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).

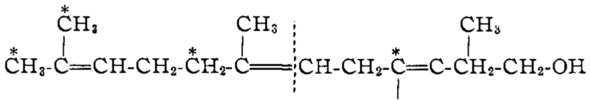
INSTITUTE FOR ATOMIC RESEARCH
AND DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
DONALD E. WILLIAMS
GABRIELE WOHLAUER
R. E. RUNDLE

RECEIVED DECEMBER 22, 1958

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

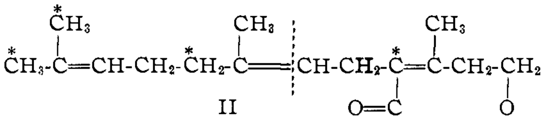
Sir:

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 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]



I

$$\overset{*}{C}H_3-\overset{\overset{\displaystyle \overset{*}{C}H_3}{|}}{C}=CH-CH_2-\overset{*}{C}H_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-\underset{\underset{\displaystyle COOH}{|}}{\overset{*}{C}}=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2-OH$$



II

$$\overset{*}{C}H_3-\overset{\overset{\displaystyle \overset{*}{C}H_3}{|}}{C}=CH-CH_2-\overset{*}{C}H_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-\underset{\underset{\displaystyle O=C}{|}}{\overset{*}{C}}=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-\underset{\underset{\displaystyle O}{|}}{CH_2}$$

A 3-mg. sample of the biosynthetic acid[8](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

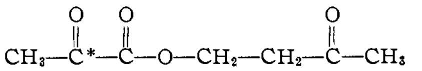
THE SPECIFIC ACTIVITIES OF THE DNP DERIVATIVES ISOLATED AFTER THE OZONOLYSIS OF THE UNSATURATED ACID

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 decarboxylation 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.



III

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

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

---

(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).

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
THE JOHNS HOPKINS SCHOOL OF MEDICINE
BALTIMORE 5, MARYLAND
JAMES W. OGILVIE, JR.[8]

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

---

(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).