and Rundle[6] predicts a PdDMG O–H stretching frequency of 2450 cm.$^{-1}$ for a collinear hydrogen bond. An examination of the infrared spectrum of PdDMG shows no important absorption band in this region; the O–H stretching band must therefore be weak and diffuse. While the previous assignment[7] of this frequency is believed incorrect, no reassignment has been made by the present authors.

[6] K. Nakamoto, M. Margoshes and R. E. Rundle, THIS JOURNAL, **77**, 6480 (1955).

[7] R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

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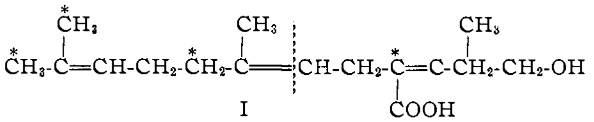
RECEIVED DECEMBER 22, 1958

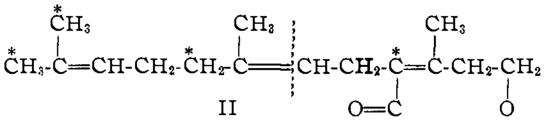
THE DEGRADATION AND STRUCTURE OF A TERPENOID ACID ENZYMATICALLY SYNTHESIZED FROM MEVALONIC ACID[1]

Sir:

In the preceding communication[2] the enzymatic conversion of mevalonic acid (MVA) to a long-chain, olefinic acid was described, and some physical and chemical properties of this acid were given. From these properties and the degradation studies, the most probable structure of this compound is the acid I which is in mobile equilibrium with its lactone II. Indicated by asterisks in I and II are the



I



II

expected locations of isotopic carbon if the conversion of MVA-2-C^{14} to this acid were to occur by the same process which is responsible for the incorporation of MVA into squalene.[3,4]

A 3-mg. sample of the biosynthetic acid,(S.A. 5,353 c./m./mg.) was ozonized, the ozonides were hydrolyzed in aqueous H_2O_2 in the presence of added carrier levulinic acid and acetone, and the 2,4-dinitrophenylhydrazone (DNP) derivatives were prepared and chromatographed. Three radioactive DNP derivatives were obtained, and these are indicated in Table I. The 67% yield of C^{14}-labeled acetone and 41% yield of C^{14}-labeled levulinic acid are sufficient to establish the structure shown to the left of the dotted vertical lines in structures I and II.

TABLE I

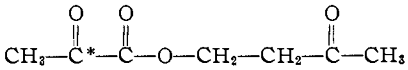
THE SPECIFIC ACTIVITIES OF THE DNP DERIVATIVES ISOLATED AFTER THE OZONOLYSIS OF THE UNSATURATED ACID

Compound	Specific activity (c./m./mg.) Found	Calculated[a]
Acetone DNP	103	153
Levulinic acid DNP	67	164
Unknown DNP	1120	

[a] Calculated on the basis of the theoretical yield of products from the ozonolysis of the acid.

In addition to the DNP derivatives of acetone and levulinic acid, 5 mg. of an unknown radioactive DNP derivative (m.p. 231–234°, dec.) which showed the characteristic insolubility of bis-2,4-dinitrophenylhydrazones was obtained. Paper chromatography of the hydrolysate resulting from the mild alkaline hydrolysis of 0.9 mg. of this unknown DNP derivative yielded three yellow spots with R_f values identical with those obtained from pyruvic DNP[5] (0.47 and 0.65) and 4-hydroxy-2-butanone DNP (0.92). Catalytic hydrogenation[5,6] of 1.9 mg. of the unknown DNP derivative and then an acid hydrolysis resulted in the formation of only one component which gave a purple color with ninhydrin after paper chromatography. This component was radioactive and had an R_f (0.24) identical with that of an authentic sample of alanine.

The foregoing data suggested that the third fragment from ozonolysis was that represented by structure III which could result from the decar-



$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{}^{*}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

III

boxylation of the corresponding ester of oxalacetic acid during the ozonolysis. The bis-DNP derivative (m.p. 231–234°, dec.) of III was synthesized by treating 4-OH-2-butanone DNP with pyruvyl chloride DNP,[7] and the product was found to be indistinguishable by chromatographic behavior and other criteria from the unknown DNP derivative.

The only structure which appears to be consistent with the above degradation data is that depicted as acid I and its lactone II.

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[1] This work was supported by grants from the U. S. Public Health Service and The Nutrition Foundation, Inc.

[2] See preceding communication, THIS JOURNAL, **81**, 754 (1959).

[3] F. Dituri, S. Gurin and J. L. Rabinowitz, *ibid.*, **79**, 2650 (1957).

[4] J. W. Cornforth, R. H. Cornforth, G. Popjak and I. Youhotsky-Gore, *Biochem. J.*, **66**, 10P (1957).

[5] G. H. N. Towers, J. F. Thompson and F. C. Steward, THIS JOURNAL, **76**, 2392 (1954).

[6] E. Kun and M. G. Hernandez, *J. Biol. Chem.*, **218**, 201 (1956).

[7] H. van Duin, *Rec. trav. chim.*, **73**, 78 (1954).

[8] U. S. Public Health Service Postdoctoral Fellow (1955–1957).

