sterically more compact CN groups of $CH_2(CN)_2$ lead to a deviation of only 1.5 powers of ten greater rate, according to equation (2), than that observed. The results listed in Table I also suggest that saturation of resonance stabilization in the ionization state contributes to the failure of equation (2) since the deviations increase with increasing values of $\Sigma\sigma_R^-$.[5]

(5) The logarithms of the ionization constants of substituted methanes (reference 4) also appear to follow equation (2) with $\rho_R \cong 30$, $\rho_I \cong 7$, and log $K_a$ of methane $\cong -40$. However, the ionization constants for $CH_3SO_2CH_3$ and $CH_3CN$ are so crude that the quantitative significance of the relationship is uncertain. Two points are worthy of comment. Nitromethane deviates (greater acidity) by about six log units, which is the same magnitude as the deviation of this compound from the norm in a plot of log $k_1$ *vs.* log $K_a$ (*cf.* Fig. 1, reference 4). Thus the deviation apparently can be attributed to the abnormally slow recombination rate of "nitrocarbanion" with hydrogen ion. On the other hand, the relationship is followed reasonably well by both $CH_2(CN)_2$ and $CH(CN)_3$. $(CH_3CO)_2CH_2$ and $(CH_3CO)_3CH$ deviate substantially (weaker acids) in the direction expected for steric inhibition of resonance in the carbanion ion.

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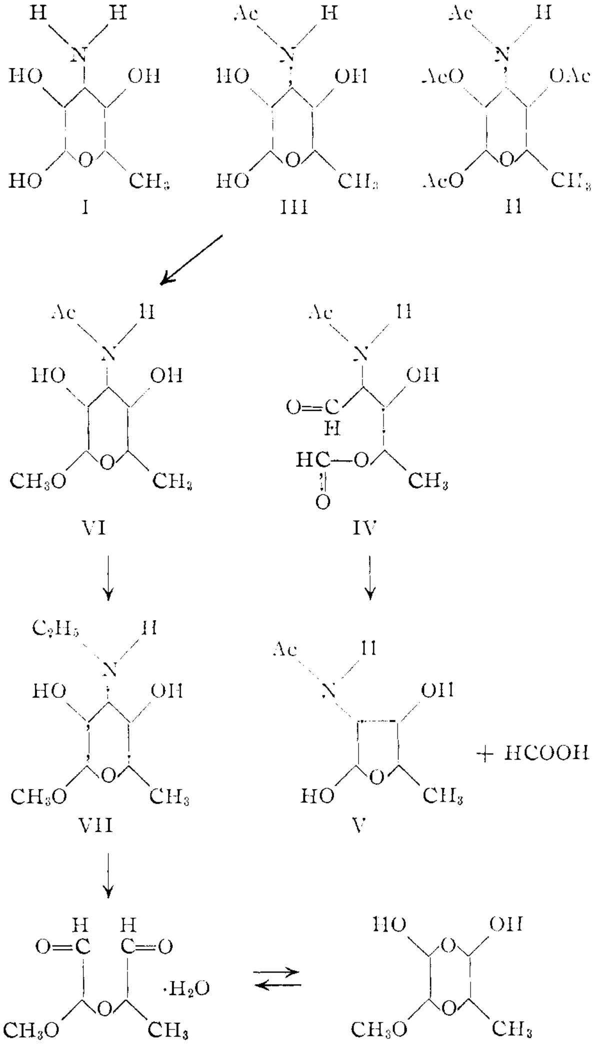
## THE STRUCTURE OF MYCOSAMINE

*Sir:*

We wish to report in this communication on the structure of an amino-sugar mycosamine,[1] which represents the nitrogen-containing moiety of the antifungal antibiotics, nystatin,[2] $C_{46}H_{77}NO_{19}$,[3,4] and amphotericin B, $C_{46}H_{73}NO_{20}$.[1,5] This amino sugar was isolated in the form of its tetraacetate[1] from the mixture of products resulting from the sulfuric acid catalyzed acetolysis of either the antibiotics or their hydrogenated derivatives. Structure I is assigned to the parent amino sugar on the basis of the following evidence:

