Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. V. Studies on the Oxidation of Dihydroshonanyl Alcohol and the Ozonolysis of Shonanic Acid.

By Nobutoshi ICHIKAWA.

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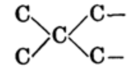
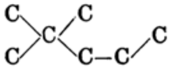
It was reported in the previous communications that the molecule of shonanic acid contains a linkage  as shown by the products of oxidation with potassium permanganate,(1) and that the elevation of boiling point accompanying its isomerisation to isoshonanic acid may be attributed to the migration of the semicyclic double bond into the ring system.(2)

Now, with a view to ascertain the presence of a semicyclic double bond and hence to establish the constitutional formula of shonanic acid, the author examined its ozonolysis as well as the oxidation of dihydroshonanyl alcohol with potassium permanganate, and was able to formulate further arrangement of atoms in the molecule of shonanic acid.

The ozonisation of shonanic acid gave a crystalline mono-ozonide, which on treatment with water gave an unsaturated acid of the formula $C_9H_{14}O_3$. This acid was found to be an unsaturated aldehydic acid and hence on further oxidation with hydrogen peroxide it gave an unsaturated dibasic acid of the formula $C_9H_{14}O_4$. The methyl ester of this dibasic acid was prepared, which on ozonolysis gave formaldehyde, formic acid and an acidic substance, which on treatment with dilute nitric acid gave dimethylmalonic acid and *asym*-dimethylsuccinic acid. When dihydroshonanyl alcohol was oxidised with dilute permanganate and then with dilute nitric acid, oxalic, *asym*-dimethylsuccinic and α,α-dimethylglutaric acids were produced.

The formation of α,α-dimethylglutaric acid reveals the presence of arrangement  in the molecule of dihydroshonanyl alcohol. As dihydroshonanyl alcohol is the alcohol derived from dihydro-

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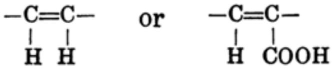
(1) This Bulletin, **12** (1937), 243.

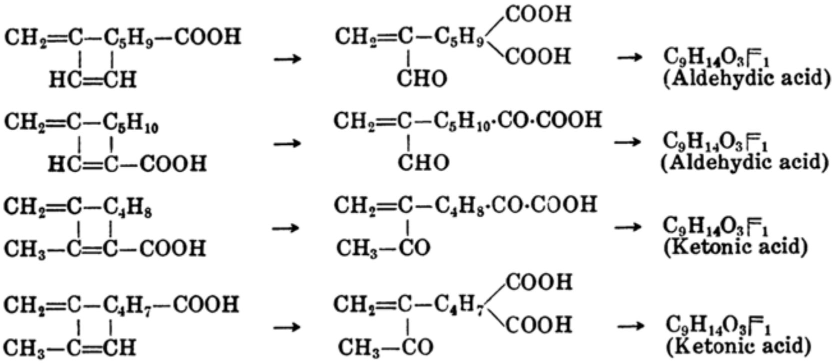
(2) *Ibid.*, **11** (1936), 759.

shonanic acid, the conclusions about its constitution may directly be adopted to dihydroshonanic, as well as to shonanic acid.

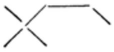
From considerations of the oxidation products mentioned above, the author has come to the following conclusions.

(1) The formation of mono-ozonide shows that the double bonds in shonanic acid are conjugated.(3)

(2) The formation of the unsaturated aldehydic acid $C_9H_{14}O_3$ cannot be explained unless the formation of the mono-ozonide takes place at the ring-forming double bond, and by presuming the ring fission to occur at this spot, this double bond must have existed either in the form  $\underset{H}{-C}=\underset{H}{C-}$ or $\underset{H}{-C}=\underset{COOH}{C-}$, otherwise the formation of the aldehydic acid becomes impossible.



(3) The formation of formaldehyde and formic acid by ozonolysis of the methyl ester of the unsaturated dibasic acid $C_9H_{14}O_4$ shows the presence of a semicyclic double bond attached to the nucleus.

Now the data for the establishment of the structural formula of shonanic acid are almost complete. (I) Shonanic acid contains a six-membered carbon ring,—proved by the formation of dinitrobenzene.(1) (II) It has within itself a skeleton  . (III) It has an exocyclic double bond attached to the ring. (IV) It has the second ethylenic linkage which is conjugated to the exocyclic one. (V) It has a carboxylic group.

