

Pyridine-2-sulfonic acid, trigonelline, 6-methylnicotinic 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 nicotinoacetate $M \times 10^{-6}$, 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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RECEIVED JULY 15, 1938

THE CHEMILUMINESCENCE OF THE CHLOROPHYLLS, 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 $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin react in the same manner, and with the same color of luminescence. The free porphyrins, porphin, and $\alpha, \beta, \gamma, \delta$ -tetraphenylporphin, 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.

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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).