 33.9 Å. There
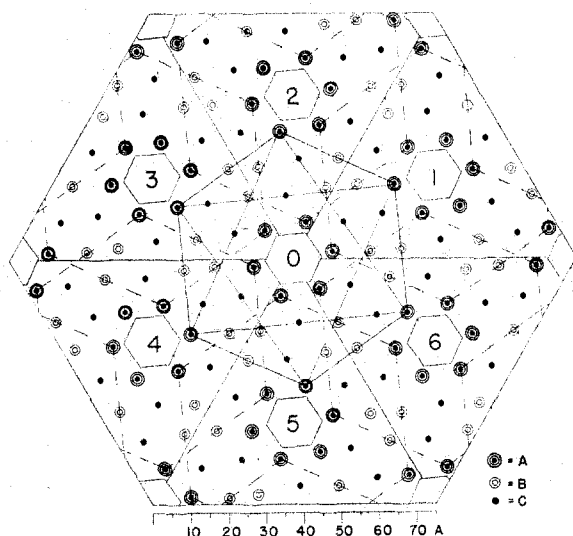

Fig. 1.—The c-plane projection of the Patterson–Harker map of the six slits of the C_2 molecule, superposed upon the corresponding projection obtained from the X-ray analysis of insulin.

are six at its corners, six at the midpoints of its sides, and six at the midpoints of lines joining alternate corners, indicated for convenience as A, B, and C, respectively.

We now notice that Crowfoot's c-plane projection also gives 18 peaks per molecule, reproduced in Fig. 1, which fall into a pleasing pattern of hexad, triad, and dyad sets. Superposing the C_2 hexagon on this diagram, we turn this hexagon about its center, through an increasing angle α until any of its points fall upon a Crowfoot peak. We find with $\alpha = 6°$ that all A peaks fit on A peaks, B peaks on B peaks, and C peaks on C peaks, as shown in Fig. 1.

This procedure allocates to the molecule at O, one A peak in each of the hexad sets surrounding the points 1, 2, 3, 4, 5, 6; the most remote B peak of each neighboring triad set; the nearer C peak of each neighboring dyad set. Drawing corresponding hexagons around other molecules, all the A, B, and C peaks are filled in. The six nearest A and B peaks around O are contributed, one each, by the molecules associated with the positions 1, 2, 3, 4, 5, 6, and none of them by the molecule at O.

So far the details of the skeleton and the positions of the side chains attached to the C_2 molecule have been left out of account. Nevertheless, the 18 peaks per molecule in Crowfoot's c-plane projection are given in the correct positions, on the assumption that there are concentrations of atoms at the six slits.

The full investigations will shortly be published.

LONG ISLAND BIOLOGICAL STATION D. M. WRINCH
COLD SPRING HARBOR, LONG ISLAND
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