A. R. Anderson[2]; maximum energy deposition extended to 7×10^{22} e.v. per g. of solution. The main products were nitrite, oxygen and hydrogen: a low yield of nitrogen was observed from concentrated solution. The 100 e.v. yield of nitrogen (G_{N_2}) from a 9.4 M solution was $(3.2 \pm 0.6) \times 10^{-3}$.

Particular attention was paid to variation of hydrogen yield with $[NO_3^-]$. Calculation of G_{H_2} in the more concentrated solutions is complicated by absorption of energy by nitrate ion, but the complication is not serious for our purposes. For example, in the worst case (15.9 M solution), assuming that all fast neutron-γ energy deposited in solution is available for water decomposition, $G_{H_2} = 0.011 \pm 0.001$. Assuming that only the energy deposited directly in the water is available, $G_{H_2} = 0.025 \pm 0.003$. A value of 0.019 ± 0.009 embraces both these extremes. At concentrations below 1 M, difference between the two G values is less than experimental error. The figure shows a

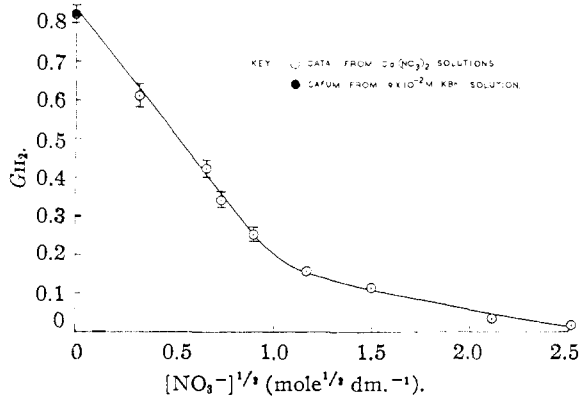

Fig. 1.—Variation of G_{H_2} with $[NO_3^-]^{1/2}$.

plot of G_{H_2} *vs.* $[NO_3^-]^{1/2}$. Linearity is evident up to $[NO_3^-]$ of about 1 M; the data over this region follow an equation of the type

$$G_{H_2} = A - k[NO_3^-]^{1/2} \qquad (1)$$

Sworski[3,4] observed this relationship to hold for variation of $G_{H_2O_2}$ with $[Br^-]$ and $[Cl^-]$. Allen and Holroyd[5] confirmed and extended the Br^- data. The data of Schwarz[6] concerning the effect of $[Cu^{++}]$ and $[NO_2^-]$ on G_{H_2} can be expressed by equation (1). The table shows values of A and k for the various solute ions M; solutions are approximately neutral unless otherwise indicated.

M =	NO_3^-	Br^-	Br^- (pH 2)	Cl^- (pH 2)	NO_2^-	Cu^{++}
A =	0.84	0.68	0.78	0.75	0.44	0.44
k =	0.65	0.65	0.93	0.88	0.30	0.60

The significance of the "one-third power" relationship has been discussed qualitatively by Sworski.[3] The parameter k affords a measure of the probability that the ion in question will react with the appropriate radical (H or OH) as it diffuses out of a "hot spot." The similarity between values of k for various ions is noteworthy. Parameter A measures the hypothetical molecular yield at zero concentration. It is different for H_2 and H_2O_2, and for various types of ionizing radiation.[7] A was measured in the present case using a 1.9×10^{-2} M KBr solution, in which the radical back reaction is adequately suppressed.[8] The value of 0.82 ± 0.02 is in good agreement with the intercept at zero $[NO_3^-]$ in the figure.

The present results may be interpreted in terms of "capture" of H atoms by NO_3^-

$$NO_3^- + H \longrightarrow NO_2 + OH^- \qquad (2)$$

From the data it may be deduced that when the "average distance" between nitrate ions is 20 Å., about half of the H atoms available for H_2 production are consumed by reaction (1). Above a concentration of 1 M (when the "average distance" between ions is about 11 Å.), G_{H_2} decreases less rapidly as $[NO_3^-]$ is increased. In 15.9 M solution (melted crystals of $Ca(NO_3)_2 \cdot 4H_2O$) more than 97% of available H atoms are intercepted.

