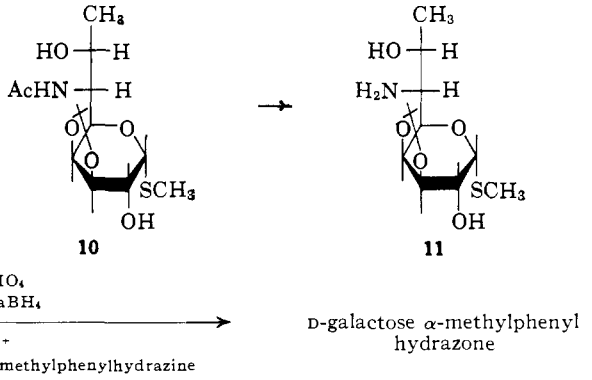
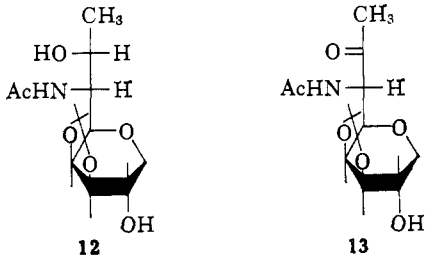
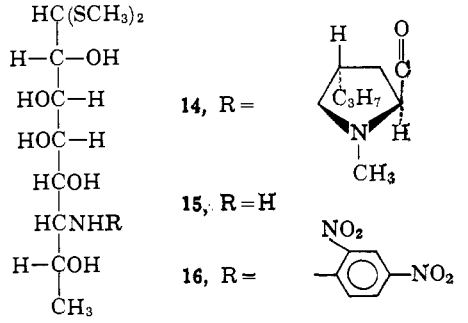
acid, and isolation as D-galactose α-methylphenylhydrazone established the D- series.



Nickel desulfurization of **10** gave **12**, $C_{13}H_{23}NO_6$. Chromic acid oxidation of **12** afforded **13**, $C_{13}H_{21}NO_6$, which gave a positive iodoform test and displayed a new n.m.r. peak, intensity 3H at δ 2.3, consistent with a methyl group adjacent to a carbonyl function. The product of borohydride reduction of **13** again gave a negative iodoform test. These data located the side-chain substituents.



Further reactions confirmed these assignments and established side-chain stereochemistry. Lincomycin was mercaptolyzed to methylthiolincomycose, **14**, $C_{19}H_{36}N_2O_6S_2$. Hydrazinolysis of **14** afforded lincosamine dimethyl dithioacetal, $C_{10}H_{23}NO_5S_2$, **15**, which was converted to the 2,4-dinitrophenyl derivative, $C_{16}H_{25}N_3O_9S_2$, **16**.



Periodate–permanganate[11] oxidation of **16** afforded 2,4-dinitrophenyl-D-allothreonine, an amorphous solid isolated by countercurrent distribution and identified by analyses and optical rotations.[12] Thus, lincomycin appears to be chemically related to celesticetin,[13,14] for which the partial structure has been published.[15]

(11) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).
(12) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1961, p. 1564.
(13) C. De Boer, A. Dietz, J. R. Wilkins, C. N., Lewis, and G. M. Savage, *Antibiotics Ann.*, 831 (1955).
(14) H. Hoeksema, G. F. Crum, and W. H. Devries, *ibid.*, 837 (1955).
(15) J. W. Hinman and H. Hoeksema, 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

Acknowledgment.—We gratefully acknowledge the analytical work of Dr. W. A. Struck and associates, and the advice and encouragement of Dr. T. E. Eble.

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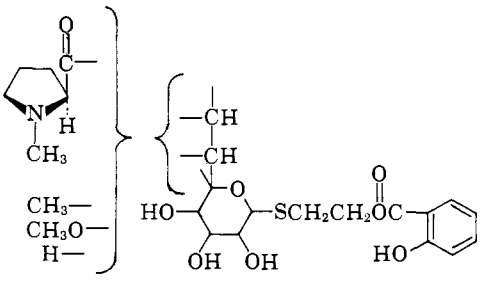
RECEIVED JULY 27, 1964

Celesticetin. IV. The Structure of Celesticetin

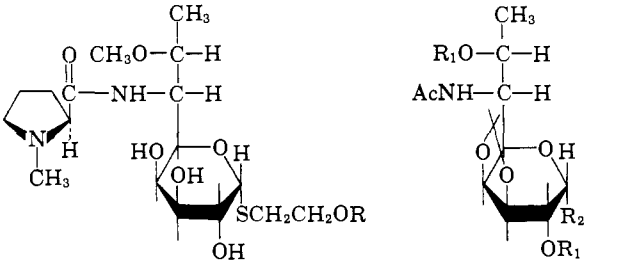
Sir:

The partial structure of the antibiotic celesticetin has been reported[1] to be **1**.



Structural studies on lincomycin[2] have shown that it is chemically related to celesticetin. The present studies now extend the comparison between the two materials and celesticetin is shown to have structure **2** and desalicetin to be **3**.

The earlier work on celesticetin did not resolve the question as to whether the octose consisted of a straight or a branched chain. The exact locations of the hygric amide and methoxyl functions were also in doubt, and the stereochemistry of the sugar was unknown. The preparation of the identical compound, **4**, from both lincomycin and celesticetin resolves these questions. Celesticetin is found to have the same carbon chain, order of substitution, and stereochemistry as lincomycin.



