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Synthetic Penicillin

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Synthetic Penicillin:  
Vincent du Vigneaud, et al. ........................................... 431, 450

Radar Observations During Meteor Showers, 9 October 1946:  
Ross Bateman, A. G. McNish, and Victor C. Pinoe 434

TECHNICAL PAPERS

The Influence of Liver L. casei Factor on Spontaneous Breast Cancer in Mice:  
B. Lewisohn, et al. .................................................. 436

Stability of Carotene in Dehydrated Carrots Impregnated With Antioxidants:  
T. E. Weier and C. R. Stocking ................................. 437

Synthetic L. casei Factor (Folic Acid) in Treating Certain Anemias in Man: Grace A. Goldsmith .... 439

NEWS AND NOTES .................................................. 440

IN THE LABORATORY

Synthetic Media for Penicillin Production:  
B. W. Stone and M. A. Farrell ............................... 445

(Photograph of Dr. H. J. Muller by courtesy of Science Service.)

Tests of Screening Effectiveness Against Insects:  
S. S. Block ............................................. 447

LETTERS TO THE EDITOR

An Experimental Compressed-Air Plant Sprayer:  
Tom Eastwood .............................................. 448

Projection of Meteor Trails on the Moon:  
James C. Bartlett, Jr. ......................................... 448

Whole-Blood Cholinesterase Determinations in Some Hematologic Dyscrasias; Low Cholinesterase Values in the Leucoses:  
R. D. Barnard, et al. .................................... 449

A Simply Constructed Biophotometer:  
Samuel A. Goldblith ..................................... 449

BOOK REVIEWS

Mathematical methods of statistics:  
Harald Cramér.  
Reviewed by J. L. Doob .............................. 450
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</thead>
<tbody>
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<td>$3.00</td>
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<tr>
<td>701-W</td>
<td>Red</td>
<td>4¾”</td>
<td>1.50</td>
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<tr>
<td>705-W</td>
<td>Amber</td>
<td>7¾”</td>
<td>1.50</td>
</tr>
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<td>Amber</td>
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Synthetic Penicillin

Vincent du Vigneaud, Frederick H. Carpenter, Robert W. Holley,
Arthur H. Livermore, and Julian R. Rachele

Department of Biochemistry, Cornell University Medical College, New York City

This report is a summary of the investigations that have led to the synthesis and isolation of G-penicillin (now termed benzylpenicillin). Most of the preliminary work, which is briefly described here, was performed by American and British chemists working under the joint auspices of the Committee on Medical Research, OSRD (Washington) and the Medical Research Council (London) (cf. Science, 1945, 102, 627). The details of this preliminary work will be published in a monograph on penicillin chemistry, now in preparation.

The isolation in crystalline form of the active synthetic product and the unequivocal proof of its identity with natural benzylpenicillin have been carried out in this Laboratory since the termination of the OSRD contracts. Complete details of this latter work will be reported following the publication of the monograph.

In the early stages of the investigation of the chemistry of penicillin, the oxazolone-thiazolidine structure I was favored by the majority of laboratories as representing the structure of penicillin. Consequently, much effort was directed toward the synthesis of compounds of Type I. An approach toward the synthesis of such compounds, which involved the condensation of an appropriate oxazolone, possessing a free or potential aldehyde group, with d-penicillamine (II) (1), was explored by several laboratories both in this country and in England. Oxazolones of Type III which possessed a potential aldehyde group were soon synthesized (2).

\[
\begin{align*}
\text{HS} & \text{C(CH}_3\text{)}_2 \\
\text{H}_2\text{N} & \text{CH} \text{COOH} \\
\text{O} & \text{CO} \\
\hline
\text{R} & \text{C} \text{N} \text{CH} \text{CH} \\
\text{O} & \text{CO} \\
\text{NH} & \text{CH} \text{COOH}
\end{align*}
\]

(III)

The formation, in such reactions, of products possessing antibiotic activity was demonstrated independently and almost simultaneously in the United States and in England and announced to the collaborating groups in the first months of 1944. The earliest record of this discovery is contained in a report from the laboratories of Merck and Company, Inc. (3), in which it was stated that "d(+)-penicillamine hydrochloride and the azlactone [(2-benzyl-4-methoxy-methylene-5(4)-oxazolone) (III, R = C_6H_5CH=; R' = CH_3)] have been reacted to give a product showing

This article was submitted for publication at the request of and through the Editorial Board of the monograph on the Chemistry of Penicillin being prepared under the auspices of the National Academy of Sciences.

The nomenclature used by the authors conforms with that to be employed in the forthcoming monograph on the Chemistry of Penicillin. According to this nomenclature G-penicillin is designated benzylpenicillin; K-, F-, and X-penicillins are designated, respectively, n-heptylpenicillin, \(A^2\)-pentenylpenicillin, and \(p\)-hydroxybenzylpenicillin. This style of nomenclature is carried over into the naming of various degradation and rearrangement products of the penicillins. For example, G-penicilloic acid is designated benzylpenicilloic acid.
exhibit the marked peaking exhibited on 9 October, remaining at approximately the lower level of 9 October throughout the period of observation.

Since meteoric particles are of very small size, radar reflections directly from them may not be expected. The effects produced are undoubtedly from tracks of highly ionized atmospheric gases and meteoric vapors produced by the impact of the meteors on the atmosphere. Velocity relative to the earth of the meteoric particles from the Draconids is of the order of $2 \times 10^5$ cm. per second. A meteoric particle having a mass of only $1$ mg. might be expected to produce of the order of $10^{15}$ ions in passing through the atmosphere if its entire kinetic energy is expended in ionization. The reflections may thus be thought of as due to scattering from a lengthy filament of highly conducting atmosphere entirely different in nature from the layers which produce regular reflections of radio waves. Thus, since the radar employed for the observations emits a polarized beam with its electric vector parallel to the plane of the horizon, discrimination between vertical and horizontal tracks is to be expected. Reflections might not be obtained from visible tracks that are perpendicular to the plane of polarization, while some invisible tracks parallel to the plane of polarization might be detected by the radar. No unusual effects were noted on the regular ionospheric records obtained during the shower.

The encouraging nature of these preliminary results indicates that radar methods of observing meteors may have a number of future applications. One such application would be the routine, continuous automatic recording of the radar echoes for determining the occurrence of meteors during overcast weather when seeing is poor and during daylight hours. It should also be possible to obtain much useful information regarding the nature and physical structure of the ionosphere with this type of radar equipment, as well as how meteor reflections may affect radio propagation and the usefulness of high frequencies.

*The Department of Scientific and Industrial Research, London, reported to Science that the 9-10 October experiments on the radio method of detection of meteors, organized by Sir Edward Appleton and R. Naismith at the Slough Radio Research Station of DSIR, were completely successful. The report said that astronomers had predicted that the earth would enter the meteor stream of the comet, Giacobini-Zinner, at about midnight, but it was not until between 3: 00 and 4: 00 A.M. on the 10th that the stream had been entered.*

The Radio Research Station first detected these echoes in 1932 and has continued to investigate them ever since. A theory was evolved that they were caused by the reflection of radio pulses from meteor trails, and evidence was progressively built up to support the theory. On this occasion the burst of echoes was on a scale greatly in excess of anything previously experienced. The methods used also permitted the average height of the meteor train to be determined, and this came out to be about 60 miles above the ground.

The report pointed out "that it was by purely scientific experiments of this kind that Sir Edward Appleton and the Radio Research Station developed the methods of detecting reflecting bodies at a distance, which later became the basis of practical radar."