



tography. Hydrolysis of this fraction gave rise to glycine. The crystalline enzyme from *Aspergillus oryzae*,⁴ also released glycinamide from arginine-vasopressin. The other fraction from the enzymatic hydrolysis was found to contain the other seven amino acids known to be present in vasopressin. This fraction gave a paper chromatographic spot close to the phenol solvent front, whereas the glycinamide showed an R_F of 0.66 in 75% phenol and 0.26 in butanol-acetic acid.

The components of a trypsin hydrolysate of arginine-vasopressin were then partially separated by countercurrent distribution between 2-butanol and 0.1% acetic acid. After 300 transfers the material was collected from those tubes in which glycinamide might be expected. The main component behaved in a fashion identical with glycinamide on the starch column with 2:1 propanol-0.5 *N* HCl as the developing agent. A sample was hydrolyzed and analyzed by starch column chromatography and glycine and ammonia were found in approximately equimolar proportions along with traces of other amino acids. The remaining material from the distribution contained the other seven amino acids of vasopressin in approximately equimolar amounts and only a small amount of glycine. Incubation of this fraction with arginase resulted in liberation of some urea, whereas arginase has no action on the intact hormone under the same conditions.

Since only those peptide bonds involving the carboxyl group of lysine or arginine are known to be hydrolyzed by trypsin,⁵ the liberation of glycinamide by trypsin from vasopressin indicates the sequence arginylglycinamide.

It has been shown that lysine-vasopressin⁶ has the same composition as arginine-vasopressin with the exception that it contains lysine instead of arginine. The trypsin hydrolysis of lysine-vasopressin has also yielded glycinamide. In view of the similarity in biological behavior of the two vasopressins, it would seem logical that the proposed structure for arginine-vasopressin represents also

(4) W. G. Crewther and F. G. Lennox, *Nature*, **165**, 680 (1950).

(5) H. Neurath and G. W. Schwert, *Chem. Rev.*, **46**, 69 (1950).

(6) E. A. Popenoe, H. C. Lawler and V. du Vigneaud, *This Journal*, **74**, 3713 (1952).

that of lysine-vasopressin,⁷ with lysine replacing the arginine.

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(7) A synthesis of the octapeptide structure here proposed for lysine-vasopressin has led to biologically active material (V. du Vigneaud, E. A. Popenoe and R. Roeske, unpublished data). The synthesis was parallel to the synthesis of oxytocin (V. du Vigneaud, C. Ressler, J. M. Swan, C. W. Roberts, P. G. Katsoyannis and S. Gordon, *This Journal*, **75**, 4879 (1953)), with ϵ -tosyllysine replacing leucine and phenylalanine replacing isoleucine in the series of reactions. The crude reaction product of the final step possessed pressor and anti-diuretic activity. The work is being continued.

(8) Appreciation is expressed to the Lederle Laboratories Division, American Cyanamid Company, for a research grant which has aided greatly in this study. Acknowledgment is also made to Parke, Davis and Company and Armour and Company for placing at our disposal posterior pituitary material used as starting material for preparation of the purified vasopressin. We are also grateful to Dr. F. G. Lennox of the Wool Textile Research Laboratory, C. S. I. R. O., Australia, for a gift of the crystalline mold enzyme.

CARBON ISOTOPE CONSTITUTION OF SOME ACETIC ACIDS

Sir:

In the course of a reinvestigation¹ of the carbon isotope effect in the decarboxylation of malonic acid, product acetic acid was to be degraded, by a modification of Phares' application² of the Schmidt reaction,³ to methylamine and carbon dioxide. During development of the modification, trial analyses were made of various commercial reagent grade acetic acids. It was found that there was considerable variation in their carbon isotope constitution.

Through the coöperation of the Carbon and Carbide Chemicals Co. we obtained a sample of glacial acetic acid made at their Niagara Falls plant by the sequence ethylene \rightarrow ethanol \rightarrow acetaldehyde \rightarrow acetic acid. The results of three determinations of the carbon isotope ratios (C^{13}/C^{12}) of carbon dioxide obtained from methylamine (R_M) and from total combustion of the acetic acid (R_D) were: $R_M = 0.010793 \pm 0.000002$; $R_D = 0.010789 \pm 0.000001$. Values obtained experimentally for the carbon isotope ratio of the original carboxyl carbon (R_C) were within a few tenths of a per cent. of that expected from the two just recorded, but were subject to much larger variation. It is believed that this spread was due to erratic inclusion of extraneous carbonate in small amount in the carbonate obtained from the degradation. It seems preferable to calculate R_C from R_M and R_D , whence $R_C = 0.010785 \pm 0.000002$, and $R_M - R_C = 0.000008 \pm 0.000002$. Evidently the symmetry of the ethylene molecule is destroyed in a step which does not distinguish between light and heavy ends of the molecule, and the subsequent reactions are sufficiently quantitative to preclude net isotope fractionation in the product.

The Celanese Corporation of America kindly supplied samples of glacial acetic acid and precursor acetaldehyde, materials made by the air oxidation

(1) F. E. Yankwich and A. L. Promislow, in preparation.