A complete account of the work, with due acknowledgments, will be published later.

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ATOMIC ENERGY RESEARCH ESTABLISHMENT
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BERKS, ENGLAND

RECEIVED JANUARY 15, 1957

A NEW POLYMERIC SULFUR-NITROGEN COMPOUND

Sir:

It has long been known that the reaction of sulfur chloride with ammonia gives sulfur nitride.[1-2] This substance, a cyclic tetramer, has the structure of an eight-membered ring composed of alternating sulfur and nitrogen atoms,[3] with four resonating double bonds. It may be reduced to the saturated analog, $H_4S_4N_4$.[4] It has been reported that the action of sulfur dichloride on ethylamine produces the corresponding N-ethyl derivative $(SNC_2H_5)_4$,[5] while other authors have found that *n*-butylamine and sulfur tetrachloride give C_4H_9-N=S=N-C_4H_9.[6] We have found that when methylamine is allowed to react with a hexane solution of sulfur dichloride, a low-molecular-weight plastic polymer having the approximate composition $(CH_3NS)_x$ is formed. Additional products are methylamine hydrochloride and an unidentified unstable yellow oil which is presumed to contain the cyclic tetramer. The polymer has been prepared in varying molecular weights, depending on how closely the relative amounts of the two reagents were controlled; *i.e.*, exact control leads to high molecular weights. In its lowest molecular weight form (*ca.* 600 as measured cryoscopically), the polymer

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may be pulled slowly into strings, but it shatters on being struck. Higher molecular weight material is more brittle.

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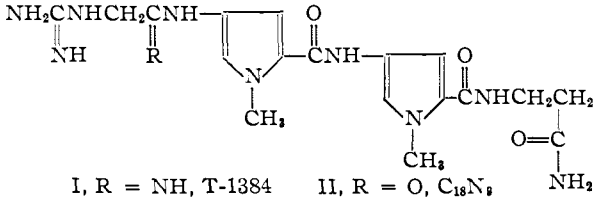
DAYTON, OHIO

RECEIVED JANUARY 7, 1957

THE STRUCTURE OF ANTIBIOTIC T-1384

Sir:

An antibiotic, designated T-1384 was isolated from an Actinomycetes type of organism by the Fermentation Biochemistry Department of these Laboratories.[1] This compound is identical with the antibiotic Netropsin,[2] $C_{32}H_{48}N_{18}O_4$.[3] Our data required the assignment of $C_{18}H_{26}N_{10}O_3$ for the empirical formula of T-1384. Subsequently, the latter empirical formula was reported for Netropsin,[4] sinanomycin,[5] and congocidine.[6] Reported herein are the data which indicate that T-1384 has structure I, β-[4-(4-guanidinoacetamidino-1-methyl-2-pyrrolecarboxamido)-1-methyl-2-pyrrolecarboxamido]-propionamide.



I, R = NH, T-1384 II, R = O, $C_{18}N_9$

Mild alkaline hydrolysis of T-1384 gave the compounds $C_{15}H_{20}N_6O_3$, $C_3H_5N_3O$ and ammonia. The C_3 compound was identified as glycocyamidine by comparison with a known sample. Apparently the same $C_{15}H_{20}N_6O_3$ compound was obtained by hydrolysis of Netropsin,[3,4] and congocidine.[6] We have now established the structure of this compound as β-[4-(4-amino-1-methyl-2-pyrrolecarboxamido)-1-methyl-2-pyrrolecarboxamido]-propionamide.

Alkaline hydrolysis (0.5 *N* NaOH) of the above C_{15} amide gave ammonia and the corresponding C_{15} acid hemihydrate, m.p. 190–105° dec., λ_{max}. 0.1 *N* HCl: 285 mμ, ε = 20,300. *Anal.* C, 52.84; H, 5.70; N, 20.11; N-CH_3, 8.31; H_2O, 2.43; neut. eq., 379, 323. The C_{15} acid and C_{15} amide both gave a positive Bratton–Marshall test[7] for an aromatic amine while their N-acetyl derivatives gave negative tests. The ultraviolet absorption spectra of these N-acetyl derivatives and T-1384 (λ_{max} 0.1 *N* HCl, 234 mμ, ε = 19,400, 300 mμ, ε = 22,400) were comparable indicating the presence of the same chromophoric system in these compounds.

