

[CONTRIBUTION FROM THE NAVAL STORES LABORATORY¹ AND THE UNIVERSITY OF FLORIDA]**The Ultraviolet Irradiation of the Cyclohexa-1,3-diene, Levopimaric Acid²**WALTER H. SCHULLER, RICHARD N. MOORE, JOHN E. HAWKINS,³ AND RAY V. LAWRENCE

Received November 29, 1961

The ultraviolet irradiation of the polycyclic cyclohexa-1,3-diene, levopimaric acid, yields photolevopimaric acid, the structure of which is considered to be the 6,14-bridged valence tautomer based on the evidence presented. An apparent correlation between the course of the reaction upon the ultraviolet irradiation of compounds containing the cyclohexa-1,3-diene moiety and the preferred conformation of a corresponding cyclohexenyl precursor is described. This correlation would seem capable of extension to certain other conjugated unsaturated cyclic systems.

The ultraviolet irradiation of various cyclic dienes has received considerable attention in recent years.^{4,5} A classic reaction of interest in this area is the ultraviolet irradiation of ergosterol⁶ to yield vitamin D. Work in this laboratory was started in 1955 on the ultraviolet irradiation of the polycyclic cyclohexa-1,3-diene, levopimaric acid (I), the major resin acid of pine gum. It had previously been reported^{7,8} that exposure of an alcohol solution of levopimaric acid to ultraviolet irradiation resulted in a change of specific rotation. The ultraviolet irradiation of one other resin acid, the conjugated heteroannular diene, abietic acid, has been investigated and reported⁹ to yield di- and tetrahydroxy abietic acids.

In the present work, the irradiation of levopimaric acid in absolute ethanol was found to give a crystalline product in crude yields up to 81%. The pure compound, termed photolevopimaric acid, m.p. 115–116° and $[\alpha]^{25D} + 79.2^\circ$ contained no conjugated unsaturation (no characteristic absorption from 220–320 $m\mu$) and was of unchanged neutralization equivalent, elemental analyses, and molecular weight as compared to the starting material. The ultraviolet (λ_{max} 210, ϵ 3620) and infrared absorption spectra (λ_{max}^{Nujol} 12.13, 12.41 μ) indicated the presence of a vinyl hydrogen on a trisubstituted double bond.^{10,11}

Heating photolevopimaric acid for forty minutes at 120° gave a 67% conversion to levopimaric

acid which was isolated and its identity confirmed on the basis of specific rotation, ultraviolet, and infrared spectrum. A plot of time vs. $\log \left(\frac{18.2 - \alpha_{272 m\mu}}{18.2} \right)$ from 5–35% conversion was a straight line, characteristic of a first-order reaction. The thermal reversibility of the light induced reaction would suggest that no gross skeletal rearrangement has occurred in the formation of photolevopimaric acid and that the C-13 carbon-to-hydrogen bond very likely remains intact during both the photochemical and thermally induced reactions.

Photolevopimaric acid was found to absorb only one mole of hydrogen on catalytic reduction to give a mixture of two compounds, separated by recrystallization. The first (26% yield) exhibited m.p. 155.5–156.5°, $[\alpha]^{26D} + 42.8^\circ$, and the second (6% yield), m.p. 203–204°, $[\alpha]^{25D} + 65.2^\circ$, while both exhibited a lack of absorption in the ultraviolet and infrared characteristic of an isolated trisubstituted double bond. Both saturated isomers were found to be of considerably greater thermal stability than photolevopimaric acid.

The loss of conjugated unsaturation on irradiation would suggest that bridging, dimerization, or a double bond shift occurs during the irradiation of levopimaric acid. Dimerization is discounted on the basis of molecular weight. No precedent is known for the shifting of a double bond out of conjugation on irradiation; nevertheless, a migration of the 8,14-double bond into the 13,14-position would represent the single possibility which would accommodate the above data. However, $\Delta^{13(14)}$ -dihydroabietic acid has been prepared^{12,13} and the reported m.p. of 174–175° ($[\alpha]^{25D} + 8.0^\circ$)¹⁴ and 170–172.5° are quite different than the values found for the hydrogenation products from photolevopimaric acid. In addition, both photolevopimaric acid hydrogenation products gave negative

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. References to specific products of commercial manufacture are for illustration only and do not constitute endorsement by the U. S. Department of Agriculture. Article not copyrighted.

