2.18; 1 methoxyl, 4.82. Found (after drying *in vacuo* at 110°): C, 65.35; H, 7.93; N, 2.29; methoxyl, 4.34.

Alkaline Cleavage of Vanilloylzygadenine. A. With Aqueous Methanolic Alkali.—Vanilloylzygadenine (200 mg.) was hydrolyzed with aqueous methanolic sodium hydroxide and the hydrolysis mixture worked up as described under procedure A for the alkaline cleavage of veratroylzygadenine. The amorphous residue (107 mg.) from the chloroform extract was found to have an infrared spectrum identical with that of the solid obtained from veratroylzygadenine by the same procedure.

The alkaline solution and water washings were worked up as above, and afforded vanillic acid (38 mg., m.p. 206–207°). The identity of the acid was demonstrated by mixed melting point and infrared spectral comparisons with an authentic sample of vanillic acid.

B. **With Alcoholic Sodium Ethoxide.**—Vanilloylzygadenine (200 mg.) was treated with alcoholic sodium ethoxide and the reaction mixture was worked up as described above in procedure B for the alkaline cleavage of veratroylzygadenine. The residue from the chloroform extract crystallized from benzene, yielding pseudozygadenine (96 mg., m.p. 168–170° (dec.)). The alkaline solution and water washings yielded vanillic acid (35 mg., m.p. 205–207°).

Methylation of Vanilloylzygadenine.—An ethereal solution of diazomethane prepared from N-nitrosomethylurea (1 g.) was added to a chloroform solution (15 ml.) of vanilloylzygadenine (100 mg.). After standing at room temperature overnight the solvents and excess diazomethane were evaporated *in vacuo*. The solid residue crystallized from absolute ethanol, yielding veratroylzygadenine (53 mg., m.p. 266–268° (dec.)). The melting point of the product was not depressed on admixture of veratroylzygadenine, and its infrared spectrum was identical with that of veratroylzygadenine. (It is evident from Fig. 1 that there are distinct differences between the spectra of vanilloylzygadenine and veratroylzygadenine.)

Isolation of Zygadenine.—The amorphous plate-0 chloroform fraction (1.8 g.) of the modified countercurrent distribution was dissolved in acetone (10 ml.). After two days, a colorless crystalline solid (320 mg.) was obtained. Recrystallization from benzene afforded clusters of needles (105 mg.), m.p. 218–220° (dec.), $[\alpha]^{22}\text{D}$ −48.5° (*c* 1.85 in chf). The mixed melting point with an authentic sample of zygadenine[15] was not depressed, and the infrared spectra of the two samples were identical.

Anal. Calcd. for $C_{27}H_{43}O_7N$: C, 65.69; H, 8.78; N, 2.84. Found (after drying *in vacuo* at 110°): C, 65.85; H, 8.72; N, 3.05.

In the recrystallization of the crude crystalline solid obtained from acetone above, a small quantity of benzene-insoluble solid (III, m.p. 265–267° (dec.)) was obtained. The amounts available were too small for rigorous purification and analysis (see discussion).

Zygadenine Triacetate.—Zygadenine (100 mg.) was acetylated with acetic anhydride and pyridine as described above for the acetylation of pseudozygadenine. The residue obtained from the chloroform extract (95 mg.) crystallized from ether as clusters of small needles, m.p. 267–270° (dec.). Recrystallization from acetone–petroleum ether yielded colorless needles (64 mg.), m.p. 273–275° (dec.), $[\alpha]^{29}\text{D}$ −55° (*c* 2.00 in chf).

Anal. Calcd. for $C_{27}H_{40}O_7N(COCH_3)_3$: C, 63.95; H, 7.97; acetyl, 20.89. Found (after drying *in vacuo* at 110°): C, 63.77; H, 8.14; acetyl, 20.63.

Isolation of Germine.—The acetone solution obtained by filtration of zygadenine and III from the plate-0 chloroform fraction in acetone was lyophilized. The solid residue (1.4 g.) was dissolved in chloroform (15 ml.) and the chloroform solution was concentrated to half its original volume by boiling on the steam-bath. Upon cooling, a colorless crystalline solid (200 mg.) separated. Recrystallization from methanol yielded heavy prisms (95 mg.) which began to sinter at 155–165° and melted at 220–225° (dec.), $[\alpha]^{24}\text{D}$ 4° (*c* 2.00 in abs. alc.). The infrared spectrum in Nujol was identical with that of an authentic specimen of germine from *Veratrum viride*.

