alous effects which will be reported in detail at a later date.

DEPARTMENT OF CHEMISTRY
STEVENS INST. OF TECHNOLOGY L. S. LEVITT
HOBOKEN, N. J. E. R. MALINOWSKI

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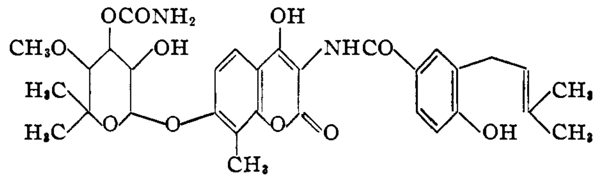
NOVOBIOCIN.[1] III. THE STRUCTURE OF NOVOBIOCIN

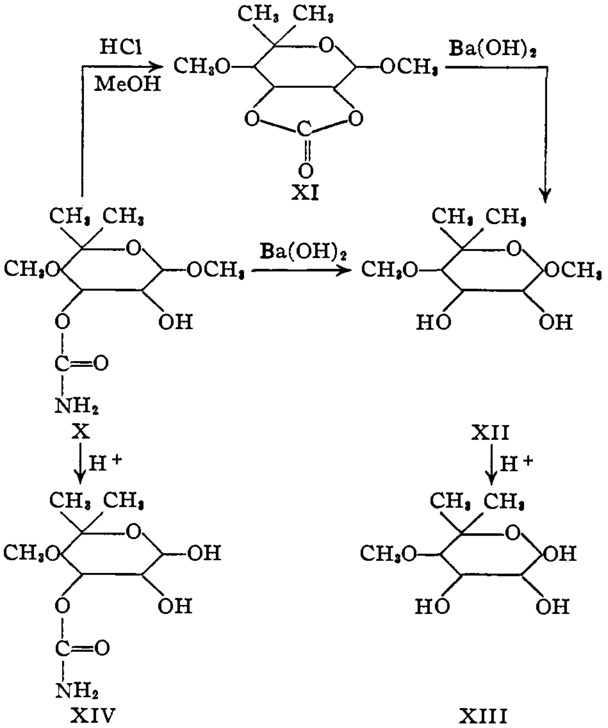
Sir:

A partial structure of the antibiotic novobiocin was proposed in the previous communication[2] in this series. The present studies deal with the structure of the sugar moiety, noviose (XII). The following results, considered with the previous findings,[2-3] permit the assignment of structure I to novobiocin.



I

The structural relationships between the methyl glycoside (X), the carbonate ester (XI), and the dihydroxy compound (XII) of the previous communication[2] are



Reaction of X with aqueous barium hydroxide at room temperature gives XII (m.p. 65–70°) in 96% yield with evolution of ammonia, and precipitation of the theoretical amount of barium carbonate (*Anal.* for XII. Calcd. for $C_9H_{18}O_5$: C, 52.41; H, 8.80; OCH_3, 30.1; C-CH_3, 14.5. Found: C, 52.67; H, 8.88; OCH_3, 26.8; C-CH_3, 2.17). Chromic acid oxidation of XII gives acetone, isolated in 46% yield as the dinitrophenylhydrazone. This confirms the presence of *gem*-dimethyl groups indicated previously[2] by infrared absorption and low C-CH_3 analyses. Compound XII, Benedict-negative, consumes one mole of periodate rapidly with the formation of a dialdehyde, which upon warming with an acid ethanol solution of 2,4-dinitrophenylhydrazine yields the dinitrophenylosazone of glyoxal in quantitative amounts and a partially characterized canary-yellow derivative, m.p. 105–106° (*Anal.* found: C, 46.66; H, 4.79). Oxidation of the dialdehyde with bromine in the presence of strontium carbonate gives a 77% yield of the expected optically active strontium salt (Calcd. for $C_9H_{14}O_7Sr \cdot 1.5H_2O$: C, 31.00; H, 4.91; OCH_3, 17.39; Sr, 25.12. Found: C, 31.18; H, 5.07; OCH_3, 19.65; Sr, 25.68).

Hydrolysis of XII in 0.5 *N* sulfuric acid at 80° for 30–45 minutes removes the glycosidic methyl group to form Benedict-positive noviose (XIII), m.p. 128–130° (Calcd. for $C_8H_{16}O_5$: C, 49.99; H, 8.39; OCH_3, 16.15; C-CH_3, 15.6. Found: C, 49.71; H, 8.50; OCH_3, 16.23; C-CH_3, 1.88). Noviose (XIII) consumes two moles of periodate with the formation of two moles of formic acid which was isolated and identified as the strontium salt. These findings establish the structures XI, XII and XIII.