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RECEIVED NOVEMBER 17, 1958

AN *OLEFINIC* FREE-RADICAL SCAVENGER FOR PHOTOCHEMICAL STUDIES IN AQUEOUS SOLUTIONS: APPLICATION TO THE PHOTOLYSIS OF HYDROGEN PEROXIDE AND ACETONE AT 2537 Å.[1]

Sir:

The use of unsaturated compounds which can undergo free-radical addition has wide application in the study of mechanisms of thermal and photochemical reactions. For photochemical reactions in water solutions the choice of an appropriate trap is severely limited by considerations of transparency and solubility. For example, acrylamide has been used successfully as a scavenger in the study of the photolysis of hydrogen peroxide solutions at 3130 Å.,[2] but it is not sufficiently transparent for use at

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[1] Sponsored by the Office of Ordnance Research, U. S. Army and by the Research Corporation.

[2] F. A. Dainton, THIS JOURNAL, **78**, 1278 (1956).

2537 Å. For wave lengths as short as 2537 Å., acrylonitrile has been used to detect free-radicals in protein photolysis.[3] However, at concentrations where this molecule successfully traps free-radicals, subsequent polymerization proceeds to such an extent as to change the properties of the solution seriously, and therefore we have, found it unsuitable for quantitative studies.

We wish to report the use of allyl alcohol, water soluble and transparent at 2537 Å., as a scavenger for free radicals formed in the photolysis of hydrogen peroxide and acetone in aqueous solutions. Allyl alcohol proved to be efficient in capturing free-radicals and polymerization was limited to low molecular weight water soluble products which did not appreciably change the properties of the system.

The quantum yield for the decomposition of hydrogen peroxide at 2537 Å. in water solution at high intensity and low concentration, limiting or non-chain conditions, is reported in recent studies as 0.98[4] and 1.00.[5] In the presence of a free-radical scavenger, the generally accepted mechanism gives a quantum yield which is just half that found in the absence of the scavenger. We have determined the quantum yield at concentrations of H_2O_2 in the range 0.002–0.02 mole per liter at intensities in the range 8–50 $\times 10^{-18}$ quanta per liter per second. At 25° the quantum yield in the absence of allyl alcohol is 0.94 ± 0.06. The quantum yields decreased as the concentration of allyl alcohol increased until a minimum value was obtained for an allyl alcohol concentration of about 0.001 *M*. From 0.001 to 1 M alcohol, the highest concentration used, there was no change in the rate of peroxide decomposition. The quantum yield obtained was 0.54 ± 0.05. Evidence that the principal reaction products were three isomeric forms of tetrahydroxyhexane was obtained. This indicates that the mechanism is the addition of hydroxyl radicals to allyl alcohol in either the 2 or 3 position with subsequent association of the resultant diol free-radicals. In fact this process appears promising as a synthetic method for the tetrahydroxyhexanes.

For aqueous acetone systems, knowledge of the photochemistry is much less complete, and the system is more complex. The effect of allyl alcohol on the gaseous products and on the acetic acid formed in solution at 25° are shown in Table I. Irradiation time and intensity were kept constant. These results show that allyl alcohol can act as a free-radical scavenger also in this system.

TABLE I

PHOTOLYSIS OF 0.1 *M* AQUEOUS ACETONE AT 2537 Å.

Allyl alcohol, m./l.	Moles of product $\times 10^4$			
	Methane	Ethane	Carbon monoxide	Acetic acid
0	1.04	0.26	0.031	0.45
0.06	0.27	.02	.023	.23
0.12	0.13	.01	.013	.03

Further work on these systems is continuing and will be reported in a detailed paper.

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[3] E. K. Rideal and R. Roberts, *Proc. Roy. Soc.* (*London*), **A205**, 391 (1951).

[4] J. P. Hunt and H. Taube, THIS JOURNAL, **74**, 5999 (1952).

[5] J. H. Baxendale and J. A. Wilson, *Trans. Faraday Soc.*, **53**, 344 (1957).

BOOK REVIEWS

Electromagnetic Isotope Separators and Applications of Electromagnetically Enriched Isotopes. By J. KOCH (Editor), University of Copenhagen, R. H. V. M. DAWTON and M. L. SMITH, Atomic Energy Research Establishment, Harwell, and W. WALCHER, University of Marburg/Lahn. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y., 1958. xi + 314 pp. 15.5 × 23 cm. Price, $7.50.

With the increasing interest among nuclear chemistry and physics laboratories in pure isotopic species for critical research applications, the appearance of the above book is both timely and informative. It is not an exhaustive treatise on the engineering details of isotope separator construction, but does contain an account from well-qualified authors on the construction, operation, technique, and research applications of medium size separators as well as chapters pertaining to the large separators at both Oak Ridge and Harwell.

The presentation of the subject matter is well organized. The authors have essentially divided the book into three main headings. The first section is on the history of early equipment and experiments in both natural and radioactive isotope separation, which culminates with a chapter on details of the instruments located in Marburg, Copenhagen, Stockholm, Uppsala, Saclay and Gothenburg. The second section is devoted to large separators in the United States and in Britain and also includes the equipment located at Amsterdam. In this section is a chapter on operational experience in the separation of over sixty of the elements. The chapter on enriched isotope applications is particularly good. Since the literature on applications is prolific, the authors have chosen to expand on a few selected examples such as energy level and scattering studies, neutron cross section work, carrier-free radioactive tracers, and the broad applications to various optical and microwave spectroscopic research. The third section gives a very readable discussion of sector fields and their focusing properties, high current ion source construction, and space charge problems associated with the design of isotope separators.

The book is highly recommended to the potential worker contemplating efforts in this field and to the specialists for the excellent general coverage and a rather complete reference to existing literature.

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