

Crystals, six-sided rods, appear when the sodium chloride concentration is 0.105 *M*.

TABLE I

CONSTANTS FOR THE GLYCOPROTEIN	
Hexose/protein (protein is taken as nitrogen $\times 6.25$ )	0.053
Hexosamine/protein	0.038
$E_{1\text{cm.}}^{1\%}$ at 277 $\mu$	11.1
Biuret color of protein portion (albumin = 1.00)	0.98
Sedimentation constant (2% soln)	14.6 Svedbergs
Electrophoretic mobility barbiturate $\text{pH } 8.6, \Gamma/2 \text{ } 0.1$	$-3.92 \times 10^{-5}$ cm. <sup>2</sup> /volt sec.

A suspension of crystals in saline was dried and weighed; 93% was composed of protein, carbohydrate and calculated salt, a further indication that the crystals are protein in nature.

The crystallized glycoprotein is ultracentrifugally homogeneous although the sedimentation diagram indicates slight denaturation during solution. Marked ultracentrifugal changes consistent with denaturation occur if the crystals are suspended in distilled water. Freezing and thawing cause the formation of two new well-defined ultracentrifugal components. In a typical experiment at a protein concentration of 2%, 9% of a component of  $S_{20,w} = 21.4$  and 3% of a component of  $S_{20,w} = 9.8$  were found.

DIVISION OF LABORATORIES AND RESEARCH RAY K. BROWN  
NEW YORK STATE DEPARTMENT OF HEALTH  
ALBANY, NEW YORK WINFIELD H. BAKER  
ALAN PETERKOFSKY  
DOROTHY L. KAUFFMAN

RECEIVED JUNE 21, 1954

### THE TRANSFORMATION OF PSEUDOSAPOGENINS TO STEROID ALKALOIDS<sup>1</sup>

Sir:

In pursuit of studies directed toward the synthesis of steroid alkaloids of skeletal formulations characteristic of natural products,<sup>2</sup> pseudosapogenins have been investigated as starting materials. Pseudosarsapogenin, I,<sup>3,4</sup> has been converted, following treatment with *p*-toluenesulfonyl chloride and pyridine, to an iodo derivative, m.p. 60–62° [Anal.<sup>5</sup> Calcd. for  $C_{27}H_{43}O_2I$ : C, 61.59; H, 8.23; I, 24.12. Found: C, 61.38; H, 8.42; I, 24.25] which has been transformed with potassium phthalimide in dimethylformamide to the C.27 phthalimido derivative II, m.p. 187–188° [Anal. Calcd. for  $C_{35}H_{47}NO_4$ : C, 77.02; H, 8.68; N, 2.57. Found: C, 76.71; H, 8.64; N, 2.81]. Cleavage with hydrazine and subsequent treatment with

(1) Supported in part by the United States Public Health Service and the Eugene Higgins Trust of Harvard University.

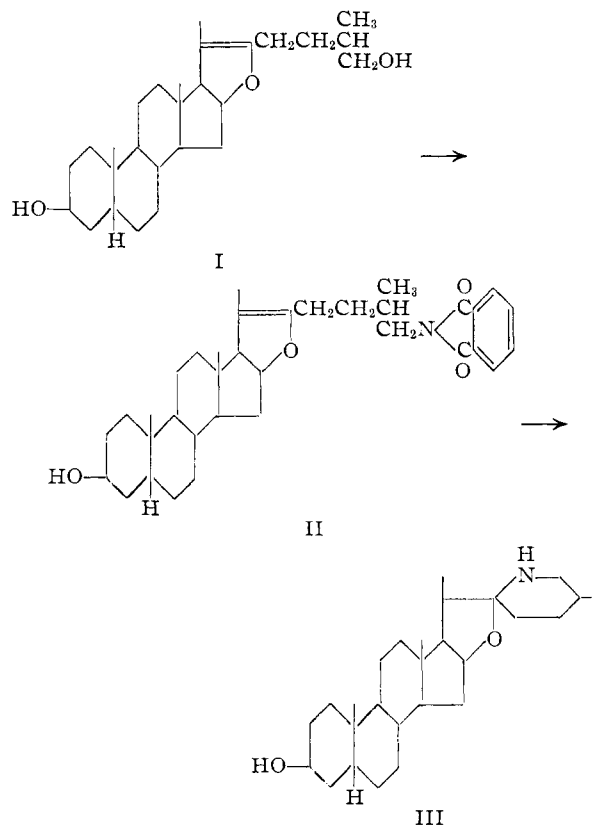
(2) F. C. Uhle, *THIS JOURNAL*, **73**, 883 (1951); **75**, 2280 (1953).