Hydrolysis of X with 0.5 *N* sulfuric acid at 80° for *ca.* one hour removes the glycosidic methyl group without appreciable hydrolysis of the carbamate to give 3-(O)-carbamylnoviose (XIV), m.p. 124–126° (Calcd. for $C_9H_{17}NO_6$: C, 45.95; H, 7.29; N, 5.96. Found: C, 45.95; H, 7.66; N, 5.92). The purity of XIV was established by a 340-transfer countercurrent distribution analysis using 1-butanol and water as the solvent system. While pure X does not react with periodate according to the Fleury and Lange procedure,[4] XIV consumes one mole within 30 minutes with the formation of one mole of formic acid. Excluding the possibility of carbamate migration, which appears unlikely in view of the excellent yields and clean-cut periodate results, the carbamate is assigned to carbon no. 3 of XIV. This permits the identification of novobiocin as 7-[4-(carbamoyloxy)-tetrahydro-3-hydroxy-5-methoxy-6,6-dimethylpyran-2-yloxy]-4-hydroxy-3-[4-hydroxy-3-(3-methyl-2-butenyl)-benzamido]-8-methylcoumarin[5] (I).

Although carbamate occurrence in nature appears to be rare, recent studies indicate the role of the carbamyl group in the biochemical synthesis of citrulline from ornithine.[6,7] The isolation of O-carbamyl-D-serine from the culture medium of a new *Streptomyces* species has been reported.[8]

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[1] The Upjohn Company Registered Trade Mark for novobiocin is Albamycin.

[2] J. W. Hinman, H. Hoeksema, E. L. Caron and W. G. Jackson, THIS JOURNAL, **78**, 1072 (1956).

[3] H. Hoeksema, J. L. Johnson and J. W. Hinman, *ibid.*, **77**, 6710 (1955).

[4] P. F. Fleury and J. Lange, *J. Pharm. Chim.*, **17**, 107, 196 (1933).

[5] We are indebted to W. Russell Stemen, Associate Editor of Chemical Abstracts, for this name.

[6] S. Grisolia and P. P. Cohen, *J. Biol. Chem.*, **198**, 561 (1952); **204**, 753 (1953).

[7] M. E. Jones, L. Spector and F. Lipmann, *Fed. Proc.*, **14**, 232 (1955).

[8] G. Hagemann, L. Pénasse and J. Teillon, *Biochim. et Biophys. Acta*, **17**, 240 (1955).

Novobiocin appears to be the first recorded example of the natural occurrence of a carbamate ester of a sugar derivative.

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RESEACH LABORATORIES
THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

HERMAN HOEKSEMA
E. LOUIS CARON
JACK W. HINMAN

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THE COMBUSTION OF CARBON SUBNITRIDE, C_4N_2, AND A CHEMICAL METHOD FOR THE PRODUCTION OF CONTINUOUS TEMPERATURES IN THE RANGE OF 5000–6000°K.[1]

Sir:

A flame temperature of slightly over 5000°K. was reached by combusting cyanogen with oxygen under pressure.[2] The high temperature is due to the high endothermic heat of formation of cyanogen (−73.60 kcal./mole gas at 25°) and the great thermal stability of the combustion products, *i.e.*, CO and N_2.

It was obvious that if a compound existed with a still higher endothermic heat of formation than cyanogen, which also could be combusted to CO and N_2, higher flame temperatures could be attained. A whole series of such compounds exist. They are the dinitriles of acetylene-dicarboxylic and polyacetylene-dicarboxylic acids or dicyanoacetylene and dicyano-polyacetylenes. Their general structural formula is $N \vdots C \cdot (C \vdots C)_n \cdot C \vdots N$.

The first member of the series ($n = 1$) or C_4N_2 was isolated by Charles Moureu and Jacques C. Bongrand[3] and named carbon subnitride.

C_4N_2 is a water-white liquid with a b.p. 76.5°, m.p. 20.5° and d^{25}_4 0.9703. It has a high endothermic heat of formation, −149.81 kcal./mole gas at 25°, and can explode to carbon powder and nitrogen. The subsequent members have not been described in the literature, but the dicarboxylic acids, from which they are derived, have been known since A. v. Bayer's[4] classical researches.

A still higher temperature can be obtained by combining an endothermic fuel with an endothermic oxidizer; in the above case the obvious substitute would be ozone for O_2. Dr. A. Streng recently succeeded in measuring flame velocities of pure O_3–O_2 mixtures in the range of 17–55 mole% O_3 and successfully burned such mixtures with H_2, CO and $(CN)_2$.