Chromatographic fractionation on alumina of the chloroform soluble portion of the acetolysis products yielded tetraacetylmycosamine (II, m.p. 159–161°, $[\alpha]^{23}D$ +39° (*c*, 1.0 in ethanol); calcd. for $C_6H_9NO_4.4CH_3CO$: C, 50.75; H, 6.39; N, 4.23; acetyl (total), 52.0. Found: C, 50.40; H, 6.44; N, 4.26; acetyl, 50.9), hydrolyzable by barium methoxide in methanol to N-acetylmycosamine[1] (III, m.p. 191–192°, $[\alpha]^{23}D$ −46° (*c*, 1.0 in ethanol); calcd. for $C_6H_{12}NO_4{\cdot}CH_3CO$: C, 46.82; H, 7.37; N, 6.83; N-acetyl, 21.0. Found: C, 46.58; H, 7.22; N, 7.07; N-acetyl, 21.2), which reduces hot Fehling solution only slowly and gives a positive iodoform test. Treatment of III with periodic acid (consumption 1 mole) yielded 2-acetamido-3-hydroxy-4-formoxypentanal IV (amorphous, calcd. for $C_8H_{13}NO_5$: C, 47.29; H, 6.45; N, 6.85. Found: C, 47.22; H, 6.84; N, 6.93) which gives a positive Morgan-Elson test for 2-acetamido aldoses, reduces Fehling solution more readily than III, and consumes one mole of base to yield formic acid and the 2-acetamido-2,5-dideoxypentose, V (m.p. 128–130°, $[\alpha]^{23}D$ −81° (*c*, 1.0 in ethanol); calcd. for $C_7H_{13}NO_4$: C, 47.99; H, 7.48; N, 8.00. Found: C, 47.86; H, 7.41; N, 8.09).



Furthermore, methyl N-acetylmycosaminide VI (m.p. 168–170°, $[\alpha]^{23}D$ +47° (*c*, 0.9 in ethanol); calcd. for $C_9H_{17}NO_5$: C, 49.30; H, 7.82; N, 6.39; $OCH_3$, 14.1. Found: C, 49.00; H, 7.56; N, 6.13; $OCH_3$, 13.5), obtained from III with methanolic hydrogen chloride, was reduced with lithium aluminum hydride to methyl N-ethylmycosaminide, VII, (m.p. 90.5–92.5°, $[\alpha]^{23}D$ +25° (*c*, 1.0 in water); calcd. for $C_9H_{19}NO_4$: C, 52.66; H, 9.33; N, 6.83; mol. weight, 205. Found: C, 52.51; H, 9.19; N, 6.84; neut. eq. (perchloric acid titration), 211), and this base was degraded with sodium periodate (2 moles) to the known[6] D′-methoxy-D-methyldiglycolic aldehyde VIII (m.p. 99–102°, $[\alpha]^{23}D$ +131 (*c*, 0.5 in water); calcd. for

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(1) J. D. Dutcher, M. B. Young, J. H. Sherman, W. E. Hibbits and D. R. Walters, "Antibiotics Annual," 1956–1957, Medical Encyclopedia, Inc., New York, N. Y., 1956, p. 866.

(2) The E. R. Squibb and Sons trademark for nystatin is "Mycostatin."

(3) J. D. Dutcher, G. Boyack and S. Fox, "Antibiotics Annual," 1953–1956, Medical Encyclopedia, Inc., New York, 1953, p. 191.

(4) J. D. Dutcher, D. R. Walters and O. P. Wintersteiner, "Therapy of Fungus Diseases," Little, Brown and Company, Boston, Mass., 1955, p. 168.

(5) J. Vandeputte, J. L. Wachtel and E. T. Stiller, "Antibiotics Annual," 1955–1956, Medical Encyclopedia, Inc., 1956, p. 587.

(6) W. D. Maclay, R. M. Hann and C. S. Hudson, THIS JOURNAL, **61**, 1650 (1939).

$C_6H_{10}O_4.H_2O$[7]: C, 43.88; H, 7.37; $OCH_3$, 18.9. Found: C, 44.40; H, 7.21; $OCH_3$, 18.3). Direct comparison of the oxidation product with a specimen of the dialdehyde (m.p. 99–101°, $[\alpha]^{23}_D$ +137° (*c*, 1.0 in water); found for $C_6H_{10}O_4 \cdot H_2O$: C, 44.48; H, 7.20) prepared in the described manner from α-methyl-6-deoxyglucopyranoside[6,8] left no doubt about their identity (no melting point depression; identical infrared spectrum). These results, besides completing the proof for structure I for mycosamine, permit assignment of the D-configuration to carbon atom 5. The stereochemistry of the remaining asymmetric centers is under investigation.

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(7) Maclay, *et al.*,[6] observed that the molecule of water indicated by the analysis could not be removed by subliming the substance *in vacuo* at 65°, and hence refer to it as "water of constitution." This view is borne out by our finding that the infrared spectrum (Nujol) of the dialdehyde lacks a carbonyl band in the 6 μ region. It is clear, therefore, that in the solid state it exists in the lactal form VIIIb rather than in the dialdehyde form VIIIa.

