loses a considerable portion of its label when treated with mercaptoethanol. This effect is shown in the last column of the table.

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RECEIVED NOVEMBER 27, 1950

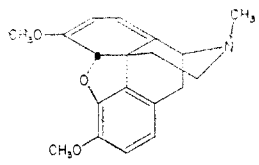
THE STRUCTURE OF PHENOLIC DIHYDROTHEBAINE AND OF β-DIHYDROTHEBAINE

Sir:

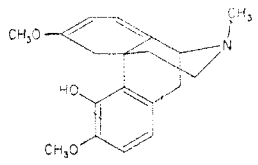
Thebaine (I) gives with sodium and alcohol,[1,2] as well as with sodium and liquid ammonia,[3] a phenolic dihydro compound, called phenolic dihydrothebaine, to which structure II has been assigned. This formulation is not compatible with the ultraviolet absorption spectrum of the compound which shows the low extinction coefficient associated with the guaiacol system ($\lambda_{max.}$ 282 mμ, log ε 3.3) without the additional presence of a conjugated alkoxydiene (compare thebaine hydrochloride, $\lambda_{max.}$ 283 mμ, log ε 3.8). The formation of a conjugated diene in good yield by a sodium and alcohol reduction is also not in accord with expectations.

The infrared absorption spectrum of phenolic dihydrothebaine has now been recorded and allows the assignment to the substance of structure III. This spectrum shows two sharp very characteristic bands at 5.9 and 6.0 μ which have been shown in this Laboratory to be characteristic of the unconjugated dihydroanisole system, while there is no band associated with the 1-alkoxy-1,3-diene between 6.1 and 6.2 μ. The new structure obviously fits all the accumulated data on the chemistry of the compound but requires interchange of the structures assigned[2] to "$\Delta^{5,6}$-dihydrothebainone methyl enolate" and "$\Delta^{6,7}$-dihydrothebainone enol methyl ether."

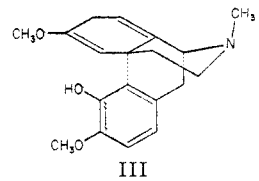
Recently, Schmid and Karrer[4] have proposed that the lithium aluminum hydride reduction product of thebaine, also a phenolic dihydro compound, which they called β-dihydrothebaine has structure IV with the unnatural configuration at C_{14}.



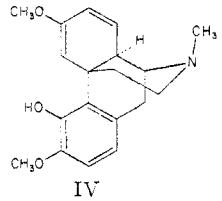
I



II



III



IV

This view is difficult to reconcile with the stereochemistry of thebaine or the formation of dihydrothebainol-6-methyl ether on further catalytic hydrogenation. It is indeed apparent that Schmid and Karrer's substance has the structure formerly assigned to phenolic dihydrothebaine and is II, a fact in accord with the ultraviolet spectrum of the compound ($\lambda_{max.}$ 284 mμ, log ε 4.05). In agreement with this view it has now been found that the substance shows the same infrared spectrum as thebaine in the relevant region.

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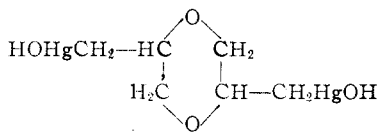
(1) M. Freund and C. Holtoff, *Ber.*, **32**, 168 (1899).
(2) L. Small and G. L. Browning, *J. Org. Chem.*, **3**, 618 (1939).
(3) K. W. Bentley and R. Robinson, *Experientia*, **6**, 363 (1950).
(4) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **33**, 863 (1950).