By putting these facts together, it remains now to determine the position of $=CH_2$ and $-COOH$ and the second ethylenic linkage in the dimethylcyclohexene nucleus. Thus there are 12 cases which fulfil the above requirements, viz.:

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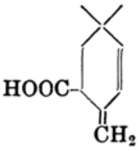
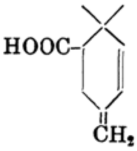
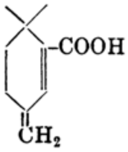
(3) Houben-Weyl, "Die Methoden der organischen Chemie," 3. Aufl., Bd. III, 409, 454.



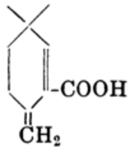
I.



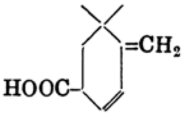
II.



VII.



VIII.



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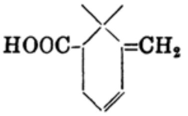

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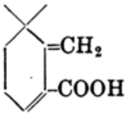

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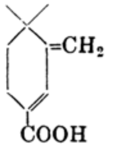
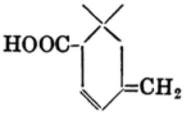
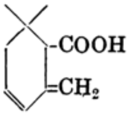


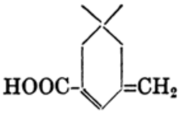
X.



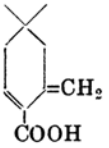
V.



VI.

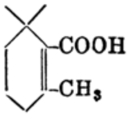


XI.

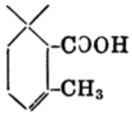


XII.

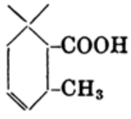
Among these formulæ those without an asymmetric carbon atom must be excluded as shonanic acid is optically active. Thus the formulæ I–VI remain to be inspected. And furthermore VI should be excluded for the following reason. If VI denotes shonanic acid, dihydroshonanic acid should be identical with one of the following substances, whereas dihydroshonanic acid proves to be a distinctly different substance.



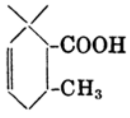
β-Cyclogeranic acid(4)
m.p. 93–94°



α-Cyclogeranic acid(5)
m.p. 106°



Δ^3-Cyclogeranic acid(6)
m.p. 75–76° or 83–84°



Δ^1-Cyclogeranic acid(7)
m.p. 102-102.5°

Thus it follows that one of the first five formulæ (I–V) should represent the constitution of shonanic acid.

Experimental.

I. Oxidation of dihydroshonanyl alcohol.

The substance was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol as previously reported.(8) It showed the following properties: b.p. 103–

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(4) Tiemann, *Ber.*, **33** (1900), 3723.
(5) Tiemann, *Ber.*, **31** (1898), 827.
(6) Merling, *Ber.*, **41** (1908), 2066.
(7) Merling, *Chem. Zentr.*, **77** (1906), II, 1694.
(8) This Bulletin, **12** (1937), 253.

104°/7 mm., 229°/760 mm.; d_4^{30} 0.9328; n_D^{30} 1.4832; α_D^{18} −2.24°; M.R. obs. 47.17, calculated for $C_{10}H_{18}O\,|\!\overline{=}_1$ 47.12.

20 g. of the substance was mixed with 1000 c.c. of 2% sodium hydroxide solution and then 3000 c.c. of 3.2% potassium permanganate solution was added drop by drop with vigorous stirring, the temperature of the reaction mixture being maintained at 20–25°. After all the permanganate had been consumed, the reaction mixture was saturated with carbon dioxide, and then warmed on the water-bath at 40–50° for an hour. Manganese dioxide precipitated was filtered off while hot and the filtrate was evaporated on the water-bath nearly to dryness and was acidified with dilute sulphuric acid. The organic acid set free was extracted with ether and dried over anhydrous sodium sulphate. After distilling off the solvent, there remained a sticky, slightly yellowish liquid, which amounted to 15 g. The substance was acidic, sparingly soluble in water and gradually acquired reddish yellow tint on exposure to the air. It was then warmed with 400 c.c. of dilute nitric acid ($d = 1.12$), evaporated on the water-bath, and ultimately under reduced pressure to remove traces of nitric acid present. The product thus obtained was a pale yellow viscous substance which was difficultly soluble in ether, chloroform and petroleum ether, but soluble in water, alcohol and warm benzene. On testing it with Schiff's reagent and Tollens' solution it proved to be perfectly free from aldehyde. On standing in cold some crystalline substance made appearance, which was spread over a porous plate previously cooled in an ice-box and stood over night in cold in order to remove the adhering fluid matter. The crystalline substance, which amounted to 7 g., was a colourless powder melting at 73–118° without any purification. The liquid portion absorbed by the porous plate was recovered by extracting it with ether, the details of which are described later.