(8) J. Compton, This Journal, 60, 398 (1938).

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# BOOK REVIEWS

**The Principles and Applications of Polarography and other Electroanalytical Processes.** BY G. W. C. MILNER, M. Sc., F.R.I.C., A. Inst. P., Atomic Energy Research Establishment, Harwell. Longmans, Green and Co., Inc., 55 Fifth Avenue, New York 3, N. Y. 1957. xxvii + 729 pp. 15 × 22 cm. Price, $17.50.

The polarographic literature has become so extensive that one must admire anyone who has the patience to prepare a comprehensive review of it, especially when his work has to compete with well-established books in the same language. However, three significant features of Milner's book distinguish it from other books on classical polarography. Firstly, the book covers the literature up to the end of 1955 whereas the coverage stops five years earlier in the book of Kolthoff and Lingane (see also Zuman's recent book, in German, on applications to organic chemistry and biochemistry). Secondly, Milner's book contains chapters contributed by J. E. B. Randles (University of Birmingham) in which the polarographic theory is presented from the point of view of electrochemical kinetics. Lastly, a large number of procedures are given for practical applications, especially in inorganic chemical analysis.

The book includes 29 chapters divided in four parts: theory and methodology, inorganic and organic polarography, and amperometric titrations. Controlled-potential electrolysis and coulometric methods are covered at the end of part one.

Fundamentals are discussed in Chapters 3 to 5 written by Randles. These chapters cover an excellent discussion of the classical theory of diffusion currents, a treatment of current-potential curves, and the best survey of phenomena related to polarographic maxima this reviewer has read in English. The analysis of current-potential curves is based on current ideas in electrochemical kinetics and definitely departs from the usual treatment involving solely equilibrium considerations (Nernst equation). This most welcome change from the conventional presentation may prove a little disconcerting to some readers who will not find some of the derivations they have become accustomed to. An original method is presented for adaptation of the equation for irreversible waves for the plane electrode to the dropping mercury electrode. Unfortunately, the rather rigorous treatment of this problem by Koutecky is only cited and not discussed at all although the analysis of experimental irreversible waves by this method is very simple.

Dr. Randle's contribution is excellent but it is written at a level which may deter practical analytical chemists—who will probably constitute the great majority of readers—from gaining the full benefit from its reading. In particular, examples of the application of theory to the analysis of reversible and irreversible waves would have helped some readers.

Some newer polarographic methods are covered in Chapter 7: derivative and differential polarography, oscillographic polarography (by Randles), new types of electrodes, and polarography in non-aqueous media. The coverage of the different voltammetric methods related to polarography is not up-to-date, and does not stress fundamentals. The omission of square wave polarography, which was developed at Harwell (1952), is quite surprising in a book written by someone from the same institution. (The author points out in the preface the significance of the method in trace analysis but that is all.) Rotated electrodes are only mentioned briefly in Chapter 7 and fundamentals are not covered.

The coverage in the descriptive part seems critical and complete. Half-wave potentials are listed in the text but, in general, are not summarized in tables at least in the inorganic part. Numerous applications to practical inorganic analysis are discussed in detail.

There is a detailed subject index but no author index.

In conclusion, this book will prove valuable to those interested in the applications of polarography. Readers with their primary interest in fundamentals will find the chapters by Randles on the theory of current-potential curves most stimulating.

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**The Condensed Chemical Dictionary.** Fifth Edition, completely revised and enlarged by ARTHUR AND ELIZABETH ROSE, State College, Pennsylvania. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y., 1956. xix + 1200 pp. 16.5 × 23 cm. Price, $12.50.

The title page of the new Fifth Edition describes the Condensed Chemical Dictionary as "a reference volume for all requiring quick access to essential data regarding chemicals and other substances used in manufacturing and research, and to terms in general use in chemistry and the process industries." On the jacket we find the statement: "Here, indeed, is a *practical* book for busy chemists, engineers, consultants, purchasing agents, executives—for anyone in any line of activity who needs a convenient source of accurate, up to-date chemical information."

A moderately careful inspection of this dictionary indicates that these descriptions are accurate. This is a reference work more suited to the needs of the industrial chemist and chemical businessman than to those of the research worker. As such, it represents an excellent effort on the part of the editors and should find widespread utility.

The dictionary section contains over 30,000 entries arranged on 1200 double-column pages. The typography and layout are very good. Each main heading is in boldface with the second and following lines of descriptive material indented below it. Liberal use of sub-headings and appropriate paragraphing within entries make for ease of searching