A DIMER OF HUMAN SERUM ALBUMIN WITH A BIFUNCTIONAL MERCURY COMPOUND

Sir:

A bifunctional organic mercurial[1] of the formula



has been successfully employed to link together two molecules of mercaptalbumin, a protein first isolated as a mercury dimer by reaction with mercuric chloride.[2,3] For brevity we denote the protein as AlbSH and the mercurial as HoHg-RHgOH. By light scattering measurements[4] and ultracentrifugal analysis,[5] evidence has been obtained that the reaction proceeds by the following scheme:

$$\text{AlbSH} + \text{HOHgRHgOH} \rightleftharpoons \text{AlbSHgRHgOH} + \text{H}_2\text{O} \quad (1)$$

$$\text{AlbSHgRHgOH} + \text{AlbSH} \rightleftharpoons \text{AlbSHgRHgSAlb} + \text{H}_2\text{O} \quad (2)$$

Turbidity measurements of a 1% solution of mercaptalbumin at *p*H 4.75 and Γ/2 0.05 showed a rapid increase to 1.8–1.9 times the initial value, within three minutes after the addition of 0.5 mole of the mercurial per mole of mercaptalbumin. This indicates that the total reaction described by steps 1 and 2 proceeds much more rapidly than the corresponding reaction of AlbSH with $HgCl_2$, which requires many hours to reach equilibrium.[6] Subsequent ultracentrifugal analysis showed a single boundary sedimenting faster than normal serum albumin (s = 4.6 S) and comparable to the analogous mercury dimer (s = 6.5 S).[3] The reaction proceeded more slowly at *p*H 6. Dimer formation was reversed, in part or completely, by reagents competing for the mercurial, such as sul-

(1) For preparation and proof of structure see: E. Biilmann, *Ber.*, **33**, 1641 (1900); *ibid.*, **35**, 2587 (1902); and J. Sand, *ibid.*, **34**, 1385 (1901).
(2) W. L. Hughes, Jr., THIS JOURNAL, **69**, 1838 (1947).
(3) W. L. Hughes, Jr., "Protein Mercaptides," *Cold Spring Harbor Symposia on Quantitative Biology*, **XIV**, 79 (1950).
(4) For method see: J. T. Edsall, H. Edelhoch, R. Lontie, and P. R. Morrison, THIS JOURNAL, **72**, 4641 (1950).
(5) Ultracentrifugal analyses were carried out by C. Gordon, and computed by Miss V. Gossard, under the supervision of Dr. J. L. Oncley.
(6) W. L. Hughes, Jr., R. Straessle, H. Edelhoch and J. T. Edsall, Abstracts of Papers, 117th Meeting of the American Chemical Society, 1950, 51C.

fide, cyanide- and iodide ion, or by substances competing for the sulfhydryl group, such as methylmercuric nitrate, mercuric ion, and excess of the mercurial itself.

The dimer has an appreciably smaller solubility than the monomer. This property in conjunction with the rapid rate of dimer formation has proved useful in the isolation of the mercaptalbumin fraction of human serum albumin. The mercaptalbumin may be recovered by precipitating the mercurial as its very insoluble iodide.

Theoretical implications of the marked effects of mercurial structure on the kinetics of dimerization are being further studied in this laboratory.

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RECEIVED DECEMBER 22, 1950

BOOK REVIEWS

Annual Review of Biochemistry. Volume XIX. J. MURRAY LUCK, Editor, Stanford University, HUBERT S. LORING, Associate Editor, Stanford University, and GORDON MACKINNEY, Associate Editor, University of California. Annual Reviews, Inc., Stanford, California. 1950. xi + 596 pp. 16 × 23 cm. Price, $6.00.

The high quality and great usefulness of the Annual Review series is well attested by the launching of three new reviews (Physical Chemistry, Plant Physiology and Psychology) in 1950. The current volume (XIX) of Annual Review of Biochemistry contains fewer pages than preceding issues, but the amount of material is about the same since a smaller type has been used. The number of chapters (22) is slightly lower than that of previous years, probably as the result of the establishment of other reviews in related fields. However, the number of references cited (somewhat over 4700) is about the same as that of the preceding volume.