(1) **Investigation of crystalline substances.** (a) *Oxalic acid.* The crystalline substance (7 g.) obtained above was boiled with 30 c.c. of chloroform, filtered while hot, washed with chloroform and dried in vacuo. It showed a m.p. 96–99°. On recrystallization from hot water it was obtained in colourless needles melting at 101°. It was identified as oxalic acid by mixed melting point.

(b) asym-*Dimethylsuccinic acid.* The above filtrate, on evaporating chloroform deposited a white crystalline powder melting at 133°. This was boiled with a little water and after quenching, needle crystals of oxalic acid were filtered off. The filtrate was evaporated and then cooled with freezing mixture, when prismatic needles with m.p. 134–136° were obtained. Another recrystallization from benzene furnished colourless needles melting at 139°. The substance was soluble in water, alcohol, benzene and chloroform. Acid value 767.4, calculated for $C_6H_{10}O_4$ 767.1. (Found: C, 48.87; H, 6.82. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%. Analysis of the silver salt: Ag, 60.02. Calculated for $C_6H_8O_4Ag_2$: Ag, 59.97%.)

Among the acids represented by $C_6H_{10}O_4$, *asym*-dimethylsuccinic acid melts at the same temperature (139–140°) as the substance under investigation, whose identity with the former was confirmed by observing the melting point of the mixture.⁽⁹⁾

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(9) *asym*-Dimethylsuccinic acid used for the trial was prepared by oxidation of dimethyl-dihydroresorcin according to the description of Vorländer and Gärtner [*Ann.*, **304** (1899), 5, 15].

(2) **Investigation of the liquid portion.** The liquid portion was recovered by extracting the porous plate broken into small bits with ether. The substance thus recovered was a viscous fluid with yellowish tint and amounted to 7.3 g. As the purification by vacuum distillation was ineffective, it was esterified by boiling it with 40 c.c. of ethyl alcohol containing 6% hydrochloric acid and the ester thus prepared was fractionated in vacuo.

(a) *Acetic acid.* As the ethyl alcohol recovered from the esterification mixture smelled of ethyl acetate, it was boiled with 5 c.c. of 50% potassium hydroxide solution under reflux condenser, and the remainder after removal of alcohol was evaporated nearly to dryness and acidified with 5N sulphuric acid and extracted with ether. From the ethereal solution about 0.8 g. of liquid acidic substance bearing the characteristic odour of acetic acid was obtained. The silver salt prepared from its neutralized solution contained 64.65% of the silver agreeing well with the theoretical silver content of the silver acetate.

(b) *α,α-Dimethylglutaric acid.* The ester portion thus obtained was dissolved in ether, washed with water and 5% sodium hydroxide solution successively in order to remove any traces of ethyl alcohol and unchanged acidic substances, dried over anhydrous sodium sulphate and the solvent was distilled off. The reddish brown matter remaining behind amounted to ca. 8 g., which was fractionally distilled under 10 mm.

Fr. No.	B.p.	Wt.(g.)
1	80–86°/10 mm.	1.2
2	86–95°/10 mm.	0.7
3	95–105°/10 mm.	—
4	105–107°/10 mm.	4.0
5	107°/10 mm.—105°/3 mm.	1.0
6	105–135°/3 mm.	0.6

Fraction 1 had the following properties: b.p. 185–187°/770 mm.; d_4^{20} 1.088; n_D^{20} 1.4160; M.R. obs. 33.67, calculated for $C_6H_{10}O_4$ 33.10. (Found: C, 49.08; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The physical constants of the fraction agree well with those of diethyl oxalate (b.p. 186°/755 mm.; d_4^{20} 1.0793; n_D^{20} 1.4104)⁽¹⁰⁾ and the free acid obtained by saponification melted at 101°, which was found to be identical with oxalic acid melting in admixture with authentic specimen.