Anal. Calcd. for $C_{27}H_{43}O_8N$: C, 63.63; H, 8.50. Found (after drying *in vacuo* at 110°): C, 63.96; H, 8.62.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Structure of Umbellulone Dibromide[1]

BY RICHARD H. EASTMAN AND AARON OKEN

RECEIVED JUNE 9, 1952

Structures for umbellulone dibromide, bromodihydroumbellulone and some of their congeners are proposed on the basis of degradation and ultraviolet and infrared absorption spectroscopy.

When the crude product obtained by treating umbellulone (I) with bromine in carbon tetrachloride solution is distilled, decomposition with evolution of hydrogen bromide occurs, and two bromine-containing products are obtained[2]: a crystalline solid, $C_{10}H_{14}OBr_2$, umbellulone dibromide, and an oil, $C_{10}H_{13}Br$. This communication provides evidence that umbellulone dibromide is 1-methyl-2-bromo-3-keto-4-bromomethyl-4-isopropylcyclopentene (II).[3]

Umbellulone dibromide is not attacked by boiling, dilute nitric acid containing silver nitrate and it does not react with bromine in boiling chloroform. The ultraviolet absorption spectrum (Table I) is that of an α,β-unsaturated ketone,[4] and the infrared absorption (Fig. 1) indicates the presence of both the C=O (5.72 μ) and C=C (6.20 μ) groups.[5] These properties are in accord with the structure II for umbellulone dibromide. In II one of the bromine atoms is unreactive toward silver ion because it is attached to a neopentyl-type system[6] and the second is unreactive on the basis of its vinyl halide character.[7] The transformations and degradation of umbellulone dibromide described below are in accord with the structure II and provide a chain of

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[1] This material is taken from the Dissertation of Aaron Oken offered in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Stanford University, where he was du Pont Fellow, 1951-1952.

[2] F. H. Lees, *J. Chem. Soc.*, **85**, 639 (1904).

[3] For early structure assignments see F. Tutin, *ibid.*, **89**, 1104 (1906).

[4] R. B. Woodward, THIS JOURNAL, **64**, 76 (1942); A. E. Gillam and T. F. West, *J. Chem. Soc.*, 815 (1941); 486 (1942).

[5] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950); H. M. Randall, R. G. Fowler, J. L. Dangl and N. Fuson, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 28.

[6] F. C. Whitmore and G. H. Fleming, THIS JOURNAL, **55**, 4161 (1933).

[7] α-Bromobenzalacetophenone does not react with alcoholic silver nitrate solution: N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

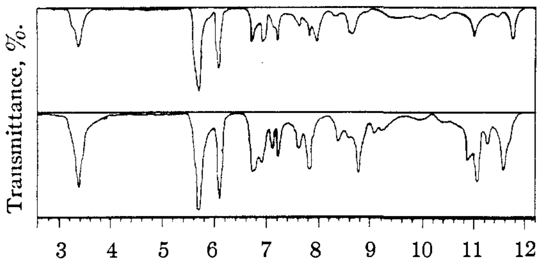


Fig. 1.—Infrared absorption spectra: top curve, umbellulone dibromide (II) in carbon tetrachloride; bottom curve, bromodihydroumbellulone (III) in carbon tetrachloride.

evidence which is difficult of interpretation on any other basis.