Since the calculated temperature of the $(CN)_2$–O_2 flame has been checked experimentally,[5] the enthalpy data for CO and N_2 can be used with confidence to calculate[6] the temperatures of C_4N_2 + O_2 and $+O_3$ flames at various pressures. They are as follows, in °K. (± 2°), for the reaction mixture specified:

	Temperature °K.		
Atm.	1.0	10	40.82 (= 600 psia)
$(C_4N_2)_g + 2O_2 \longrightarrow 4CO + N_2$;			
$\Delta H_{298°} = +254.6$	5261	5573	5748
$(C_4N_2)_g + 4/3\ O_3 \longrightarrow 4CO + N_2$;			
$\Delta H_{298°} = +299.9$	5516	5936	6100

Temperature decrease due to ionization of the combustion products can be neglected completely even at 6000°K.

C_4N_2 was burned with oxygen in both a diffusion and premixed flame in the range of $2O_2$–$4O_2$ per mole C_4N_2. The nitride burns with a bright white-blue flame similar in many respects, but *not* identical, to the $(CN)_2$–O_2 flame. The $C_4N_2 + 2O_2$ flame burns to only CO and N_2 and has a calculated temperature, as outlined previously, of 5260°K. An oxygen-rich flame, of the composition $C_4N_2 + 2.40\ O_2$ produced, in addition to CO, CO_2 and N_2, the nitrogen oxides, NO_2, N_2O_3 and mainly NO; calculated as NO, their amount equalled 0.6–0.9 mole% of the combustion products.[7]

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1475.

(2) J. B. Conway, W. F. R. Smith, W. J. Liddell and A. V. Grosse, THIS JOURNAL, **77**, 2026 (1955).

(3) C. Moureu and J. C. Bongrand, *Bull. soc. chim.*, [**V**], 846 (1909); *Ann. Chim.*, **14**, 5 (1920).

(4) A. v. Bayer, *Ber.*, **18**, 678, 1885, 2269 (1885).

(5) J. B. Conway, R. H. Wilson, Jr., and A. V. Grosse, THIS JOURNAL **75**, 499 (1953).

(6) Acknowledgment is due to Drs. Rapp and Irgon of Reaction Motors, Inc., for their accurate calculations. N.A.C.A. tables were used up to 6000°K.; above 6000°K. the data were extrapolated.

(7) Our experimental combustion and analytical techniques and results are fully described in Technical Note No. 1 (A. V. Grosse and A. D. Kirshenbaum) Report Control No. AFOSR-TN-56-13. Contract No. AF 18(600)-1475, Project No. 7-7968, dated December 15, 1955. U. S. Air Force, Office of Scientific Research, Air Research & Development Command, P. O. Box 1395, Baltimore 3, Md.

THE RESEARCH INSTITUTE OF
TEMPLE UNIVERSITY
PHILADELPHIA 44, PA.

A. D. KIRSHENBAUM
A. V. GROSSE

RECEIVED FEBRUARY 27, 1956

A NEW ATP-FORMING REACTION: THE REDUCTIVE DEAMINATION OF GLYCINE

Sir:

Extracts of the amino acid-fermenting organism, *Clostridium sticklandii* (strain HF), catalyze the formation of acetic acid and ammonia from glycine when 1,3-dithiolpropanol (DTP) is added as the reducing agent.[1] Decomposition of glycine-2-C^{14} in this system results in the formation of acetic acid labelled exclusively in the methylene carbon atom.[2] Aged preparations derived from extracts of alumina-ground dried cells exhibit dependencies on DPN and Mg^{++} (Table I). There also appears to be a requirement for pyridoxal phosphate, particularly in the absence of added DPN, but this is somewhat variable. When more highly purified enzymes prepared from sonic extracts are employed, there is almost complete dependency on orthophosphate and an adenylate nucleotide (Table II). Since AMP, ADP and ATP are equally efficient in promoting the reaction, the preparation undoubtedly contains an adenylate kinase. Arsenate substitutes for phosphate and eliminates the need for an acceptor nucleotide.

The stoichometry of the over-all process as determined by direct analysis of the reaction products

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(1) T. C. Stadtman, *3rd Int. Congr. Biochem.*, Bruxelles, p. 53 (1955).

(2) C^{14}-acetate was recovered by steam distillation, checked for purity by Duclaux distillation and degraded using the Schmidt reaction according to E. F. Phares, *Arch. Biochem. and Biophys.*, **33**, 173 (1951).