Volume XIX contains the customary chapters on enzymes and biological oxidations (3), chemistry of carbohydrates, lipids, amino acids and proteins, nucleic acids, hormones, antibiotics (7), vitamins, nutrition, metabolism of carbohydrates, fats and amino acids (6). Two chapters deal with the composition and metabolism of muscle and of neoplastic tissue; other chapters cover the composition of blood serum and plasma, the pyrrole pigments, immunochemistry and partition chromatography. Each chapter is written by a specialist in the field and summarizes the important papers which appeared between November, 1948 and December, 1949. The rapid increase in the volume of biochemical literature makes these critical reviews invaluable to teachers, students, research workers and others attempting to keep abreast of developments in the various areas of biochemistry.

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Synthetische Methoden der organischen Chemie. Repertorium 3. By W. THEILHEIMER. S. Karger, Ltd., Holbeinstrasse 22, Basel, Switzerland. (New York), 1949. viii + 412 pp. 16 × 23 cm. Price, Sfr. 40.—. (Available through Interscience Publishers, Inc., 215 Fourth Avenue, New York 15, N. Y.; price, $10.00.)

Volumes 1 and 2 of this series, covering the periods 1942–1944 and 1945–1946, have appeared in English translations. The current volume (1946–1948) and Volume 4 will be published only in the German editions but it is expected that translations will be resumed with Volume 5.

These books present a survey of new synthetic methods and modification or improvements of older methods, arranged according to the system of reaction types developed by Weygand. Reaction symbols have been devised which permit a systematic classification of the transformations involved. The individual entries state concisely the starting materials, reaction conditions, products and yields. Reference to the original work is given and often supplementary references, including citations to the early volumes of this series. The text of Volume 3 serves to some extent as a cumulative index, since it contains all of the type reaction headings of the earlier volumes, and cross references are given when no new entries are available. There is provided also a cumulative subject index (50 pp.) to the first three volumes. A short tabulation (3 pp.) of English–German translations of the principal chemical terms used in the index is included.

This type of survey is particularly useful to the research worker as a means of locating new and improved methods for specific reactions, which might otherwise be quite difficult to find in the original literature.

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Elsevier's Encyclopaedia of Organic Chemistry. Series III. **Carboisocyclic Condensed Compounds.** Volume 12B. Naphthalene A. Compounds Containing One Naphthalene Nucleus. Nitrogen Compounds. Edited by F. RADT. Elsevier Publishing Company, Inc., 215 Fourth Avenue, New York 3, N. Y. 1949. Pages 345–1052. 18 × 26 cm. Price, single volume $64.00, For subscribers to Series III $56.00, For subscribers to the complete work $48.00.

Two earlier volumes (Vols. 14 and 12A) of this encyclopaedia have been reviewed by L. F. Fieser (THIS JOURNAL, **70**, 1294(1948)) and W. A. Mosher (*ibid.*, 71, 3579 (1949)). The reader is referred to these reviews for an excellent discussion of the general plan of this monumental undertaking. The reviewer of the present volume (Vol. 12B) can only re-echo enthusiastic approval.

The present work deals with nitrogen compounds of naphthalene. The compounds are listed under the headings: Naphthalene Compounds Containing Nitro Groups; Nitrosonaphthalenes; Hydroxylaminonaphthalenes; Naphthalene Compounds containing NH_2-Groups; Naphthylnitramines; Nitrosohydroxylaminonaphthalenes; Naphthylnitrosamines; Hydrazinonaphthalanes; Diazo-Compounds; Azo-Compounds; Azoxy-Compounds; Triazo-Compounds; Hydroxytriazenes; Triazenes; and Tetrazenes.

As far as possible, derivatives of any given substance have been grouped together. Accordingly, anhydrides of dicarboxylic acids are found under the latter and not under the heterocyclic compounds containing one oxygen. Likewise, methylene ethers of dihydroxy-compounds are considered as derivatives of dihydroxy-compounds. Compounds differing only in their degree of unsaturation are described in immediate succession. Thus, 2-Naphthylhydroxylamine is followed by 5,6,7,8-Tetrahydro-2-naphthylhydroxylamine.

Functional groups in the side chain are given precedence over similar functional groups in the nucleus. Compounds containing the same functional group only once are followed