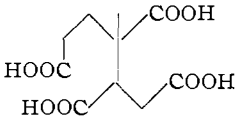
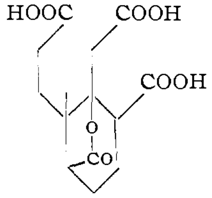
and pyridine yields germine tetraacetate,[6] stable to chromic acid, m.p. 260–261° dec.; $[\alpha]^{23}\text{D}$ −98° (c 1.57, py.). Calcd. for $C_{27}H_{39}O_8N(COCH_3)_4$: C, 62.02; H, 7.59; acetyl, 25.40. Found: C, 61.77; H, 7.50; acetyl, 25.22. Treatment of isogermine under the same conditions affords isogermine tetraacetate, m.p. 222–226°; $[\alpha]^{24}\text{D}$ −80° (c 1.63, py.). Found: C, 61.69; H, 7.49; acetyl, 25.85. Acetylation of pseudogermine under the same conditions yields pseudogermine tetraacetate, m.p. 208–220°; $[\alpha]^{24}\text{D}$ −59° (c 1.70, py.). Calcd. for $C_{27}H_{39}O_8N(COCH_3)_4 \cdot H_2O$: C, 60.41; H, 7.68; acetyl, 24.75. Found: C, 60.34; H, 7.29; acetyl, 24.44. The fact that all three isomers yield tetraacetates indicates that the ether bridge of the hemiketal system must terminate at a primary or secondary carbon atom.

Moreover acetylation of dihydrogermine[7] leads to dihydrogermine pentaacetate, stable to chromic acid, m.p. 288–290° dec.; $[\alpha]^{28}\text{D}$ −64° (c 1.41, py.). Calcd. for $C_{27}H_{40}O_8N(COCH_3)_5$: C, 61.56; H, 7.68; acetyl, 29.82. Found: C, 61.61; H, 7.72; acetyl, 29.82. This result is compatible with the view that sodium-alcohol reduction of germine proceeds by liberation and then reduction of a keto group with concomitant liberation of the hydroxyl group involved in the hemiketal ring. Since this hydroxyl group is acylable, it must be primary or secondary.

The fact that the hemiketal ring in germine is 5-membered[4] indicates that the terminus of the ether bridge of the hemiketal system must be at C_1, C_7, or C_{19}. The formation of the hexanetetracarboxylic acid IV by chromic acid oxidation of germine[1,5] shows the absence of oxygen from positions C_1 and C_{19} and fixes C_7 as the terminus of the ether bridge. The failure to detect the lactone tricarboxylic acid V among the products of chromic acid oxidation of germine[1,5] is readily explicable on the basis of partial formulation I for germine.


IV


V

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(6) Earlier reports (W. Poethke, *Arch. Pharm.*, **276**, 571 (1938); J. Fried, H. L. White and O. Wintersteiner, THIS JOURNAL, **72**, 4621 (1950)) that germine forms a pentaacetate have been found to be in error. Recent acetyl determinations both at Harvard and at the Squibb Institute agree with a tetraacetate formula.

(7) L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **149**, 451 (1943).

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RECEIVED AUGUST 16, 1954

CHOLESTEROL—A PRECURSOR OF TETRAHYDROCORTISONE IN MAN

Sir:

Cholesterol has been shown to serve as a precursor of two adrenal steroid hormones (hydrocortisone and corticosterone) *in vitro*.[1,2] This communication demonstrates that cholesterol is converted in man to an adrenal steroid metabolite, pregnane-3-α-17-α-21-triol-11,20-dione (THE), probably via Δ^4-pregnene-17-α-21-diol-3,11,20-trione (cortisone).[3] This appears to be the first report of the conversion of cholesterol to an 11-oxygenated steroid in man.