(2) Presented before the American Chemical Society, S.E.-S.W. Regional Meeting in New Orleans, Louisiana, December 7–9, 1961.

(3) Deceased.

(4) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

(5) W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959).

(6) R. J. de Kock, N. G. Minnaard, and E. Havinga, *Rec. trav. chim.*, **79**, 922 (1960).

(7) K. Kraft, *Ann.*, **520**, 133 (1935).

(8) H. Wienhaus, H. Ritter, and W. Sandermann, *Ber.*, **69B**, 2198 (1936).

(9) R. F. Brown, G. B. Bachman, and S. J. Miller, *J. Am. Chem. Soc.*, **65**, 623 (1943).

(10) P. Bladon, H. B. Henbest, and G. W. Wood, *J. Chem. Soc.*, 2737 (1952).

(11) P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2403 (1951).

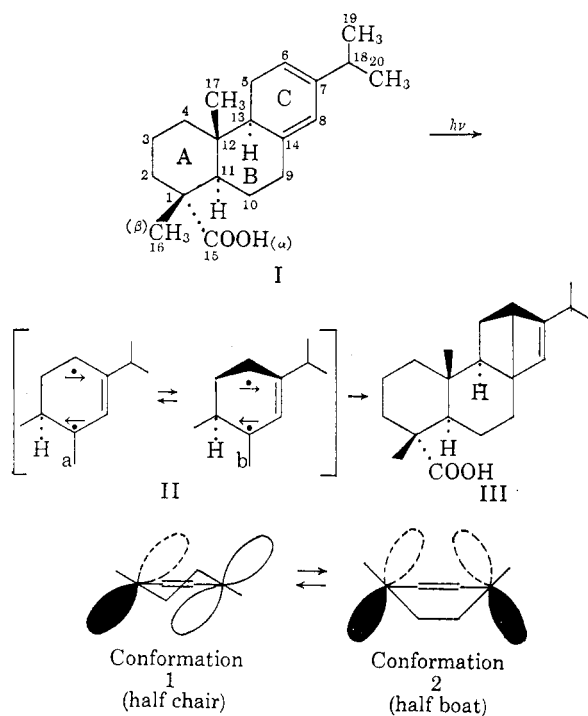
(12) J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4762 (1960).

(13) E. E. Royals, W. C. Bailey, and R. W. Kennedy, *J. Org. Chem.*, **23**, 151 (1958).

(14) E. E. Royals, W. C. Bailey, and R. W. Kennedy, unpublished results.

tetranitromethane tests for olefinic unsaturation while photolevopimaric acid exhibited a positive reaction.

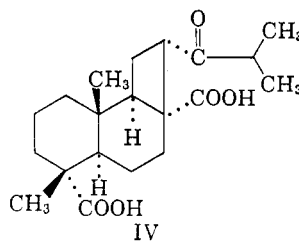
The third possibility, bridging or valence tautomer formation, as an explanation for the loss of one double bond finds as a previous example of this type of irradiation reaction the bridging of the polycyclic cyclohexa-1,3-dienes, isopyrocalciferol,⁵ and pyrocalciferol⁶ as well as a variety of other unsaturated cyclic systems, e.g., cyclohepta-1,3-diene,^{15,16} cycloheptatriene,¹⁵ cyclohepta-2,4-dien-1-ones,^{16,17} and several tropolones.^{4,18,19} The bridged products in the pyrocalciferol series, like photolevopimaric acid, are reported to be readily converted to the starting material on heating and to be of greatly increased thermal stability following hydrogenation.⁵ A parallel bridging reaction in the present case would suggest that photolevopimaric acid has the constitution III.



The experimental data are in accord with this structure. The NMR spectrum (Prof. Werner Herz, Florida State University) of photolevopimaric acid confirms the presence of a single vinyl hydrogen. The location of the peak at a relatively low field is in accord with a vinyl proton on a cyclobutene ring.^{5,15,19} The presence of a cyclopro-

pane ring (unless fully substituted) is ruled out by the absence of cyclopropane ring proton absorption. The presence of an isopropyl grouping is supported by the doubling of the absorption peaks ascribable to the C-19 and C-20 methyls, due to interaction with the tertiary hydrogen at C-18. This behavior has been previously observed in the resin acid series.^{12,20} A broad band in the allylic hydrogen region is assigned²⁰ to a single tertiary allylic hydrogen at C-18 and a triplet at a somewhat higher field is associated with a single allylic tertiary proton at C-6. Bands ascribable to the C-16 and C-17 methyl groups^{12,20} are also observed.

