

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL

XVI. THE STRUCTURES OF HEXADECATETRAENOIC AND OCTADECATRIENOIC ACIDS

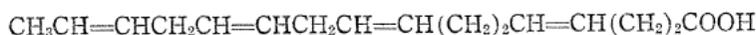
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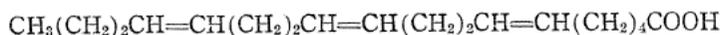
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The structures of hexadecatetraenoic and octadecatrienoic acids were formerly studied by Tsuchiya. Relating to hexadecatetraenoic acid¹⁾ he concluded from the results of the oxidation of amyl hexadecatetraenoate with potassium permanganate in acetone and the oxidation of potassium hexadecatetraenoate with permanganate in aqueous solution that the structure of this acid is either 4, 8, 11, 14- or 4, 8, 12, 15-hexadecatetraenoic acid. The same author oxidized also amyl ester of octadecatrienoic acid²⁾ with permanganate in acetone, and inferred the structure of this acid to be either 6, 10, 14-, 6, 9, 13- or 6, 10, 13-octadecatrienoic acid, of which the 6, 10, 14-structure seemed most probable reasoning by analogy with the structure of hiragonic acid (6, 10, 14-hexadecatrienoic acid).

The present authors subjected potassium hexadecatetraenoate to the oxidation with permanganate in aqueous solution and also butyl hexadecatetraenoate to the permanganate oxidation in acetone, and examined the oxidative scission product. Among dibasic acids, succinic acid was identified, and this acid was found to have been derived from the terminal group containing carboxyl as well as intermediate groups without carboxyl. Malonic acid was not separated, but the dibasic acids obtained in these experiments underwent a partial decomposition forming carbon dioxide by heating to about 140°C, and hence the presence of malonic acid in some proportion was inferred. Since hexadecatetraenoic acid has neither conjugate bonds nor allene type bonds, the results obtained above indicate that this acid should consist of the groups either (1) $\text{CH}_3\text{CH}=\text{}$, two of $=\text{CHCH}_2\text{CH}=\text{}$, $=\text{CH}(\text{CH}_2)_2\text{CH}=\text{}$, and $=\text{CH}(\text{CH}_2)_2\text{COOH}$ or (2) $\text{CH}_2=\text{}$, $=\text{CHCH}_2\text{CH}=\text{}$, two of $=\text{CH}(\text{CH}_2)_2\text{CH}=\text{}$, and $=\text{CH}(\text{CH}_2)_2\text{COOH}$. As monobasic acid in the scission product, a volatile acid which appeared to consist of acetic acid was obtained, while no formic acid was detected. These facts seem to indicate that hexadecatetraenoic acid has the groups of (1). However, acetic acid might be possibly formed by the secondary decomposition of malonic acid which is derived from the group $=\text{CHCH}_2\text{CH}=\text{}$, while formic acid which is expected to be formed from the group $\text{CH}_2=\text{}$ might undergo a further oxidation and completely disappear in these experiments. Accordingly, it is not convincingly established that hexadecatetraenoic acid has the groups of (1). The relative positions of the groups $=\text{CHCH}_2\text{CH}=\text{}$ and $=\text{CH}(\text{CH}_2)_2\text{CH}=\text{}$ in hexadecatetraenoic acid were not determined in these experiments, but if hexadecatetraenoic acid like moroctic acid (4, 8, 12, 15-octadecatetraenoic acid) be assumed to have ethylenic linkages in 4- and 8-positions, the respective groups of (1) should be arranged as follows:



As for octadecatrienoic acid, its ethyl ester was oxidized by the acetone permanganate method, and the scission product was examined. As monobasic acid, butyric acid was identified. Among dibasic acids, succinic acid and adipic acid, the latter being derived from the terminal group containing carboxyl, were separated. Hence, octadecatrienoic acid is 6, 10, 14-octadecatrienoic acid with the following formula:



Experimental

1. Hexadecatetraenoic Acid

The hexadecatetraenoic acid described in the 15th report³⁾ of this series was used for the present experiments. It had d_4^{20} 0.9364, n_D^{20} 1.4911, N.V. 225.9, and I.V. 400.9 (calculated for $\text{C}_{16}\text{H}_{24}\text{O}_2$, N.V. 225.9 and I.V. 408.8).