(3) R. E. Marker and E. Rohrmann, *ibid.*, **62**, 519 (1940).

(4) The author is indebted to Dr. James A. Moore, Parke Davis and Company, Detroit, Michigan, and to S. B. Penick and Company, New York, N. Y., for quantities of sarsapogenin and of diosgenin acetate.

(5) Microanalyses and spectroscopic determinations by Dr. S. M. Nagy and associates of the Massachusetts Institute of Technology, Cambridge, Massachusetts.

mineral acid has afforded an alkaloid III, m.p. 221–223°,  $[\alpha]_{25}^D -17.4^\circ$  (methanol) [Anal. Calcd. for  $C_{27}H_{43}NO_2$ : C, 78.02; H, 10.91; N, 3.37. Found: C, 78.23; H, 10.85; N, 3.25].



A parallel approach employing pseudodiosgenin has afforded solasodine. Although the singular lability of pseudodiosgenin and of its derivatives has, to the present, compromised repeated attempts to isolate and fully characterize the intermediates postulated for the sequence, it has been possible to transform pseudodiosgenin to solasodine as a continuous process in over-all yields of the order of ten per cent. Pseudodiosgenin-3-acetate-27-butyrate, m.p. 117–118° [Anal. Calcd. for  $C_{33}H_{50}O_5$ : C, 75.24; H, 9.57. Found: C, 75.49; H, 9.66] (from diosgenin acetate and refluxing butyric anhydride) and pseudodiosgenin dibutyrate, m.p. 78–79°,  $[\alpha]_{25}^D -16.8^\circ$  (methanol) [Anal. Calcd. for  $C_{35}H_{54}O_5$ : C, 75.77; H, 9.81. Found: C, 75.60; H, 9.61] (from diosgenin or from pseudodiosgenin and refluxing butyric anhydride) on alkaline hydrolysis at 25° have yielded pseudodiosgenin, m.p. 161–162°, which, on successive treatment with *p*-toluenesulfonyl chloride in pyridine, sodium iodide in diethyl ketone, potassium phthalimide in dimethylformamide, and hydrazine in ethanol, has afforded solasodine, m.p. 200–201°,  $[\alpha]_{25}^D -118^\circ$  (chloroform) [Anal. Calcd. for  $C_{27}H_{43}NO_2$ : C, 78.40; H, 10.48; N, 3.39. Found: C, 77.36; H, 10.52; N, 3.42] mixed melting point<sup>6</sup>

(6) The author is indebted to Prof. L. H. Briggs, Auckland University College, Auckland, New Zealand, and to Dr. Yoshio Sato of the National Institutes of Health, Bethesda, Maryland, for authentic samples of solasodine.

and infrared spectrum identical with that exhibited by an authentic specimen of naturally occurring solasodine; hydrochloride, m.p. 288–290° [*Anal.* Calcd. for  $C_{27}H_{44}NO_2Cl$ : C, 72.05; H, 9.85; N,

3.11. Found: C, 72.24; H, 9.92; N, 3.05].

DEPARTMENT OF PHARMACOLOGY  
HARVARD MEDICAL SCHOOL  
BOSTON 15, MASSACHUSETTS

FREDERICK C. UHLE

RECEIVED JULY 6, 1954

## BOOK REVIEWS

**Fluorescence of Solutions.** By E. J. BOWEN, M.A., D.Sc., F.R.S., Fellow of University College and Aldrichian Proeclor in the University of Oxford; and FRANK WOKES, Ph.D. (Lond.), B.Sc., F.R.I.C., Ph.C., Director of Ovaltine Research Labs., King's Langley, Herts., England. Longmans, Green and Co., Inc., 55 Fifth Avenue, New York 3, N. Y. 1953. vii + 91 pp. 14.5 × 22 cm. Price, \$4.65.

In the preface the authors state that this book is intended for students and practical workers who need an elementary introduction to the subject of fluorescence of solutions, together with information about methods of measurement. In accordance with this idea the subject matter is presented in a manner capable of being understood by persons with only the most elementary knowledge of chemistry and physics.

The book is divided into ten short chapters. The first chapter compares fluorescence with other radiation, the second discusses energy considerations. The third chapter on fluorescence and modern theory of wave mechanics seems the least useful in the book since that subject does not lend itself to such brief and qualitative treatment. The fourth chapter discusses some instrumental factors affecting the measurement of fluorescence. The next two chapters deal with the theory and kinetics of quenching with the discussion including various ideas about the mechanism of quenching as well as the equations which apply. The seventh chapter on the detection of fluorescence is concerned primarily with the characteristics of the various types of photocells which may be used. The next chapter describes light sources, filters and several arrangements which may be used in the measurement of fluorescence intensities. The last two chapters discuss details of measurement and methods of fluorimetric assay. These chapters include the preparation of standards, corrections for instrumental blanks, elimination of interfering substances, and recovery of experiments.