Treatment of photolevopimaric acid with ozone followed by the oxidative decomposition of the ozonide with chlorine²¹ gave a product in high yield which exhibited the correct neutralization equivalent and elemental analyses for the dibasic acid IV to be expected from the ozonolysis of



III. The NMR spectrum of the dibasic acid (Prof. W. Herz) exhibited two methyl doublets associated with the isopropyl group and split by the tertiary hydrogen of that group. The signals were superimposed on a methyl singlet corresponding to the C-17 methyl while the presence of another methyl singlet at a higher frequency was associated with the C-16 methyl. No vinyl hydrogen nor cyclopropane hydrogen signals were observed. The presence of the ketonic grouping in the oxidation product was established by the preparation of a 2,4-dinitrophenylhydrazone which exhibited an ultraviolet absorption spectrum characteristic of 2,4-dinitrophenylhydrazones of saturated ketones.²² The value of $M_D + 224$ for the dibasic acid is close to that for photolevopimaric acid, $M_D + 239$, which is consistent with the proposed structures as no asymmetric centers are formed or destroyed in the reaction as pictured.

The configurations indicated in III are based on the excessive strain of a trans fusion between ring B and the cyclobutane ring. The C-13- α assignment in I is according to Schuller and Law-

(15) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(16) O. L. Chapman and D. J. Pasto, *Chem. & Ind. (London)*, 53 (1961); 54 (1961).

(17) G. Buchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

(18) O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **82**, 3642 (1960).

(19) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *J. Am. Chem. Soc.*, **82**, 1768 (1961).

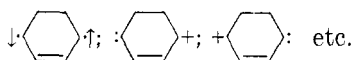
(20) W. H. Schuller and R. V. Lawrence, *J. Am. Chem. Soc.*, **83**, 2563 (1961).

(21) L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961).

(22) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold (Publishers) Ltd., London, 1955, pp. 53, 106.

rence.^{20,23} Support for the configurations as indicated in III is also found in the fact that molecular models of III in which the fusion of ring B and the cyclobutane ring is *trans* show that the 7,8-double bond would be almost completely shielded on one side by the C-17 angular methyl and the C-7 isopropyl grouping. Under these circumstances, attack by the palladium-hydrogen complex during reduction would be expected to occur almost exclusively from one side to yield essentially a single saturated product.

The ultraviolet irradiation of homoannular conjugated hexadienes has been reported to result in bridging in some cases⁵ and to ring opening to a triene in others.^{4,6,24} Photochemical excitation and the subsequent reactions of this system would seem to involve the excited singlet state.²⁵ Important resonance forms of the excited singlet state might be written^{26,27};



The presumed preferred conformations of the cyclohexenyl structures (conformations nearest those most stable in the ground state) would then seem to be logically related to the course of the reaction. This correlation might be rationalized in terms of the non-photochemical transformation of the excited state to ϵ preferred (lowest energy conformation) transition state followed by a collapse to product(s) in the ground state. The conformation differences are most easily seen in the construction of models by assuming sp^2 hybridization²⁸ for both alpha carbon atoms.

The half-chair form of cyclohexene is more stable than the half-boat form by 2.7 kcal.²⁹ due chiefly to the nonbonding interactions among the two sets of eclipsed hydrogen atoms in the half-boat form. Thus, the two most stable conformations of the cyclohexenyl resonance forms of the excited state of cyclohexa-1,3-diene⁶ would be expected to be the two symmetrical half-chair forms resulting from ring flip. These conformations are relatively similar to conformation 1 (see above) and from the direction of the bonding p orbitals, it would seem consistent to expect little tendency for sigma bond formation. The same reasoning would apply to α -phellandrene⁶ and to

α -terpinene.³⁰ Examination of models (*e.g.*, Dreiding Stereomodels) of similar resonance structures derived from ergosterol,^{5,6} lumisterol,^{5,6} methyl dehydroursolate acetate,⁴ 7-dihydrocholesterol,²⁴ 7-dehydro-19-norcholesterol,²⁴ and 19-nor- $\Delta^{5,7}$ -androsteradiene-3B-17B-diol²⁴ indicates that the preferred conformations are also similar to conformation 1 above. It may be assumed from the course of the reaction in all of the above cases, that when cyclization is not anticipated, (*i.e.*, conformation 1) collapse to the ground state occurs with opening of the 5,6-sigma bond.