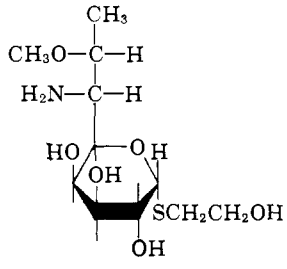
2, R = salicyloyl; celesticetin
3, R = H; desalicetin
4, R_1 = Me; R_2 = H
5, R_1 = H; R_2 = —SCH_3
6, R_1 = R_2 = H

N-Acetylmethylthiolincosaminide, **5**, has previously been prepared from lincomycin.[2] Treatment with Raney nickel desulfurized **5**, giving **6** as a crystalline

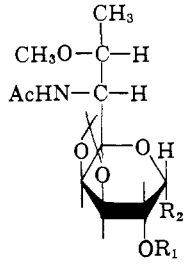
(1) H. Hoeksema and J. W. Hinman, 129th National Meeting of the American Chemical Society, Dallas, Texas, 1956; *J. Am. Chem. Soc.*, in press.
(2) H. Hoeksema, B. Bannister, R. D. Birkenmeyer, F. Kagan, B. J. Magerlein, F. A. MacKellar, W. Schroeder, G. Slomp, and R. R. Herr, *ibid.*, **86**, 4223 (1964).

substance. Methylation of the two free hydroxyls of **6** with sodium hydride and methyl iodide in dimethylformamide then gave **4** which was isolated by countercurrent distribution and crystallized.

In the celesticetin series the same group of reactions was used. Hydrazinolysis cleaved the amide and gave β-hydroxyethylthiocelestosaminide, **7**, as a crystalline compound. Acetylation with acetic anhydride in ethanol, followed without purification by treatment with acetone and sulfuric acid, afforded **8**. The latter was noncrystalline but was purified by countercurrent distribution. Raney nickel desulfurization of **8** provided the expected compound, **9**. Methylation by the earlier procedure again led to **4**, isolated by countercurrent distribution. It was identical with the corresponding compound from lincomycin by mixture melting point, analysis, infrared spectrum, and n.m.r. pattern.

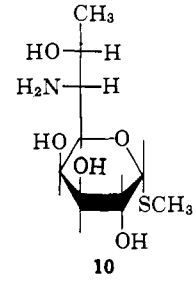


7



8, R_2 = SCH_2CH_2OH, R_1 = H
9, R_1 = R_2 = H
4, R_2 = H; R_1 = Me

The stereochemistry at carbon 1 was deduced by comparison of the n.m.r. of compound **7** with that of the corresponding material, α-methylthiolincosaminide (**10**), obtained from lincomycin. Since the J values of 4.5 c.p.s. for the doublet ascribed to the anomeric hydrogen at carbon 1 are identical for both compounds, and the remaining stereochemistry of the two compounds is the same, the thio grouping must be α as in lincomycin.



10

It is of interest to note that the same octose, substituted differently at three sites, is produced by two distinctly different actinomycetes, and that both substances are active antibiotics. The biosynthetic implications are under investigation.

Acknowledgment.—Grateful acknowledgment is made of the analytical work of W. A. Struck and associates, n.m.r. curves from George Slomp, and helpful advice from F. Kagan.

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RECEIVED SEPTEMBER 8, 1964

BOOK REVIEWS

The Inorganic Chemistry of Nitrogen. By WILLIAM L. JOLLY, University of California, Berkeley, Calif. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1964. xi + 124 pp. 12 × 24 cm. Price, $5.75.

The editors of the series of monographs of which this volume is a part, state in the foreword that these volumes fulfill the following three functions: (1) a selection of these volumes can be used as a "textbook for an advanced inorganic chemistry course that makes full use of physical chemistry prerequisites"; (2) the series in total constitutes a reference treatise of inorganic chemistry systematized by physical principles; and (3) each monograph by itself represents a specialist's introduction to a specific research field. It is the opinion of the reviewer that the present volume could very well form one of a selected series to fulfill function 1, and that this volume delightfully fulfills function 3, providing as it does an exceedingly attractive introduction to research in the inorganic compounds of nitrogen. The volume is, however, too brief and provides an insufficient number of references to the original literature to serve as an effective reference treatise.

This book is divided into eleven chapters entitled The Unique Features of Nitrogen; Elementary Nitrogen; Ammonia; Nitrogen–Halogen Compounds; the Hydronitrogens and Hydroxylamine; Nitrogen Oxides and Oxy-Acids; Sulfur–Nitrogen Compounds; Phosphorus–Nitrogen Compounds; Carbon–Nitrogen Compounds; Boron–Nitrogen Compounds; Thermodynamics of Nitrogen Compounds. This book is attractively written and reflects the broad experience of the author in nitrogen chemistry. The small size of the volume makes it inevitable that numerous topics which many inorganic chemists would consider important will be omitted, and the reviewer missed seeing some of his "pet" topics. The reviewer found few typographical or other errors.

In view of the modern character of most of the writing, it is a bit surprising to find that the author relapses into the obsolete jargon of the "solvent-system" concept of acids and bases on p. 28 in stating that "such acids (as CH_3COOH) are strong in ammonia." However, such relapses as this are rare. The reviewer is delighted to recommend this very attractive volume to all serious chemistry students as well as to professional chemists generally. Certainly, no inorganic chemist will wish to be without it.

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The Monosaccharides. By JAROSLAV STANĚK, MILOSLAV ČERNÝ, JAN KOCOUREK, and JOSEF PACÁK. Academic Press, Inc., 111 Fifth Ave., New York, N. Y. 1963. 1006 pp. 17.5 × 25 cm. Price, $32.00.

Few, if any, sub-disciplines of organic chemistry are overlapped by more varied interests than the carbohydrate field. Here the physical organic chemist, the biochemist, the immunochemist, and the industrial chemist, as well as a host of