TABLE I

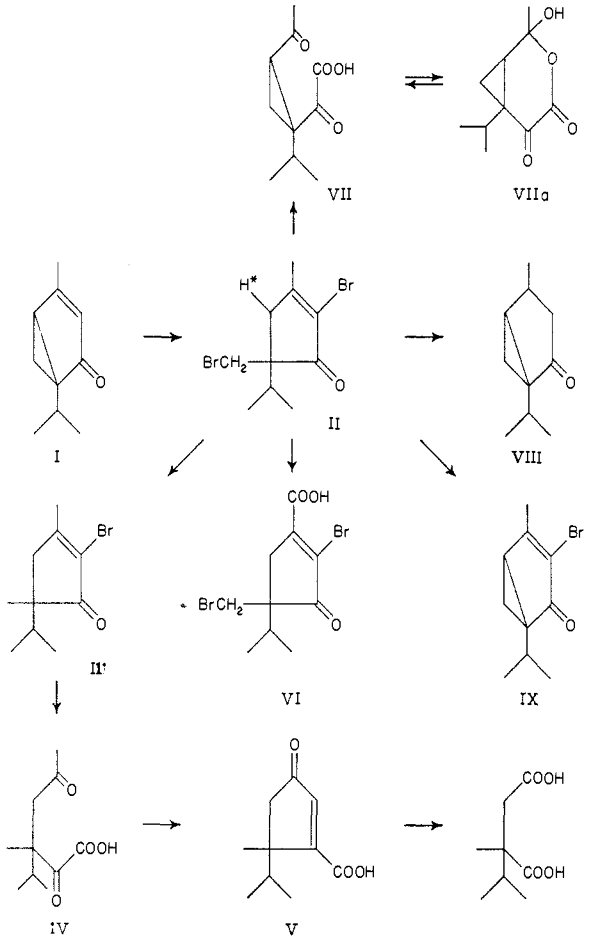
ULTRAVIOLET ABSORPTION MAXIMA

Compound	$\lambda_{\max}^{\text{alc.}}$ and log ϵ values
Umbellulone dibromide (II)	250 (4.0); 307 (2.0)
Bromodihydroumbellulone (III)	243 (4.2); 310 (2.1)
Compound V	240 (4.1)
Compound VI	262 (4.0)
Ketohomoumbellulonic acid (VII)	220 (3.3); 240 (3.9)[a]
Umbellulone (I)	220 (3.8); 265 (3.5); infl. 308 (2.3)
α-Bromoumbellulone (IX)	223 (3.8); 277 (3.5); infl. 314 (2.6)

[a] In 5% aqueous sodium hydroxide solution.

Reduction of umbellulone dibromide with zinc in acetic acid[2] or with copperized zinc in boiling alcohol yields bromodihydroumbellulone, $C_{10}H_{15}OBr$. Bromodihydroumbellulone does not react with boiling alcoholic silver nitrate or with bromine and its ultraviolet absorption spectrum (Table I) is nearly identical[8] with that of the dibromide II. Its infrared spectrum shows great similarity to that of the dibromide (II) (Fig. 1), and it is proposed from these data and the degradation discussed below that it has the structure III.

Oxidation of bromodihydroumbellulone (III) with permanganate in buffered solution produced a monobasic acid, $C_{10}H_{16}O_4$. Since this acid contained ten carbon atoms and yet was halogen-free, the neopentyl-type bromine atom was removed in the reduction of the dibromide II. The acid gave a positive iodoform reaction, was saturated toward bromine and alkaline permanganate and is assigned structure IV. When a similar oxidation was carried out but the total acidic product was treated with strong alkali before isolation by acidification, a different monobasic acid, $C_{10}H_{14}O_3$ (V), was obtained. The ultraviolet absorption spectrum of this acid (Table I) is very similar to that of VI which is a product of the oxidation of umbellulone dibromide (II) with boiling, red fuming nitric acid.[9] The acid V is the expected aldol cyclization product of IV. Oxidation of the acid V with permanganate gave a crude product that on further oxidation with nitric acid was converted into α-methyl-α-isopropylsuccinic acid, identified by comparison of its infrared absorption spectrum with that of an authentic sample.[10]



The oxidation of umbellulone dibromide (II) by permanganate in bicarbonate buffered solution produced a *halogen-free* monobasic acid, $C_{10}H_{14}O_4$.

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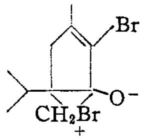
(8) An unequivocal empirical calculation of the positions of the principal absorption maxima of umbellulone dibromide and bromodihydroumbellulone cannot be made since too few compounds of this type have been studied. A. E. Gillam and T. F. West (*J. Chem. Soc.*, 486 (1942)) have shown that a correction of −11 mμ must be applied to Woodward's rules (ref. 4) when the unsaturated carbonyl chromophore occurs in a five-membered ring. The data of C. Djerassi, *et al.* (THIS JOURNAL, **73**, 3263 (1951)) indicate a bathochromic contribution of 23 mμ for bromine on the α-carbon atom of the chromophore under discussion. Using these generalizations the calculated maximum for umbellulone dibromide is at 251 mμ, in excellent agreement with the observed value of 250 mμ. The agreement is fortuitous, since it provides no explanation for the hypsochromic shift of 7 mμ between the dibromide II and bromodihydroumbellulone (III) (*cf.* Table I). Molecular models demonstrate the possibility of neighboring group interaction of the neopentyl-type bromine atom and the carbonyl group, which suggests that structures of the type IIa may effect