Examination of models of similar resonance structures derived from pyrocalfiferol⁵ and isopyrocalfiferol⁵ indicates that the preferred conformation is similar to conformation 2 above and collapse to the ground state with formation of a new sigma bond (bridging) is consistent with the direction of the bonding p orbitals and anticipated orbital overlap.

The consideration of models of similar resonance structures derived from levopimaric acid indicates that the effect of the fused A-B ring system on only one side of the cyclohexenyl ring system is to yield two preferred (rings A and B in chair forms) unsymmetrical conformations 1 and 2 (IIa,b; see above) in contrast to the monocyclics. Conformations IIa and IIb would appear to differ very little in energy content, however, as the single C-13-hydrogen atom is not eclipsed by either of the C-5-hydrogen atoms in either conformation. Cyclization of conformation 2 (IIb) yielding III, would thus seem to indicate that bridging is the preferred course of the general reaction as opposed to ring opening to a triene.

The extension of this general approach to more complicated conjugated unsaturated ring systems appears possible. The observed *ring opening* on irradiation of cyclohexa-2,4-dien-1-ones⁴ and 3,5-cycloheptadien-1-ones³¹ is in accord with the observation that molecular models of the presumed cyclohexenyl resonance structures indicate that the conformation involving the minimum amount of nonbonding interactions between hydrogen atoms is similar to conformation 1 with respect to the relative directions of the bonding p orbitals. The *bridging* of the tropolones^{4,18,19} cyclohepta-1,3-dienes,^{15,18,32} cyclohepta-1,3,5-triene,¹⁵ and cyclohepta-2,4-dien-1-ones,^{16,17} is again in accord with the observation that molecular models

(23) W. H. Schuller and R. V. Lawrence, *Chem. & Ind. (London)*, 105 (1961).

(24) L. Velluz, B. Goffinet, and G. Amiard, *Tetrahedron*, **4**, 241 (1958).

(25) E. Havinga, R. J. DeKock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960).

(26) J. P. Simons, *Quart. Rev. (London)*, **13**, 3 (1959).

(27) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley Sons, Inc., New York, 1955, Chap. 6 and 7.

(28) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, 1959, pp. 685-687; 338-339.

(29) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948).

(30) W. H. Schuller and R. V. Lawrence, unpublished results. The ultraviolet irradiation of an ethanol solution of α -terpinene (λ_{\max} 266 $m\mu$) results in a steady increase in absorption with the development of λ_{\max} 252, 261 (major peak) and 271 $m\mu$. *trans*-2,5-dimethylhexatriene-(1.3.5) exhibits λ_{\max} 252, 261 (major peak), 272 $m\mu$, as reported by K. Alder and H. von Brachel, *Ann.*, **608**, 195 (1957).

(31) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961).

(32) J. Rigaudy and P. Courtot, *Tetrahedron Letters*, **3**, 95 (1961).

of the presumed cyclohexenyl resonance structures indicate that the conformation involving the minimum number of nonbonding interactions between hydrogen atoms is similar to conformation 2 with respect to the relative directions of the bonding p orbitals. Thus, the above approach might be found useful in predicting the results from compounds not yet irradiated.

It has been shown that the irradiation of levopimaric acid with visible light in the presence of a photosensitizing dye and an excess of oxygen gives the transannular peroxide, 6,14-peroxy- $\Delta^{7(8)}$ -dihydroabiatic acid.³³ It was thus of present interest to determine the behavior of levopimaric acid on irradiation with ultraviolet light in the presence of an excess of oxygen. The reaction resulted in the destruction of the conjugated diene system. A crude solid was obtained which appeared to be a mixture of dehydroabiatic acid and of peroxides, some of which were apparently hydroperoxides (reduced by bisulfite²⁰); however, no pure compounds could be isolated. Treatment of the product with base did not result in the development of absorption from 220–320 $m\mu$; thus the absence of 6,14-peroxy- $\Delta^{7(8)}$ -dihydroabiatic acid can be assumed.³³ This would tend to strengthen the notion that the irradiation of levopimaric acid with ultraviolet light yields a singlet²⁵ rather than a triplet excited state.