Hydrolysis of the C_{15} acid with 5 *N* sodium or barium hydroxide gave about *1.5 moles* of a C_6-$H_8N_2O_2$ compound, isolated as the $^1/_2$ H_2SO_4 salt, 187–202° dec. *Anal.* C, 37.79; H, 4.79; N, 14.54; S, 8.24; N-CH_3, 4.54; neut. eq., 99.8; λ_{max}. 0.1 *N* HCl: 260 mμ, ε = 9,800. The N-acetyl derivative of the C_6 compound (m.p. 200° dec. λmax. 0.1 *N* HCl: 232 mμ, ε = 13,200; 280 mμ, ε = 7,100) gave on heating 1 mole of carbon dioxide and an N-acetyl compound, $C_7H_{10}N_2O$, m.p. 119–120°. *Anal.* C, 60.36; H, 7.30; N, 19.82; N-CH_3, 7.85; N-acetyl, 31.32.

The presence of an N-methyl group, which had been indicated by our analysis of T-1384, was confirmed by the isolation and characterization of methylamine following the oxidation of the C_6 compound with acidic peroxide. The similarity of the ultraviolet absorption spectrum of the N-acetyl C_5 compound to N-ethylpyrrole,[8] the empirical formula, a positive Ehrlich test, and a positive Bratton–Marshall test[7] after hydrolysis suggested that the C_5 fragment was 3-amino-1-methylpyrrole.

The ease with which the C_6 compound was decarboxylated suggested an α-carboxyl group. Comparison of the C_6 fragment with a synthetic sample of 4 amino-1-methyl-2-pyrrolecarboxylic acid[9] showed them to be identical.

From the filtrates of the C_6 preparation was isolated β-alanine as its 2,4-dinitrophenyl derivative, m.p. 144–146°. *Anal.* C, 42.52; H, 3.69; N, 16.32. This derivative was identified by comparison with an authentic synthetic sample.

Hydrolysis data on the C_{15} acid had shown it to contain two moles of 4-amino-1-methyl-2-pyrrolecarboxylic acid and one mole of β-alanine. Since the C_{15} acid could not be decarboxylated readily and since it gave a positive test for an aromatic amine, the order of its fragments were postulated to be C_6—C_6—β-alanine. This order was also suggested by the ultraviolet absorption data. The structures of the C_{15} acid and amide were established to be β-[4-(4-amino-1-methyl-2-pyrrolecarboxamido)-1-methyl-2-pyrrolecarboxamido]-propionic acid and the corresponding propionamide by comparison with synthetic samples.[9]

When T-1384 sulfate was treated with one equivalent of barium hydroxide at room temperature for 3 hours, there was produced ammonia and a new compound $C_{18}H_{25}N_9O_4 \cdot {}^1/_2H_2SO_4 \cdot {}^1/_2H_2O$, m.p. 200° dec. *Anal.* C, 43.88; H, 5.77; N, 25.12; S, 3.38. λ max. 0.1 *N* HCl: 234 mμ, ε = 19,600; 299 mμ, ε = 21,500. From spectral and hydrolytic data this $C_{18}N_9$ compound is postulated to be the N-guanidinoacetyl derivative of the C_{15} amide, β-[4-(4-guanidinoacetamido-1-methyl-2-pyrrolecarboxamido)-1-methyl-2-pyrrolecarboxamido]-propionamide, structure II. A comparison of the $C_{18}N_9$ compound with a synthetic sample[9] of II confirmed its structure.

All features of the structure of T-1384 now have been established except the position and nature of the group giving rise to ammonia upon very mild hydrolysis. Potentiometric titration of T-1384

(1) S. De Voe, C. Ervin and N. Bohonos, unpublished data.

(2) Netropsin is the Trademark of Chas. Pfizer and Co. We wish to thank Dr. A. C. Finlay of Chas. Pfizer and Co. for a sample of Netropsin which was shown to be identical with T-1384 by chromatography and by spectral comparisons.

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