IIa

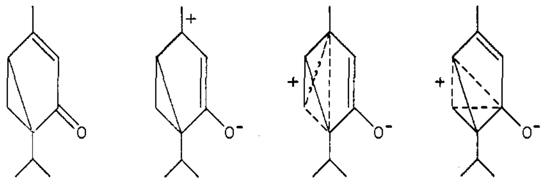
the absorption. Similar interactions have been proposed to account for spectroscopic anomalies in related cases (W. D. Kumler, L. A. Strait and E. L. Alpen, *ibid.*, **72**, 1463, 4558 (1950); S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1145 (1952)), and in application here lead to the conclusion that an α-bromo substituent on an α,β-unsaturated carbonyl system in a five-membered ring produces a bathochromic shift of 16 mμ rather than 23 mμ as found for the six-membered case.

(9) The bathochromic shift of 26 mμ in going from V to VI is in accord with the α-bromo substitution in VI (see footnote).

(10) J. Porath, *Arkiv Kemi*, **1**, 385 (1949); *C. A.*, **44**, 3898 (1950).

This acid was saturated to permanganate and bromine, was an α-keto acid as evidenced by evolution of a molar quantity of carbon dioxide on treatment with lead tetraacetate in acetic acid solution,[11] and gave iodoform on treatment with hypoiodite. The only structure possible for this acid is VII, formed from the dibromide II by oxidation and concomitant cyclization in the presence of alkali. The cyclization presents no difficulties of interpretation since the starred hydrogen atom in the formula of the dibromide II is activated by the carbonyl group (and the bromine atom) through the double bond. Similar cyclopropane ring formations are reported to occur with great ease in analogous structures.[12] The unreactivity of the bromine atom on the neopentyl-type system toward silver ion, an extramolecular reagent, has no bearing on this intramolecular nucleophilic displacement of bromide ion[13] in which the ion formed by removal of the starred hydrogen in II is very favorably located for attack on the bromomethyl group. The ultraviolet absorption spectrum of VII is unusual (Table I), but not unreasonable for the structure assigned in which a carbonyl group is conjugated[14] through the cyclopropane ring with an α-keto acid function. The shift in the spectrum of VII when it is converted into its conjugate base (Table I) suggests that the compound may exist at least in part in the hemiacetal-lactol modification VIIa in neutral solution.[15]

Two further reactions of the dibromide provide conclusive evidence for the facile reformation of the cyclopropane ring under alkaline conditions. When the dibromide II was treated with Raney nickel alloy in aqueous alcoholic alkali solution, β-dihydroumbellulone[16] (VIII) was produced; and, treatment of the dibromide with potassium acetate in boiling alcohol yielded α-bromoumbellulone (IX). The structure of the latter is inferred from the close correspondence of its ultraviolet absorption spectrum to the characteristic spectrum of umbellulone (I) (Table I). In this regard it may be pointed out that both umbellulone and its α-bromo derivative may be regarded as analogs of the cyclopentadienone (or cyclopentadienylium oxide) system[17] in which one of the double bonds has been replaced by a three-membered ring. In view of recent work[18] with cyclopropyl derivatives, umbellulone and its α-bromoderivative should be regarded as hybrids of the following types of structures



The extent of the interaction of the electrons of the cyclopropane ring with the α,β-unsaturated carbonyl system can be judged from the ultraviolet spectra of I and X which are quite atypical (Table I); and, from a chemical point of view, by our observation that the bromine atom in α-bromoumbellulone is highly unreactive toward alcoholic alkali, acetate ion and piperidine. This latter behavior is in contrast to the usual reactivity of α-bromo-α,β-unsaturated ketones to these reagents,[19] and is explained by the contribution of the non-classical[18] structures above which reduce the electrophilic character of the β-carbon atom so as to inhibit or prevent the Michael addition which has been shown to be the first step in the replacement of the bromine atom in such systems.[20]

We wish to express our gratitude to John H. Wise of the Stanford Chemistry Department for assisting us in the determination of the infrared absorption spectra; and we wish to thank Mr. Gene Heckathorn, of Heckathorn and Company, Richmond, California, and Mr. William P. Simmons for a gift of the oil of the California bay tree (*Umbellularia californica*) which made this work possible.