TABLE I
PHOTOLEVOPIMARIC ACID

Hydrogen Assignment	τ
Vinyl hydrogen	4.25 (1) ^a (center of multiplet)
Tertiary allylic hydrogen on C-18	7.25 (1) ^a (broad band)
Tertiary allylic hydrogen on C-6	7.70 (1) ^a (center of triplet)
Ring hydrogens	8.0–8.5
Hydrogens on C-16 methyl	8.66 (3) ^a (singlet)
Hydrogens on C-17 methyl (angular)	8.87 (3) ^a (singlet)
Hydrogens on C-19 and C-20 methyls	8.87 and 8.88 (3) ^a (doublet overlapping C-17 singlet) 8.98 and 9.02 (3) ^a (doublet)

^a Numbers in parentheses indicate number of protons represented by the peak.

EXPERIMENTAL³⁴

Preparation of photolevopimaric acid (III). A solution of 0.906 g. of levopimaric acid in 30 ml. of absolute ethanol (0.10 M) was charged to a fused quartz actinometer cell 75 mm. in

diameter, 10 mm. thick, of 32 ml. capacity and with a bottle mouth opening at the top. No effort was made to exclude air from the reaction mixture other than that the reactor was stoppered before irradiation was begun. The vessel was irradiated at a right angle to the face with an unfiltered (transmits from 185–400 $m\mu$) Hanovia quartz high pressure mercury-vapor arc lamp (100 watts; Model 30600) at a distance of 30 cm. The reaction was followed by the change in specific rotation and also by frequent determinations of the absorption spectrum from 220–320 $m\mu$. The reaction was found to be of zero order for the first three quarters (45-hr. irradiation) of the observable change in specific rotation and the decrease in absorption at 272 $m\mu$, after which the rate progressively decreased to the final values (85 hr. irradiation) $[\alpha]^{25D} +40^\circ$ and $\alpha_{272 m\mu}$ 0.8, with no characteristic absorption from 220–320 $m\mu$ exhibited by the reaction mixture. Water was added short of turbidity and the solution allowed to stand. The product precipitated to give 0.73 g. (81%) of crude material, m.p. 95–106°. One recrystallization from aqueous ethanol gave 0.42 g. (46%) of m.p. 112–114°.

The irradiation, when carried out with the same lamp equipped with a Vycor heat-deflecting filter No. 7910 (transmits 210–up $m\mu$) and a nickel oxide filter No. 9863 (transmits 230–420 $m\mu$) at a distance of 10 cm. from lamp to actinometer cell gave a solution of final $[\alpha]^{25D} +60^\circ$; on addition of water 0.62 g. (68%) of needles were obtained m.p. 113–114.5°. One recrystallization from aqueous ethanol gave 0.54 g. (60%) of m.p. 115–116°, unchanged on further recrystallization; $[\alpha]^{25D} +79.2^\circ$ (c 0.97); $M_D +239$; no characteristic absorption from 220–320 $m\mu$; λ_{max} 210 $m\mu$, ϵ 3620; λ_{max}^{Nujol} 12.13, 12.41 μ ; positive tetranitromethane test for unsaturation.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.4; H, 10.0; neut. equiv. 302. Found: C, 79.4, 79.5; H, 10.0, 10.1; neut. equiv. 304; molecular weight *via* the Signer method³⁵ employing absolute ether as the solvent and levopimaric acid as the reference compound: 302, 302.

The irradiation, when carried out at 0.2 M and 0.3 M concentrations, employing the Hanovia lamp equipped with filters transmitting from 230–420 $m\mu$, gave yields of 66% (m.p. 109.5–111°; after one recrystallization from ethanol, yield 47% and m.p. 112–114°) and 71% (m.p. 112.4–114°), respectively.

Irradiation of an *n*-heptane solution of levopimaric acid resulted in essentially the same changes in specific rotation and ultraviolet spectrum although the rate of change was somewhat slower.

The methyl ester of photolevopimaric acid was prepared employing diazomethane; however, the ester could not be crystallized.

The use of a red-purple filter No. 5874 (transmits 305–410 $m\mu$) with the above Hanovia lamp did not bring about a transformation of levopimaric acid to photolevopimaric acid.

Thermal isomerization of photolevopimaric acid. A sample of photolevopimaric acid was heated for 5 min. at 200° in an oil bath. The ultraviolet spectrum of the solid changed from one showing no selective absorption to one exhibiting λ_{max} 241, 252, and 266 $m\mu$.