Fraction 4 had the following properties: b.p. 233–235°/770 mm.; d_4^{20} 0.9956; n_D^{20} 1.4293; M.R. obs. 55.97, calculated for $C_{11}H_{20}O_4$ 56.42. (Found: C, 61.07; H, 9.21. Calculated for $C_{10}H_{20}O_4$: C, 61.11; H, 9.26%.) The analytical data showed that the substance represents a compound corresponding to the diethyl ester of a dibasic acid of the formula $C_7H_{12}O_4$. The substance was saponified by warming 3 g. of the sample with 2 g. of potassium hydroxide, 8 c.c. of water and 100 c.c. of ethyl alcohol for an

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(10) Delfes, *Jahresbericht über die Fortschritte der Chemie*, **1854**, 26; Brühl, *Ann.*, **203** (1880), 27.

hour. The excess of alcohol was distilled off and the remainder was evaporated to a smaller bulk and was acidified with dilute hydrochloric acid and the organic acid thus set free was extracted 4 times with chloroform using 10 c.c. each time. The chloroform solution was collected, dried over anhydrous sodium sulphate and the solvent distilled off. The sticky liquid acid remaining behind was then warmed with 5 c.c. of conc. hydrochloric acid and then cooled with freezing mixture, when the substance became crystalline and melted at 67°. It was purified twice by precipitation from benzene solution with the addition of light petroleum ether. Thus its melting point attained 83°. (Found: C, 52.29; H, 7.56. Calculated for $C_7H_{12}O_4$: C, 52.50; H, 7.50%.) It is clear that the acid under investigation is a dibasic acid of the formula $C_7H_{12}O_4$ and the melting point of the sample is proximate to those of α,α-dimethylglutaric acid⁽¹¹⁾ (m.p. 83–84°, diethyl ester b.p. 235–236°), α,β-dimethylglutaric acid⁽¹²⁾ (m.p. 84–84.5°) or *d*-β-methyladipic acid⁽¹³⁾ (m.p. 84.5°). Among these three acids *d*-β-methyladipic acid can be excluded for the reason that it is insoluble in cold benzene, and furthermore its diethyl ester has a quite different boiling point⁽¹⁴⁾ (b.p. 257°) from that of the diethyl ester in question. Reminding that dimethylmalonic acid and *asym*-dimethylsuccinic acid were found among the oxidation products of shonanic acid and dihydroshonanyl alcohol respectively, it should be expected that the present dibasic acid is α,α-dimethylglutaric acid. Now, it was found to be identical with α,α-dimethylglutaric acid by examining the melting point in admixture with the authentic sample prepared from ionone by oxidation as described by Tiemann.⁽¹⁵⁾

II. Ozonolysis of shonanic acid.

(1) **Preparation of mono-ozonide of shonanic acid.** To a well-cooled solution of the acid (10 g.) dissolved in carbon tetrachloride (100 c.c.), a current of ozonized oxygen containing ca. 3% ozone was passed through at a rate of 15–20 liters per hour until the absorption of ozone has ceased. The ozonide obtained was crystalline and floated on the surface of the solvent, which was filtered off, washed several times with carbon tetrachloride, spread over porous plate to remove the adhering solvent and finally dried in vacuo. The yield of the ozonide amounted to about 12 g., which is approximately the theoretical value calculated as mono-ozonide ($C_{10}H_{14}O_2 \cdot O_3 \vDash_1$). The mono-ozonide showed the decomposition point 82° and when perfectly dry it decomposed vigorously with evolution of heat. It was quite insoluble in chloroform, benzene, carbon tetrachloride and ether, and was attacked very slowly by water at ordinary temperature but more rapidly at elevated temperature (above 60°).

(2) **Decomposition of the ozonide.** The ozonide was gently heated on the water-bath at about 75° with 5 times of its volume of water in a current of hydrogen and the decomposition products thus obtained were examined. The hydrogen gas escaping from the decomposition flask was introduced into ice-cold distilled water

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(11) Kishner, *Chem. Zentr.*, **79** (1908), II, 1859; Blaise, *Bull. soc. chim.*, [3], **21** (1899), 626.

(12) Blaise, *Bull. soc. chim.*, [3], **29** (1903), 333.

(13) Semmler, *Ber.*, **25** (1892), 3516.

(14) Markownikow, *Chem. Zentr.*, **74** (1903), II, 288.