Experimental

Isolation of Umbellulone (I).—Umbellulone was separated from the oil of the California bay tree by the elegant bisulfite extraction method of Wienhaus and Todenhöfer.[16] Our material had n^{20}D 1.4842, $[\alpha]^{25}$D −39.4° (pure liquid, 1-dm. tube), b.p. 99–100° at 15 mm., and the ultraviolet absorption spectrum[21] in alcohol solution reported in Table I.

Umbellulone Dibromide (II).—Umbellulone dibromide was prepared by the method of Lees.[2] We obtained the material in 25% yield, with the following properties: m.p.[22] 118–119°, $[\alpha]^{25}$D +6.8° ($CHCl_3$, *c* 2, 2-dm. tube). The reported[2] constants are m.p. 119–119.5, $[\alpha]$D +6.9° ($CHCl_3$, *c* 2).

Anal.[23] Calcd. for $C_{10}H_{14}Br_2O$: C, 38.73; H, 4.55. Found: C, 38.80; H, 4.49.

The dibromide reduced neutral permanganate solution but did not react with boiling alcoholic silver nitrate, bromine in carbon tetrachloride or sodium iodide in acetone. The dibromide was dissolved in 10% alcoholic sulfuric acid to give a colorless solution. Dilution of the solution with water after 48 hours produced a quantitative yield of the dibromide of m.p. 118–119° and $[\alpha]^{25}$D +6.5° ($CHCl_3$, *c* 2.2).

The ultraviolet absorption spectrum of the dibromide in alcohol solution is reported in Table I and the infrared absorption is shown in Fig. 1.

Oxidation of Umbellulone Dibromide. A. With Red, Fuming Nitric Acid.—To 10 g. of the dibromide cooled in an ice–salt-bath was added 7 ml. of red, fuming nitric acid. The solution which resulted was brought to room temperature and warmed gently as the reaction moderated. Additional acid was then added and the mixture was finally heated on the steam-bath until the majority of the acid had evaporated. The residue, dissolved in ether, was extracted thoroughly with dilute sodium bicarbonate solution. Acidification of the bicarbonate extract, ether extraction and solvent removal gave 5.5 g. of crystalline solid which had m.p. 145–146° after one crystallization from hexane. The material was unreactive toward silver nitrate in alcohol, was shown to contain halogen by sodium fusion, and rapidly decolorized neutral permanganate.

Anal. Calcd. for $C_{10}H_{12}Br_2O_3$: C, 35.34; H, 3.56;

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[11] E. Baer, THIS JOURNAL, **62**, 1597 (1940).

[12] V. Prelog, W. Bauer, G. H. Cookson and G. Westoo, *Helv. Chem. Acta*, **34**, 736 (1951); M. Idzkowska and E. Wagner, *Chem. Zentr.*, **69**, 494 (1898).

[13] P. D. Bartlett and L. S. Rosen, THIS JOURNAL, **64**, 543 (1942).

[14] I. M. Klotz, *ibid.*, **66**, 88 (1944).

[15] *Cf.* R. B. Woodward and R. H. Eastman, *ibid.*, **72**, 399 (1950).

[16] H. Wienhaus and K. Todenhöfer, *Schimmel's Berichte*, 285 (1929).

[17] *Cf.* J. D. Knight and D. J. Cram, THIS JOURNAL, **73**, 4136 (1951); C. F. Koelsch and T. A. Geissman, *J. Org. Chem.*, **3**, 480 (1938).

[18] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 4542 (1951); C. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[19] N. Pauli and H. Lieck, *Ber.*, **33**, 501 (1900).

[20] N. H. Cromwell and D. J. Cram, THIS JOURNAL, **65**, 301 (1943).

[21] The ultraviolet absorption has been measured previously by A. E. Gillam and T. F. West (*J. Chem. Soc.*, 98 (1945)).

[22] Melting points are not corrected.

[23] Analyses are by Microchemical Specialties Co., Berkeley, California.

neut. equiv., 340. Found: C, 35.19; H, 3.55; neut. equiv., 345.

This acid is assigned structure VI. The ultraviolet absorption spectrum is reported in Table I.

