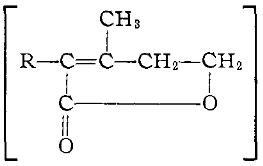
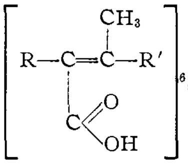
The methyl ester was prepared, purified by vapor phase chromatography, and found to have an absorption maximum at 228 mµ. The infrared spectrum of the acid was characterized by three absorption maxima in the 5 to 7 µ region. These maxima and their tentative assignments are

5.80 µ 

5.91 µ  [6], and 6.09 µ (C=C)[6]

The acid when chromatographed on filter paper in an ethanol–ammonia system[7] migrated as a single spot and had an R_f of 0.75. This spot could be detected by its radioactivity, by spraying with brom thymol blue, or by the decolorization of $KMnO_4$.

Preliminary experiments have indicated that the isolated acid is rather poorly converted to nonsaponifiable lipids by rat liver homogenates. It seems possible that the acid may exist in an activated form prior to isolation or that some minor structural modification, such as a double bond migration, may have occurred during the isolation and purification procedures.

The structure of the isolated acid has been determined and is reported in the following communication.[5]

[6] J. Cason, N. K. Freeman and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951).

[7] E. P. Kennedy and H. A. Barker, *Anal. Chem.*, **23**, 1033 (1951).

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RECEIVED NOVEMBER 17, 1958

CRYSTAL STRUCTURES OF NICKEL AND PALLADIUM DIMETHYLGLYOXIMES[1]

Sir:

Both palladium and nickel dimethylglyoximes (PdDMG and NiDMG) crystallize in the space group Ibam and are nearly isostructural. For NiDMG the intensity data of Godycki[2] were used for least squares refinement on the IBM 650 computer. The nickel scattering factor was corrected for anomalous dispersion.[3] Intensity data from the [*hk*0] and [*hkl*] planes of PdDMG were taken with a Norelco proportional counter using copper radiation. Details of the structure determination have been given previously.[1] Values of the atomic parameters and of the reliability index, *R*, for the two structures are given in Table I, which lists the intramolecular distances and their standard deviations. The lattice constants are a = 16.68 and 16.85, b = 10.44 and 10.49, and c = 6.49 and 6.52 Å. for NiDMG and PdDMG, respectively.

TABLE I

ATOMIC PARAMETERS

Atom	Parameter	NiDMG	Std. dev.	PdDMG	Std. dev.
$\mathrm{O_{I}}$	x	0.1577	0.0009	0.1618	0.0012
	y	.0991	.0014	.0960	.0020
$\mathrm{O_{II}}$	x	.0543	.0009	.0500	.0012
	y	.2589	.0015	.2654	.0021
$\mathrm{N_{I}}$	x	.1111	.0009	.1179	.0013
	y	.9931	.0019	.9901	.0025
$\mathrm{N_{II}}$	x	.9909	.0011	.9868	.0014
	y	.1765	.0014	.1829	.0022
$\mathrm{C_{I}}$	x	.0808	.0013	.0864	.0017
	y	.7741	.0022	.7744	.0028
$\mathrm{C_{II}}$	x	.1440	.0013	.1471	.0018
	y	.8813	.0020	.8748	.0028
$\mathrm{C_{III}}$	x	.0988	.0015	.1076	.0019
	y	.6334	.0024	.6305	.0031
$\mathrm{C_{IV}}$	x	.2348	.0015	.2373	.0020
	y	.8575	.0023	.8522	.0031
	R	.124		.065	

$R = \Sigma||F_0| - |F||/\Sigma|F_0|$

TABLE II

INTRAMOLECULAR DISTANCES (Å).

Distance	NiDMG	Std. dev.	PdDMG	Std. dev.
$\mathrm{M–N_{I}}$	1.85	0.015	1.99	0.020
$\mathrm{M–N_{II}}$	1.85	.015	1.93	.021
$\mathrm{O_{I}–O_{II}}$	2.40	.021	2.59	.030
$\mathrm{O_{I}–N_{I}}$	1.35	.023	1.33	.031
$\mathrm{O_{II}–N_{II}}$	1.36	.023	1.37	.031
$\mathrm{N_{I}–C_{II}}$	1.29	.028	1.31	.038
$\mathrm{N_{II}–C_{I}}$	1.30	.028	1.31	.037
$\mathrm{C_{I}–C_{II}}$	1.54	.031	1.47	.041
$\mathrm{C_{I}–C_{III}}$	1.50	.033	1.55	.044
$\mathrm{C_{II}–C_{IV}}$	1.53	.033	1.54	.045

The PdDMG molecule appears to be less symmetrical than the NiDMG molecule. The two crystallographically different Pd–N and N–O distances differ from each other; the difference appears to be significant for the Pd–N distances. The hydrogen bonded O–O distance in PdDMG is also significantly greater than the corresponding distance in NiDMG. The observed difference in symmetry would be the expected result if NiDMG possessed a symmetrical hydrogen bond and PdDMG an unsymmetrical one, leading to nonequivalence of N–O and Pd–N distances in the latter. It has been estimated by Huggins[4] that at hydrogen bonded O–O distances of 2.65 Å. and below, the hydrogen bond should become symmetrical. This work, as well as recent neutron diffraction results,[5] indicates that Huggins' critical distance is perhaps somewhat high, but does support the thesis of a single potential minimum below a certain O–O distance, and suggests that this limit has been reached in NiDMG.

On the basis of the observed O–O distance, the empirical correlation of Nakamoto, Margoshes

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[1] Contribution No. 698. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[3] C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

[4] M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

[5] G. E. Bacon and R. S. Pease, *Proc. Roy. Soc.* (*London*), **A230**, 359 (1955).

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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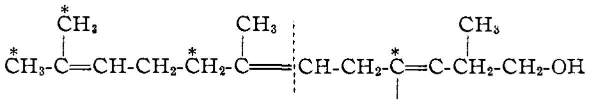
RECEIVED DECEMBER 22, 1958

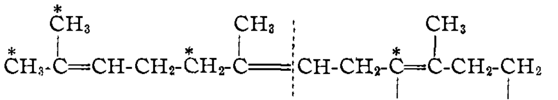
THE DEGRADATION AND STRUCTURE OF A TERPENOID ACID ENZYMATICALLY SYNTHESIZED FROM MEVALONIC ACID[1]

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,[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.

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.

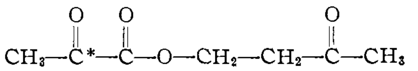
TABLE I

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.

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



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

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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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).