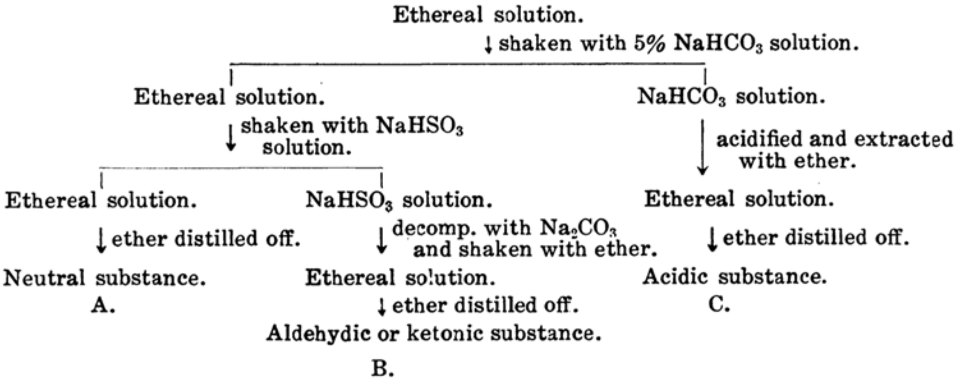
(15) Tiemann, *Ber.*, **31** (1898), 862.

in order to catch any soluble matter produced, and then into a saturated solution of barium hydroxide. Carbon dioxide was evolved and precipitated barium carbonate, which amounted to ca. 3.8 g. per 10 g. of the ozonide.

When the decomposition was over the presence of aldehydic substance in the water trap was tested with Schiff's reagent as well as with Tollens' solution which gave negative results. The iodoform reaction was also negative.

The oily product remaining in the decomposition flask was distilled in steam, and the distillate gave positive reaction with Schiff's reagent as well as with Tollens' solution whilst it gave no iodoform reaction showing the absence of acetone or acetaldehyde therein. The dimedon test was also thoroughly negative, showing the absence of formaldehyde in the distillate. The strong positive aldehydic reaction shown even by the first running may be attributed to the very nature of the product in question.

The product which came over with steam was then extracted with ether and was treated according to the following scheme.



Finally the substance was found to accumulate in C, and the portions going to A or B very minute.

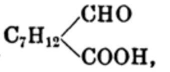
(3) **The investigation of the acidic substance (C).** The yield of the acidic substance amounted to 24 g. from 50 g. of the ozonide. It showed all the characteristic properties of an aldehyde but the attempt to obtain its semicarbazone in crystalline state was not successful. As the purification of the substance by distillation in vacuo was not attained, the aldehyde group present was first oxidised to acid group, the resulting acid esterified and the ester fractionated in vacuo. The substance thus purified was subjected to more minute examinations.

Oxidation of the aldehydic acid. 20 g. of the aldehydic acid was dissolved in 200 c.c. of 10% sodium hydroxide solution and was oxidised with 22 c.c. of perhydrol (30%) at 40–45°, when the reddish colour of the solution changed gradually to a yellowish tint, and the solution gave no more positive result with Tollens' solution. The solution was then evaporated to a smaller bulk in an atmosphere of carbon dioxide, acidified with dilute sulphuric acid and the organic acid thus liberated was extracted with ether. Yield 16 g.

Preparation of the methyl ester. The acid obtained above was esterified by heating with 100 g. of methyl alcohol containing 3% hydrochloric acid on the water-bath for 2 hours and the product was extracted as usual and fractionally distilled under reduced pressure.

Fr.	1	b.p. 86–109°/19 mm.	3 c.c.
	2	b.p. 109°/19 mm.–142°/7 mm.	9 c.c.
	3	b.p. 142–147°/7 mm.	4 c.c.

The main fraction (2) was once more rectified when it showed the following properties. (Yield 7 c.c.) B.p. 138–140°/7 mm.; d_4^{30} 1.073; n_D^{30} 1.4733. (Found: C, 61.57; H, 8.52. Calculated for $C_{11}H_{18}O_4$: C, 61.68; H, 8.41%.)