B. **With Buffered Permanganate.**—A solution of 1.7 g. of potassium permanganate in 100 ml. of 80% acetone was added dropwise to a stirred solution of 1.5 g. of umbellulone dibromide and 0.8 g. of sodium bicarbonate in 50 ml. of 80% acetone. A permanent pink color remained after 92 ml. of the permanganate solution had been added. The mixture was filtered, the residue was leached and the combined filtrate and washings were evaporated at reduced pressure until the acetone had been removed. The aqueous residue was extracted with ether, acidified with dilute hydrochloric acid and again extracted with ether. Evaporation of the second ether extract yielded 0.24 g. of white crystals. After three crystallizations from a mixture of hexane and isopropyl alcohol the material had m.p. 145°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.62; H, 7.12; neut. equiv., 198. Found: C, 60.36; H, 7.12; neut. equiv., 202.

This material dissolved reluctantly in dilute sodium bicarbonate but readily in dilute sodium hydroxide. The Beilstein test for halogen was negative as was the Baeyer test for unsaturation. Iodoform was obtained when the compound was treated with sodium hypoiodite. When lead tetraacetate was added to a solution prepared by dissolving the compound in a small volume of sodium hydroxide solution then adding excess glacial acetic acid, slightly more than one mole of carbon dioxide per mole of compound was evolved. The compound is assigned structure VII (or VIIa), ketohomoumbellulonic acid.

Formation of α-Bromoumbellulone (IX) from Umbellulone Dibromide.—A solution of 31 g. of umbellulone dibromide and 49 g. of potassium acetate in 200 ml. of alcohol was boiled under reflux for 24 hours. The solvent was removed by distillation and the residual oil was distilled. At 17 mm., 7.3 g. of oil distilled in the range 145–156°. A sample for analysis was collected at b.p. 142–143° at 16 mm.

Anal. Calcd. for $C_{10}H_{13}BrO$: C, 52.40; H, 5.72. Found: C, 52.78; H, 5.72.

The compound contained halogen as shown by sodium fusion and is assigned the structure IX, α-bromoumbellulone.[24] The ultraviolet absorption spectrum is reported in Table I.

Reduction of Umbellulone Dibromide. A. With Raney Nickel Alloy.—To a solution of 15.5 g. of the dibromide in 50 ml. of methanol was added 50 g. of alloy. The slurry was stirred and cooled in an ice-bath while a solution of 50 g. of sodium hydroxide in 250 ml. of water was slowly added. When the vigor of the reaction permitted, the mixture was heated on the steam-bath for a period of 4 hours. Steam distillation of the mixture produced 6.4 g. of a colorless oil. The oil was treated with excess semicarbazide acetate in ethanol to yield 3.4 g. of white crystals of m.p. 130–146°. Crystallization from aqueous alcohol gave material of m.p. 155.5–156.0°. A mixed melting point with authentic β-dihydroumbellulone semicarbazone[16] (m.p. 157–158.5°) showed no depression and the ultraviolet absorption spectra of the two samples were identical.

B. **With Copperized Zinc.**—The zinc was prepared by washing 30 g. of zinc dust with 100 ml. of 5% sulfuric acid, then thoroughly with water. The zinc dust was then treated with 1100 ml. of 2% copper sulfate solution for a few minutes and washed with water and alcohol.

A solution of 9.3 g. of umbellulone dibromide in 50 ml. of alcohol was boiled under reflux for 20 hours with 25 g. of the copperized zinc. After filtration the solution was poured into 300 ml. of water and the precipitate which formed was collected and crystallized from aqueous alcohol to yield 2.2 g. of bromodihydroumbellulone, m.p. 57–59°. The compound showed no depression in a mixed melting point with a sample (m.p. 56.5–58.5°) prepared by the zinc–acetic acid reduction method used by Lees.[2]

Bromodihydroumbellulone is assigned structure III. The ultraviolet and infrared absorption spectra are reported in Table I and Fig. 1. Our samples had $[\alpha]^{25}D$ −58° (alcohol, *c* 6.7, 2-dm. tube). A sample (0.25 g.) was dissolved in 3 ml. of 10% alcoholic sulfuric acid. After the solution had stood 48 hours, the compound (0.20 g., m.p. 57–58.5°) was recovered by dilution with water. The recovered material had $[\alpha]^{25}D$ −58° (alcohol, *c* 6.3, 2-dm. tube). A mixture of the recovered material and untreated bromodihydroumbellulone showed no depression in melting point.