A solution was made of 4.24 μc. of 4-C^{14}-cholesterol[4] (5 μc/mg.) and 33.8 μc. of cholesterol-t[5,6] (7.3 μc./mg.) in 2.3 g. of propylene glycol and added to 30 ml. of sterile human plasma. The mixture was given intravenously to a male arthritic patient. Cholesterol with two labels was chosen in this experiment in order to determine whether or not the side chain of cholesterol-t is utilized in steroid hormone production. A 24-hour urine sample was collected on the second day after the administration of the radiocholesterol and a crude neutral steroid extract prepared.[7] The extract was subjected to paper partition chromatography[8] for seven days and the steroid, with the same mobility as that of THE, was then eluted and rechromatographed for five days in the same system.[9] The lower of two well-defined areas[10] (corresponding to the movement of pure THE[11]) was cut out and eluted with methanol. An aliquot was mixed with pure THE and found to travel as a single spot in the above solvent system.[12] The remainder, 2.8 mg., was converted to the diacetate and mixed with 10.09 mg. of pure THE diacetate, m.p. 233–234°. Following vacuum sublimation and five recrystallizations from methanol, the THE diacetate melted at 232–233.5°. The ultraviolet spectrum of this material in sulfuric acid after two hours was identical with that given by pure THE diacetate treated in the same manner.[13] The mixture of labeled THE diacetate and carrier, 5.01 mg. (Sample A) was dissolved in 50 ml. of toluene containing 100 mg. of 2,5-diphenyloxazole.[14]

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(1) A. Zaffaroni, O. Hechter and G. Pincus, THIS JOURNAL, **73**, 1930 (1951).

(2) O. Hechter, M. M. Solomon, A. Zaffaroni and G. Pincus, *Arch. Biochem. Biophys.*, **46**, 201 (1953).

(3) S. Burstein, K. Savard and R. I. Dorfman, *Endocrinology*, **52**, 448 (1953).

(4) Procured from Radioactive Products, Inc., Detroit, Michigan.

(5) This was generously supplied by R. G. Gould, Los Alamos Scientific Laboratory.

(6) Oppenhauer oxidation and equilibration with alkali indicated that 37.5% of the tritium was located at positions 2, 3, 4 and 6. The remainder of the tritium probably was located at positions 24, 25, 26 and 27 (see D. Fukushima and T. F. Gallagher, *J. Biol. Chem.*, **198**, 861 (1952)).

(7). B. Baggett, R. A. Kinsella, Jr., and E. A. Doisy, *ibid.*, **203**, 1013 (1953).

(8) R. B. Burton, A. Zaffaroni and E. H. Keutman, *ibid.*, **188**, 763 (1951).

(9) For the rechromatography the sheets were impregnated with propylene glycol diluted with methanol 1:2 and 1 mg. of steroid per sheet was applied.

(10) In this run the lower area was 6 to 8 cm. from the starting line, while in later 7-day runs it appeared from 13 to 15 cm. from the origin.

(11) We are grateful to Dr. Karl Pfister of Merck, Inc., for supplies of this steroid.

(12) In other runs aliquots were removed at this point, mixed with authentic THE and run for six days in the benzene–formamide system.[8] On development only one spot was observed. Other aliquots were converted to THE diacetate and were found to have the same mobility as pure THE diacetate in the benzene-formamide system.

(13) A. Zaffaroni, THIS JOURNAL, **72**, 3828 (1950).

(14) F. N. Hayes and R. G. Gould, *Science*, **117**, 480 (1953).

TABLE I

SPECIFIC ACTIVITY OF THE DIACETATE

Sample	Mg. counted	DPM tritium/mg.	DPM C^{14}/mg.
A	5.01	75	20.4
B	3.28	125	23.1
C	2.88	131	19.4

Sample B: the filtrates of the recrystallizations of A were combined, vacuum sublimed, and recrystallized once from methanol, m.p. 232–233°. Sample C: the toluene of B was distilled off under high vacuum, and the 2,5-diphenyloxazole was removed by vacuum sublimation. The THE diacetate remaining was vacuum sublimed and recrystallized once from methanol, m.p. 232°.

The radiocarbon and tritium were then counted in a liquid scintillation counter[15] capable of counting the pulses due to the carbon-14 and tritium at the same time. Then the pulses due to tritium were screened out and only those coming from the carbon-14 were counted. The tritium counts were obtained by difference.[16] The specific activities were calculated and are shown in the table.

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(15) The instrument was developed for us by the Packard Instrument Co., La Grange, Illinois.

(16) Details regarding the method of counting both carbon-14 and tritium in the same sample will be published later.