The substance was undoubtedly unsaturated since it absorbed bromine and decolourlized permanganate solution in cold. Its empirical formula corresponded with $C_{2.7}H_{4.6}O$, but since it is a dimethyl ester of a dibasic acid, it must contain two $COOCH_3$ groups. It naturally follows that the formula of this acid should be $(C_{2.7}H_{4.6}O)_4$ or $C_{11}H_{18}O_4$ approximately. The experimental data concerning the molecular weight agreed fairly well with this formula, viz.: 0.2577 g. subst. absorbed 0.1856 g. of bromine, while $C_{11}H_{18}O_4$ requires 0.1927 g. 0.3858 g. subst. absorbed 45.1 c.c. of hydrogen (0°, 760 mm.), while $C_{11}H_{18}O_4$ requires 40.4 c.c. Saponification value 517.8, calculated for $C_{11}H_{18}O_4$ 523.4. Thus the free acid should be represented by $C_9H_{14}O_4\ulcorner^{=}_{1}$ or $C_7H_{12}(COOH)_2$, and the foregoing aldehydic acid by $C_9H_{14}O_3$ or  $C_7H_{12}\begin{cases}CHO\\COOH,\end{cases}$ presumably aliphatic with one ethylenic linkage. The position of the double bond was determined by ozonolysis of the dimethyl ester of the former.

(4) **Ozonolysis of dimethyl ester of the acid $C_9H_{14}O_4$.** The methyl ester (10 g.) was dissolved in carbon tetrachloride (100 c.c.) and 3% ozonized oxygen made to bubble through until the solution became inactive against bromine. At the end of the reaction the solution was heated in a flask with 50 c.c. of water on the water-bath in a current of CO_2-free air and made to distil slowly. The decomposition of the ozonide set in with the distillation of carbon tetrachloride. In order to catch any water soluble substance such as formaldehyde, acetaldehyde or acetone, which may have been produced during the decomposition of the ozonide, a gas-washer containing a little water was put in place of the receiver and the air escaping out of this receiver was once more introduced into another gas-washer with a little water and then into barium hydroxide solution to detect carbon dioxide.

Carbon dioxide. The formation of carbon dioxide was recognized by the formation of barium carbonate in the gas-washer.

Formaldehyde. The water and carbon tetrachloride in the gas-washer was separated and the aqueous layer tested with Schiff's reagent as well as with Tollens' solution. When 8 c.c. of the aqueous distillate was mixed with 5 c.c. of alcoholic dimedon solution (10%) needle crystals of formaldimedon made appearance, which was filtered off, washed with water, and dried. It melted at 185°, and another recrystallization from alcohol furnished colourless needles melting at 191° alone and

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(16) Fenton and Sisson, *J. Chem. Soc.*, **91** (1907), 690.

in admixture with pure specimen of formaldimedon. Thus the presence of formaldehyde was recognized.

Identification of formic acid. The residual liquid product in the decomposition flask was then extracted with ether and was saponified with alcoholic potash. The resulting acidic substance gave positive reaction with Schiff's reagent as well as Tollens' solution and it deposited mercurous chloride when heated with concentrated mercuric chloride solution.

The liquid acid obtained (8 g.) was stirred 3 times with 10 c.c. of water each time for about an hour and the water layer separated was neutralized with aqueous ammonia and evaporated to ca. 10 c.c. A portion of this solution when heated with mercuric chloride solution deposited mercurous chloride, while it showed a reducing action on Tollens' solution. The neutral solution was acidified with dilute hydrochloric acid and was extracted with ether several times.

The ethereal solution thus obtained was then mixed with about 10 c.c. of water and warmed on the water-bath and the ether was expelled. The residual aqueous solution was digested with magnesium powder at ordinary temperature and filtered.(16) From the filtrate on mixing with alcoholic dimedon solution, formaldimedon melting at 191° was obtained, which shows that the original solution contained formic acid.

Oxidation of the liquid acid obtained from the ozonide. The liquid acidic substance, after removal of formic acid, amounted to 6.5 g. It was warmed with 320 c.c. of dilute nitric acid ($d = 1.12$) on the boiling water-bath for 5 hours and then evaporated to syrup and extracted with ether. From the ethereal solution an oily substance was precipitated by the addition of light petroleum ether, which gradually turned into a crystalline mass on cooling. The mass softened at 111° and melted at 131° without any purification. By fractional recrystallization from a mixture of light petroleum ether and benzene (2:3) two kinds of crystalline acids were obtained, the one crystallizing at first melted at 123–129° and the other at 173–178° (with decomposition). By three successive purifications from the same solvent two acids with m.p. 139° and m.p. 186–187° (with decomp.) were obtained. The former had the formula $C_6H_{10}O_4$ and was identified as *asym*-dimethylsuccinic acid by melting in admixture with an authentic specimen. (Found: C, 49.12; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The latter melting at 186–187° (with decomp.) had the composition $C_5H_8O_4$ and was found to be identical with dimethylmalonic acid by examining the melting point of the mixture of the sample with an authentic specimen.

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