This book will be of little interest to the advanced student but will be of great help to the beginning student or to the technician who wishes to know more about the basic principles underlying the study of fluorescence. For the latter purpose the selection of material is good and the presentation clear. The book is also excellent in its mechanical features.

UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA

G. K. ROLLEFSON

**The Physical Chemistry of the Silicates.** By WILHELM EITEL, Director of Silicate Research, University of Toledo. The University of Chicago Press, 5750 Ellis Avenue, Chicago 37, Illinois. 1954. xvii + 1592 pp. 18 × 25 cm. Price, \$30.00.

The first edition of "Physikalische Chemie der Silikate" by Wilhelm Eitel appeared in Germany in 1929 when the work of W. L. Bragg on crystal lattices was in its infancy and the knowledge of ionic bonds in silicates was extremely limited.

The second edition appeared in Leipzig in 1941, augmented principally through significant studies of silicate systems made in the Geophysical Laboratory in Washington, and great forward strides made in the field of hydraulic cements. The richly illustrated German volume was lithographed in 1944 and distributed in America "in the Public Interest by Authority of the Alien Property Custodian."

The former director of the Kaiser Wilhelm Institut für Silikatforschung of Berlin, now director of the Institute of Silicate Research in the University of Toledo, also authors

the present edition of "The Physical Chemistry of the Silicates" in English.

The volume is divided into five sections. Section A (3 chapters) considers crystalline structure, the glassy state, colloidal systems. Chapter I deals with the  $SiO_4$  group in tetrahedral arrangements, including special structures, islands, group complexes, chain structures, layer structures, framework structures; discusses isomorphism and effects on crystalline solutions; structures for silicates and the structure of clay minerals. Chapter II is on the fused and glassy states with a study of their physicochemical properties and constitution. In Chapter III we encounter colloids, the investigative methods pertaining thereto and the effects of the colloidal state on various ceramic materials.

The two chapters of Section B on fusion and polymorphic equilibria in dry silicate systems include, in Chapter I, general remarks, methods for measuring fusing points, supercooling and heating, crystallization and inversions; in Chapter II, special silicate combinations, from  $SiO_2$  through binary and polynary systems.

Section C deals with silicate systems that involve volatiles; also zeolites and permutites. Chapter I is concerned with gas absorption and evolution, the participation of the host ( $SiO_2$ , etc.) in heterogeneous gas reactions; fluorides in the melt; equilibria between  $SiO_2$  and carbonates (normally and under pressure); hydrothermal syntheses with quantitative equilibria; resorption and weathering; solubility. Chapter II covers silicate hydrates of zeolite and permutite types; dehydration and types of water binding with changes in structure; gas and liquid sorption, base exchange.

Section D has three chapters on solid-state reactions and their ceramic uses. Chapter I discusses sintering, the kinetics and reactions in contacting solids and material migration, consequent structural defects; silicate syntheses; inversions; gas-atmosphere influences; electrolytic conductance and thermal effects in solid powders; radioactive tracer studies. Chapter II deals with thermal changes in clays; mullite formation in fired clays, porcelains and refractories; other ceramic bodies; silica glass. Chapter III concerns itself with hydraulic cements, formation and constitution of Portland cement clinkers, their microscopic and X-ray studies, phase equilibria, effects of ferric oxide, alkalies, fluorides, and the role of magnesia, lime and alumina; finally hydration of cements is considered under various conditions.

Section E on silicate melts as "Industrial Glasses and Slags" in Chapter I tells of the making of these and states general tendencies and properties. Chapter II gives a brief treatment of industrial slags.

There follows a 20 page key to industrial periodicals on silicate research, a subject index, an index to mineral and rock species, an index on special silicate equilibria, an alphabetical index of silicate and related systems, one of chemical compounds and finally an author index. The author index and the subject index refer to sections and paragraph numbers and not to pages.

There are five sections as in the American printing of the third German edition and similar indexes but the treatment of the subject is more elaborate and complete. The new volume is twice as large. The volume has received careful preparation and editing and is well illustrated. Although the volume was published in 1954, there are no references beyond 1952. As the first publication of its kind in the English language it will find a welcome spot in glass, enamel, refractory, mineralogical and other libraries.

UNIVERSITY OF PITTSBURGH  
PITTSBURGH, PENNSYLVANIA

ALEXANDER SILVERMAN