Oxidation of Bromodihydroumbellulone. A. With Potassium Permanganate.—A solution of 5 g. of bromodihydroumbellulone (III) in a mixture of 100 ml. of acetone and 40 ml. of water was treated with a 3.5% solution of potassium permanganate in acetone until a permanent pink color remained in the solution. The mixture was filtered, acidified with dilute sulfuric acid and concentrated under reduced pressure. The concentrate was extracted with ether and the extract was dried and freed of solvent. The oil residue was distilled, yielding 0.4 g., b.p. 80–130° at 5 mm., and 1.4 g., b.p. 136–140° at 5 mm. Redistillation of the higher-boiling fraction gave 0.9 g. of a viscous oil at b.p. 123–125° at 2–3 mm. This product was soluble in dilute bicarbonate, gave a negative Beilstein test, was saturated to permanganate and gave a precipitate of iodoform on treatment with hypoiodite.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05; neut. equiv., 200. Found: C, 59.64; H, 8.21; neut. equiv., 202.

A semicarbazone melting at 209–210° was prepared. This acid is assigned structure IV.

In a similar oxidation of 2.3 g. of bromodihydroumbellulone carried out in wholly aqueous medium using 2.3 g. of potassium permanganate and 4 g. of sodium bicarbonate as buffer, 20 g. of sodium hydroxide dissolved in 20 ml. of water was added to the filtrate from the manganese dioxide. The solution was kept at 70° for one-half hour, then acidified and cooled. Filtration gave 0.85 g. of a white solid of m.p. 189–191°. One crystallization from aqueous acetic acid produced 0.60 g. of nearly white needles of m.p. 194–195.5° (cor.).

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.93; H, 7.74; neut. equiv., 182. Found: C, 66.07; H, 7.83; neut. equiv., 187.

This acid instantly decolorized permanganate, gave a negative Beilstein test, and is assigned structure V. The ultraviolet absorption spectrum is reported in Table I.

α-Methyl-α-isopropylsuccinic Acid.—Two-tenths of a gram of 1-carboxy-3-keto-5-methyl-5-isopropylcyclopentene (V) from oxidation of bromodihydroumbellulone (see above) was dissolved in 10 ml. of 50% acetic acid and oxidized by the addition of 0.4 g. of pulverized potassium permanganate in portions. Sodium sulfite and dilute hydrochloric acid were added to destroy the manganic acetate complex and the resulting colorless solution was evaporated to dryness. Extraction of the residue with hot ethyl acetate followed by solvent removal and trituration of the residue with ethyl acetate and hexane gave 0.020 g. of white, acidic material of m.p. 119–126°. This material was dissolved in 0.5 ml. of concentrated nitric acid and the solution was boiled down to near-dryness. Final traces of solvent were removed at reduced pressure and the residue was crystallized twice from ethyl acetate and hexane giving 0.010 g. of white, acidic needles, m.p. 131.5–133°. The infrared absorption of this material was identical with that of an authentic sample of *dl*-α-methyl-α-isopropylsuccinic acid prepared from methyl isopropyl ketone, cyanoacetic ester and potassium cyanide according to the method of Porath.[10] Our synthetic material had m.p. 152.5–153.5°.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.15; H, 8.09; neut equiv., 87. Found: C, 55.01; H, 7.98; neut. equiv., 88.5.

Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman model DU spectrophotometer. The sensitivity knob was kept three and one-half turns from the extreme clockwise position, the instrument was balanced by varying the slit width and density readings were taken at maximum intervals of 5 mμ.

The infrared absorption spectra were obtained using a Perkin–Elmer model 12c infrared spectrophotometer with sodium chloride optics. Wave lengths are correct to 0.05 μ and transmission to ±10%.

STANFORD, CALIF.

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[24] One of us (R. H. E.) with James C. Selover has since prepared α-bromoumbellulone (m.p. 30–31°) by piperidine dehydrohalogenation of an *unstable* umbellulone dibromide, prepared by careful bromination of the ketone at low temperature. When the oily sample from the potassium acetate treatment was seeded with that from the dehydrohalogenation it crystallized and showed m.p. 28–31°. A mixture had m.p. 29–31°.