(a) *Oxidation of potassium hexadecatetraenoate with potassium permanganate in aqueous solution.* Hexadecatetraenoic acid (0.15 g) was added with 15 cc of water which contains a slight excess of potassium hydroxide necessary to neutralize the acid. The solution was cooled with ice, and 35 cc of a 3% solution of potassium permanganate was gradually added while stirring. After standing over a night, a current of sulfur dioxide was passed into the solution until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The insoluble substances were removed by filtration. The filtrate was neutralized, evaporated to dryness, acidified with sulfuric acid, and extracted twice with ether using 200 cc each time. The ether solution was washed with a saturated solution of sodium chloride, and ether was distilled. The residue (0.1 g) was treated with petroleum ether. The portion soluble in petroleum ether had an odor of acetic acid, and its neutral aqueous solution showed a red coloration with ferric chloride. The portion insoluble in petroleum ether yielded a crystalline solid of M.P. 177-178°C after recrystallization from ethanol-petroleum ether. It showed no depression of melting point when mixed with a specimen of succinic acid (M.P. 182-183°C) in various proportions. The substance recovered from the mother liquor of recrystallization partly decomposed at about 140°C, forming carbon dioxide. The ether and petroleum ether which were recovered by distillation in the above experiments had an odor of acetic acid. The portion soluble in petroleum ether, and the ether and petroleum ether recovered in these experiments were tested for formic acid by several known reactions, but the results were negative.

(b) *Oxidation of butyl hexadecatetraenoate with potassium permanganate in acetone.* Butyl ester (0.18 g) prepared from hexadecatetraenoic acid was dissolved in 10 cc of acetone, 1.5 g of powdered potassium permanganate was added in small portions, and the mixture was refluxed for 5 hours. Acetone was distilled, 20 cc of water was added, and a current of sulfur dioxide was passed into the mixture until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The mixture was then filtered through a wet filter paper, and the oily substance (A) and the aqueous solution (B) were separated. The oily substance (A) on the filter paper was collected by using ether, and the ether so-

lution was washed with a solution of sodium carbonate, by which the acidic substance in the ether solution was separated as sodium salt from the ether solution. The carbonate solution was acidified with sulfuric acid, and the oily substance (monoester of dibasic acid) liberated was collected by using ether. Yield 0.05 g. This was saponified and acidified, and the free dibasic acid (0.02 g) was extracted with a relatively large amount of ether. It was a crystalline solid, and had M.P. 176–177°C. No depression of melting point was observed when mixed with succinic acid in various proportions.

The aqueous solution (B) was extracted twice with ether using 200 cc each time, the ether solution was washed twice with a saturated solution of sodium chloride, and the ether was distilled. The residue obtained was separated into two portions by using petroleum ether. The portion (0.03 g) soluble in petroleum ether was liquid and had an odor of acetic acid. Its neutral aqueous solution showed a red coloration with ferric chloride. Tests for formic acid were negative. The portion (0.07 g) insoluble in petroleum ether, after being washed with a little cold ether, had M.P. 165–167°C, and yielded succinic acid of M.P. 178–179°C after recrystallization from ethanol-petroleum ether. The ether and petroleum ether recovered in the above experiments had an odor of acetic acid.

2. Octadecatrienoic Acid

The octadecatrienoic acid described in the 15th report³⁾ of this series was used for these experiments. It had d_4^{20} 0.9226, n_D^{20} 1.4796, N.V. 202.3, and I.V. 279.5 (calculated for $C_{18}H_{30}O_2$, N.V. 201.5 and I.V. 273.5).