A sample of photolevopimaric acid weighing 0.128 g., was placed in a small test tube and immersed in a constant temperature oil bath at 120°. The reaction was followed for 20 min. by the removal of small amounts of product at intervals and measurement of the ultraviolet spectrum over the range 220–320 $m\mu$ in ethanol. The data are given as minutes, $\alpha_{272 m\mu}^{max}$, and conversion to levopimaric acid in per

(34) All melting points uncorrected. All specific rotations and ultraviolet absorption spectra in 95% ethanol unless otherwise designated.

(35) E. P. Clark, *Ind. Eng. Chem. Anal. Ed.*, **13**, 820 (1941).

(33) R. N. Moore and R. V. Lawrence, *J. Am. Chem. Soc.*, **80**, 1438 (1958); **81**, 458 (1959).

cent: 0, 0.29, 1.6; 3, 0.73, 4.0; 6, 2.43, 13.3; 9, 4.00, 22.0; 12, 5.12; 28.1; 15, 6.39, 35.1; 20, 7.90, 43.4.

Isolation of levopimaric acid (I) from the thermal isomerization of photolevopimaric acid. A sample of pure photolevopimaric acid weighing 0.30 g. was placed in a small test tube and immersed in a constant temperature oil bath at 120° for 40 min. The product, λ_{\max} 272 m μ , α 12.19 (corresponds to a 67% conversion to levopimaric acid), was dissolved in a little alcohol and the levopimaric acid precipitated as the 2-amino-2-methylpropanol salt, 0.18 g. (46% yield in terms of conversion of irradiation product to levopimaric acid); λ_{\max} 272 m μ , α 13.43 (essentially pure). The salt was reslurried in 2 ml. of alcohol and acidified with 2 drops of acetic acid. A little water was added and the levopimaric acid precipitated. The acid was recrystallized once from alcohol-water and vacuum-dried, yield 0.08 g. (58% from salt); $[\alpha]^{25D}$ -279° (c 1.0); λ_{\max} 272 m μ , α 18.2; infrared spectrum essentially identical to the spectrum of pure levopimaric acid.

Hydrogenation of photolevopimaric acid. To a pre-reduced dispersion of 0.200 g. of 5% palladium-on-carbon was added 0.400 g. of photolevopimaric acid. One equivalent of hydrogen was absorbed in 35 min.; essentially no further increase in hydrogen uptake occurred during the next 1.5 hr. The catalyst was removed by filtration and water added to the filtrate. On cooling a crystalline product came down, yield 0.27 g. (68%). This was dissolved in the minimum amount of boiling absolute ethanol; first crop: yield 0.05 g. (13%); m.p. 183-185°. A few drops of water was added to the mother liquor and on cooling, second crop: yield 0.165 g. (41%); m.p. 153-155°.

The low-melting isomer was recrystallized from aqueous ethanol: Yield 0.105 g. (26%), m.p. 155.5-156.5° (unchanged on further recrystallization from ethanol); $[\alpha]^{25D}$ +42.8° (c 0.77); no appreciable absorption through 205 m μ ; no bands at 12.13 and 12.41 μ ; negative tetranitromethane test for unsaturation.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.9; H, 10.6; neut. equiv. 304.5. Found: C, 79.1; H, 10.4; neut. equiv. 303.

The high-melting isomer was recrystallized from 95% ethanol: yield 0.022 g. (6%); m.p. 203-204° (unchanged on further recrystallization from alcohol); $[\alpha]^{25D}$ +65.2° (c 0.43); no bands at 12.13, 12.41 μ ; negative tetranitromethane test for unsaturation.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.9; H, 10.6; neut. equiv. 304.5. Found: C, 79.1; H, 10.6; neut. equiv. 304.5.

Thermal stability of hydrogenated photolevopimaric acid. A 0.010-g. sample of hydrogenated photolevopimaric acid (m.p. 155.5-156.6°) was placed in a small centrifuge tube, the tube flushed with nitrogen, stoppered, and held in an oil bath at 160° for 40 min. After one recrystallization from alcohol, the product weighed 0.0070 g. (70% recovery), and exhibited m.p. 153-155°.

A 0.0068-g. sample of hydrogenated photolevopimaric acid (m.p. 203-204°) was placed in a small centrifuge tube, the tube flushed with nitrogen, stoppered, and held in an oil bath at 207° for 5 min. After one recrystallization from alcohol, the product weighed 0.0042 g. (62%) and exhibited m.p. 196-200°.