(2) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(3) K. F. Schmidt, *Ber.*, **87B**, 704 (1924).

of propane and butane mixtures in their Bishop, Texas, plant. Four determinations of the carbon isotope ratios of this acetic acid gave the following averages: $R_M = 0.010896 \pm 0.000004$; $R_D = 0.010839 \pm 0.000004$. Upon combination, these data yield: $R_C = 0.010782 \pm 0.000006$; $R_M - R_C = 0.000114 \pm 0.000007$. The results obtained for the acetaldehyde were similar, but subject to larger error: $R_M - R_C = 0.000100 \pm 0.000020$. In the air oxidation process, it would appear that little if any discrimination between C^{12} and C^{13} in the aldehyde groups occurred during the oxidation of that compound, but that most of the difference in isotopic constitution of the acetic acid carbon atoms arose antecedent to that oxidation, most probably in the step in which the symmetry of the

original hydrocarbon molecule is destroyed. This is a particularly interesting result because of the reported essentially random distribution of the carbon isotopes in petroleum hydrocarbons.

Samples of acetic acid and related compounds from other sources are being examined. It is hoped that the findings will assist in the understanding of the complicated oxidations involved in the production of these materials in nature and in commerce.

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BOOK REVIEWS

Elsevier's Encyclopaedia of Organic Chemistry. Series III—Carboisocyclic Condensed Compounds. Vol. 14—Supplement 2, Triterpenes. By F. RADT AND DORA STERN (Editors). Elsevier Publishing Co., 402 Lovett Boulevard, Houston, Texas. 1952. xxxii + pp. 939s-1346s. 18 × 26 cm. Price, Single Issue \$40; Series Subr. \$35; Set Subr. \$30.

In view of the recent extensive developments in the chemistry of tetracyclic and higher cyclic compounds, a field covered in volume 14 of this series, the appearance of a supplement is most timely. To date, two such supplements have been published, the first covering compounds of this series excluding triterpenes and sterols and the present volume which includes only the chemistry of the triterpenes. The authors state that a supplement covering steroids will appear subsequently.

The triterpene Supplement covers the field between the years of 1937 and 1946. In most cases, however, the important work reported by early 1952 also has been included. The expansion made in this book over the original volume can be illustrated by the following figures; the entire discussion of the triterpenes was only 85 pages in the original volume whereas the Supplement contains 400. A typical expansion is to be found in the tetracyclic triterpenes where the chemistry of lanosterol has increased from 2 to 53 pages.

The general arrangement of this Supplement follows that employed for the original edition (for a review see *THIS JOURNAL*, 70, 1294 (1948)) and, in addition, certain desirable features have been added. At the top of every other page, a skeletal structure complete with the ring numbering employed has been inserted. Each section has a general flow sheet of the transformations reported, complete with reaction conditions, literature references and the supplement page number where the compound will be found discussed in detail. Again, the preparation of these reaction schemes has been done in a wonderful manner and the clarity of the set-up is to be commended.

With regard to nomenclature and ring numbering, the authors have employed that used by the workers in the field. For example, the tetracyclic triterpene lanosterol has been indexed as a C_{30} -sterol. As a result of this change which has only been in the literature for a year, the ring numbering in the Supplement will be different from that in the majority of papers in the literature quoted. The compounds related to euphol, however, have been retained as derivatives of triterpenes.

An additional section has been added to the Supplement which looks ahead to the future when the interconversions

between arbitrary series have become so numerous that the compounds will be arranged on the basis of ring structure. Accordingly, 26 pages have been devoted to listing, systematically, the triterpenes as derivatives of polycyclic aromatic hydrocarbons.

In view of the completeness, clarity and timeliness of this supplementary edition, it will be of great value to workers in the field of triterpenes and related subjects.

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Experimental Nuclear Physics. Volume I. Edited by E. SEGRE. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1953. ix + 789 pp. 15.5 × 23.5 cm. Price, \$15.00.

The Preface to this wonderful book gives its purpose as that of "bringing the experimentalist up to date in experimental techniques, point out to him the significant facts and data, and indicate the broad lines of theoretical interpretation." The reviewer believes this is exactly the end accomplished.

The sections are five in number, the first, written by Hans H. Staub, being on Detection Methods—Geiger counters, scintillation counters, crystal counters, proportional counters, ionization chambers, cloud chambers, photographic plates and Cerenkov counters, as well as the principles of the ionization of gases by ions and electrons, the behavior of electronic instruments, and typical constructions and methods of operation of the instruments described. The second part, written by H. A. Bethe and Julius Ashkin, on the Passage of Radiations through Matter, has the usual completeness and authority of Bethe treatises on this subject. The third part is a beautifully written and up-to-date account of Nuclear Moments and Statistics, by Norman F. Ramsey. Part IV, also by Ramsey, is on theoretical nuclear two-body problems and nuclear structure. This of all the sections was least pleasing to the reviewer, but it is understandable and interesting. Part V, by K. T. Bainbridge, on mass spectroscopy and isotopic abundances and masses, is magnificent in its clarity and precision and completeness.

The reviewer, a physical radiochemist, is completely convinced that this book should be in the hands of all experimental physicists and most radiochemists. It probably will prove to be the first of an indispensable series. As far