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RECEIVED AUGUST 9, 1954

BOOK REVIEWS

Energy Transfer in Hot Gases. Sixth Conference, U. S. Bureau of Standards. By the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. 1954. iii + 126 pp. 15 × 23.5 cm. $1.50.

The 50th anniversary of the Bureau of Standards was celebrated in part by a series of 12 conferences devoted to different aspects of the Bureau's program of fundamental and applied research. The present volume consists of a rather noteworthy set of 16 papers presented at the sixth of these conferences devoted to consideration of radiation and energy transfer processes occurring in hot gases. As may be anticipated the subject is of current interest to scientists working in what are normally considered quite separate fields and this diversity is represented by contributions from many well-known authorities in such fields as photochemistry, spectroscopy, combustion, fuels, kinetics, astrophysics and aeronautics. What is most impressive, however, is not the diversity represented by these authors, but rather the way in which a common interest has so effectively integrated their different disciplines into an impressive attack on some very difficult and important problems of molecular dynamics.

The first paper by A. G. Gaydon on "Processes of Electronic Excitation in Relation to Flame Spectra" provides an excellent introduction to the remainder of the volume. It summarizes very nicely the excitation processes occurring in flames and their relevance to the problems of flame temperature measurement. In a later paper, S. S. Penner has reviewed the theoretical background involved in the infrared emissivity of diatomic gases. B. Lewis adds a very interesting paper on the theory of flames with particular emphasis on empirical models which have been successful in accounting for combustion waves. A brief paper by B. Karlovitz presents an interesting treatment of turbulence in flames and an important application to heat transfer from such flames.

One of the important problems in flames is, of course, the measurement and interpretation of temperatures and there are a number of very stimulating experimental papers on this subject by R. H. Tourrin, G. A. Hornbeck and R. C. Herman, H. P. Broida, S. S. Penner and M. Gilbert and D. Weber, G. H. Dieke and H. M. Crosswhite, S. Silverman and W. S. Benedict and E. K. Plyler. Among these, the first one and the last two are of particular interest because of the use of the rather new techniques made available from infrared work.

P. J. Dyne discusses some of the problems of identification of radical and molecular species responsible for emission in fluorescence and discharges. Closer to the chemical viewpoint is a very interesting discussion of flame induced chemiluminescence at interfaces by J. R. Arthur and D. T. A. Townend. Quite spectacular H_2–F_2 flame experiments are described by R. H. Wilson, Jr., J. B. Conway, A. Engelbrecht and A. V. Grosse. This reaction appears to give the hottest flame yet recorded (4300°K.).

The last paper by H. K. Sen represents an attempt at a new explanation of the anomalous temperature observed in the photosphere and chromosphere of stars, based on the existence of shock waves in these regions.

This brief volume represents an important contribution to a rapidly growing and important field. Many of the interesting phenomena are still only partially understood and there is still disagreement about some of the basic data. Nevertheless, to workers in the field this will be for some time a stimulating and useful presentation and the Bureau is to be commended for making these papers conveniently available at reasonable cost.

In conclusion the reviewer wishes to make clear to the lay reader that despite its origin and title, the present volume is not a discussion of the political atmosphere in our nation's capitol.

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The Biochemistry of the Nucleic Acids. 2nd Edition. By J. N. DAVIDSON, D.Sc., M.D. (Edin.), F.R.I.C. Gardiner Professor of Physiological Chemistry in the University of Glasgow. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1954. viii + 200 pp. 11 × 17 cm. Price, $2.25.

This pocket-sized Methuen Monograph offers the only modern summary of the status of the rapidly expanding body of information about nucleic acids, and fulfills the author's promise of a book for "chemists who wish to know something about the biological aspects of the subject, and of biologists who wish to learn a little about the chemical aspects." It emphasizes the biological and metabolic aspects of the subject, particularly on a cellular level. The important changes in concepts of the composition and structure of the polynucleotides, the many developments relating deoxyribonucleic acids to chromosomal material and the multitude of views on the possible functions of ribonucleic acids are all clearly presented. It is as up to date as is practical and the usefulness has been increased in this edition by placing the bibliographies after each chapter. The next edition could be improved by the inclusion of an author index, and by some distinguishing mark on its spine to differentiate it from previous editions. The concise, but re-