Ozonolysis of photolevopimaric acid. A solution of 0.302 g. (0.001 mole) of photolevopimaric acid in 30 ml. of absolute methanol was cooled to -70° and treated with ozone until uptake ceased (approximately 1 mole of ozone absorbed). Water (20 ml.) and methanol (10 ml.) were added and the solution held at 0°. Chlorine gas (about 0.3 g.) was added and the solution, containing excess chlorine, stored overnight

in the refrigerator. The solution was concentrated under strongly reduced pressure whereupon the product crystallized; weight 0.31 g. (86%); $[\alpha]^{25D}$ +57.8° (c 0.53). Recrystallization from aqueous methanol gave 0.21 g.; $[\alpha]^{25D}$ +63.7° (c 0.46); M_D +224; essentially no change in rotation on subsequent recrystallization from absolute methanol; m.p. 201.5° dec. with evolution of gas; negative halide test on sodium fusion; λ_{\max}^{Nujol} no bands in 3- μ region; no characteristic absorption from 220-320 m μ .

Anal. Calcd. for $C_{20}H_{30}O_5$: C, 68.5; H, 8.6; neut. equiv. 175.2. Found: C, 68.3; H, 8.8; neut. equiv. 176.8.

The 2,4-dinitrophenylhydrazone was prepared in essentially quantitative yield and after recrystallization of the flaky yellow derivative from aqueous ethanol, m.p. 175-177° dec. with evolution of gas; λ_{\max}^{Nujol} 366 m μ , ϵ 21,830.

Anal. Calcd. for $C_{26}H_{34}O_8N_4$: C, 58.85; H, 6.5; N, 10.6. Found: C, 58.6; H, 6.6; N, 10.6.

The irradiation of levopimaric acid in the presence of excess oxygen. A solution of 1.51 g. of levopimaric acid in 25 ml. of absolute ethanol (0.2 M) was placed in a fused quartz actinometer cell and irradiated from a distance of 15 cm. with a Hanovia lamp containing filters transmitting light of 230-420 m μ . A gas delivery tube extended to the bottom of the solution and a steady stream of oxygen passed through the solution during irradiation. Ethanol was added occasionally to keep the volume at 25 ml. The reaction was followed by the change in $[\alpha]^{25D}$ and for the first 12 hr. (about one half of the total observable change) the rate of change was independent of the concentration of resin acid. The rate then progressively decreased and leveled off after 48 hr. with no characteristic absorption observed from 220-320 m μ . The solution was concentrated and water added; first crop 0.380 g.; second crop 0.18 g.; third crop 0.265 g.

First crop: m.p. 145-145.5°; recrystallized from ethanol to give 0.28 g.; m.p. 146-147°, $[\alpha]^{25D}$ +64.7° (c 0.82), λ_{\max}^{Nujol} 6.68 μ , 12.23 μ , no band in 3- μ region, λ_{\max} 268 m μ (α 1.34), 275 m μ (α 1.20), no titratable peroxide.

Second crop: m.p. 131.5-135° with dec. and evolution of gas, $[\alpha]^{25D}$ +29° (c 0.98), 0.164 equiv. titratable peroxide/equiv. resin acid, λ_{\max}^{Nujol} 3.0 (w), (6.68) (w), 12.25 (s), μ ; treatment with excess bisulfite²⁰ substantially reduced the peroxide content, treatment with excess sodium hydroxide²³ resulted in little change in absorption from 220-320 m μ .

Third crop: $[\alpha]^{25D}$ -12.7° (c 0.827), 0.287 equiv. peroxide/equiv. resin acid, λ_{\max}^{Nujol} 3.0 (s), no bands in 6.7- nor 12.2- μ regions, treatment with excess bisulfite²⁰ substantially reduced the peroxide content, treatment with excess of base²³ resulted in little change in absorption from 220-320 m μ .

NMR absorption spectra. [Prof. Werner Herz, Florida State University, Tallahassee, Fla.] The spectrum of photolevopimaric acid was run as a 10% solution in deuterated chloroform at 60 mc employing tetramethylsilane as the internal standard with frequencies determined by the side band technique. No absorption was noted in the cyclopropyl ring proton region of $\tau = 9.2-10.0$.

The spectrum of the dibasic acid IV was obtained in trifluoroacetic acid. Methyl signals were found at 46, 47.5, 50.5, 42, and 60 c.p.s.

Acknowledgment. The authors wish to thank Mr. L. E. Brown, Southern Utilization Research and Development Division, for the elemental analyses.

OLUSTEE, FLA.
GAINESVILLE, FLA.