Ethyl ester (1.5 g) prepared from octadecatrienoic acid was dissolved in 15 cc of acetone, 12 g of powdered potassium permanganate was added in small portions, and the mixture was refluxed for 5 hours. Acetone was then distilled, 20 cc of water was added, and a current of sulfur dioxide was passed into the mixture until the excess of permanganate was reduced. The mixture was filtered through a wet filter paper, on which oily substances and insoluble oxides of manganese remained. The material on the filter paper was washed with 50 cc of water, and then extracted with ether, giving 0.8 g of oily substances (a). The filtrate and washing were combined, neutralized with a solution of potassium hydroxide, and extracted with ether. By these treatments, non-acidic substances contained in the aqueous solution were removed to the ether solution. The aqueous solution was concentrated to about 30 cc volume, acidified with sulfuric acid, and extracted three times with ether using 200 cc each time. The ether solution was washed with a saturated solution of sodium chloride, and the ether was distilled, leaving 0.5 g of residue which was then separated into 0.15 g of petroleum ether soluble portion (b) and 0.35 g of petroleum ether insoluble portion (c). The ether and petroleum ether recovered in the above experiments were washed with a solution of sodium carbonate, after which the latter was concentrated and acidified with sulfuric acid. The product, being distilled by adding a small amount of potassium permanganate, gave 50 cc of aqueous distillate (d).

(a) *Oily substances.* These were dissolved in ether, and washed with a solution of sodium carbonate. The aqueous layer was separated and acidified with sulfuric acid, resulting 0.3 g of oily liquid. Its N.V. 319.5 is close to the calculated value (322.1) for monoethyl adipate. The free acid liberated by hydrolysis of the oily liquid gave a crystalline solid of M.P. 148–149°C and N.V. 765.5 after two recrystal-

lizations from ethanol-petroleum ether. No depression of melting point was observed when mixed with a specimen of adipic acid of M.P. 152-153°C.

(b) *Petroleum ether soluble portion.* This portion still contained a minor amount of solid substances which were insoluble in petroleum ether. The liquid portion obtained by a repeated treatment with petroleum ether had N.V. 630.3 which is close to the calculated value (636.8) for butyric acid. Hydroxamic acid prepared from this liquid acid and butyl hydroxamic acid in ethanol were compared by the paper chromatography⁴⁾ with the results given in Table 1 which indicate that the liquid acid consists of butyric acid.

TABLE 1

	R_f		Coloration
	Hydroxamic acid from liquid acid	Butyl hydroxamic acid	
Ascending method	0.74	0.75	Purple
Descending method	0.78	0.80	Purple

Notes—Filter paper: "Toyo Filter Paper" No. 2; developer: butanol; temperature: 26-28°C; chromogenetic reagent: 10% solution of ferric chloride in ethanol.

(c) *Petroleum ether insoluble portion.* This portion, after being washed with a little cold ether, melted at 170-173°C. It gave, after two recrystallizations from ethanol-petroleum ether, succinic acid of M.P. 180-181°C and N.V. 947.6 (calculated, 950.3). The crystalline solid recovered from the mother liquor of recrystallizations evolved no carbon dioxide when heated to about 150°C.

(d) *Aqueous distillate.* This was faintly acidic. The neutralized solution showed a faint red coloration with ferric chloride, but the amount of potassium hydroxide required to neutralize 50 cc of aqueous distillate was only 0.0017 g.

Summary

1. Potassium hexadecatetraenoate was oxidized with potassium permanganate in an alkaline aqueous solution. Also butyl hexadecatetraenoate was oxidized with permanganate in acetone. It was inferred from the results of an examination of the oxidative scission product that hexadecatetraenoic acid consists of the groups, $\text{CH}_3\text{CH}=\text{}$, two of $=\text{CHCH}_2\text{CH}=\text{}$, $=\text{CH}(\text{CH}_2)_2\text{CH}=\text{}$, and $=\text{CH}(\text{CH}_2)_2\text{COOH}$. If hexadecatetraenoic acid, like morotic acid (4, 8, 12, 15-octadecatetraenoic acid) be assumed to have ethylenic linkages at 4- and 8-positions, its structure is likely to be 4, 8, 11, 14-hexadecatetraenoic acid.

2. Ethyl octadecatrienoate was oxidized with potassium permanganate in acetone. The results of an examination of the oxidative scission product established that the structure of this acid is 6, 10, 14-octadecatrienoic acid.

References

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