Reaction of Hydrogen Peroxide on Fatty Acid Esters under Pressure. III. Oxidation of Methyl 9, 10-Dihydroxystearate

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The reaction of hydrogen peroxide on methyl oleate(1) and on saturated fatty acid methyl esters(2) under pressure has already been reported in detail. The present research was carried out with the intention of finding the kinds of compounds formed by the action of hydrogen peroxide on methyl 9, 10-dihydroxystearate produced by the oxidation of methyl oleate with potassium permanganate and of following up the course of the reaction in the oxidation with hydrogen peroxide as mentioned above.

When methyl oleate is oxidized under pressure by the use of hydrogen peroxide, the position between 9 and 10 having a double bond is oxidized. In this case, however, the formation of 9, 10-dihydroxystearic acid is not observed, but substances coming from cutting off the carbon chain of methyl oleate at the position between 9 and 10 are formed. Moreover, various lower homologues of monobasic and dibasic fatty acid are formed. These are presumably produced by the oxidation at the other position of the carbon chain.

Expecting that the position between 9 and 10 where a double bond exists initially in methyl oleate is most liable to be oxidized in the oxidation of methyl 9, 10-dihydroxystearate and consequently C_9-aldehyde and C_9-fatty acid may be formed with relatively good yields. Methyl 9, 10-dihydroxystearate was subjected to the action of a 30% hydrogen peroxide solution under pressure.

The results obtained in this reaction were like those in the oxidation of saturated fatty acid methyl esters under a similar condition, excepting that the position between 9 and 10 was oxidized.

Experimental

Methyl 9, 10-Dihydroxystearate. — Commercial oleic acid was separated into solid acid and liquid acid through the lead-salt-ethanol process. The liquid acid was converted into lithium salt. This

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1) H. Kameoka, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, 63, 741 (1960).

2) H. Kameoka, ibid., 63, 744 (1960).

lithium salt, insoluble in a 50% ethanol solution, was filtered out and then changed to free fatty acid. The free fatty acid was subjected to the fractional distillation in a current of carbon dioxide gas three times. The distillate at the distillation temperature of 163~165°C/1 mmHg was oxidized in an aqueous alkaline solution of potassium permanganate, and sulfur dioxide gas was passed into the solution. After filtrating the aqueous solution, the remaining white substance was thoroughly washed with petroleum ether. This substance was recrystallized from a solution of 80% ethanol several times. The resulting crystalline substance having its melting point at 131~132°C and its neutralization value at 177.0 was esterified with methanol and sulfuric acid. The ester was recrystallized from an 80% ethanol solution once more. The ester thus prepared had an acid value 0.0, a saponification value 167.2, a hydroxyl value 334.5 and a melting point 104~105°C, and it was used as the sample of this research.

Hydrogen Peroxide.—A 30% solution was used.

Reaction under Pressure.—The sample (methyl 9,10-dihydroxystearate) and a 30% hydrogen peroxide solution were enclosed in an autoclave (a capacity of 100 cc.) made of stainless steel, having an electromagnetic stirrer. The initial pressure in each test was maintained at 0 kg./cm^2. By heating the autoclave, the inside temperature and pressure of it were raised. In this case, heating was controlled in such a way that it may take about 1.5 hr. to reach the temperature shown in Table I, and the pressure was also raised up to the values given in Table I. The reaction time indicates the length of time held within the range of these temperatures and pressures. The conditions of reaction are shown in Table I.

Treatment of the Reaction Products. — Having been allowed to stand overnight after the completion of the reaction, the autoclave was opened. The reaction mixture was taken into a separating funnel. The interior of the autoclave was then thoroughly washed with distilled water and petroleum ether. The washing solutions used were also taken into the separating funnel. The content in the separating funnel was extracted with petroleum ether. In this way the content was separated into the soluble portion [A] and the insoluble portion [B].

As the petroleum ether soluble portion [A], a rather viscous oily substance was obtained after entirely removing the petroleum ether by distillation. This substance, after its constants were measured,

TABLE I. CONDITIONS OF REACTION

Reaction No.	Sample wt., g.	30% H_2O_2 g.	Initial press. kg./cm^2	Press. kg./cm^2	Temp. °C	Final press. kg./cm^2	Reaction time min.	Stir. r. p. m.
1	5.0	50	0	65~ 80	100~110	40	90	60
2	5.0	50	0	110~120	130~140	75	120	60
3	5.0	60	0	130~145	138~146	65	120	60
4	5.0	50	0	115~120	145~155	70	180	60
5	6.8	50	0	110~125	145~155	65	180	60
6	10.2	50	0	100~110	125~140	60	120	60
7	10.2	50	0	120~135	140~150	60	180	60

TABLE II. TABLE OF THE SYSTEMATIC SEPARATION OF THE REACTION PRODUCTS

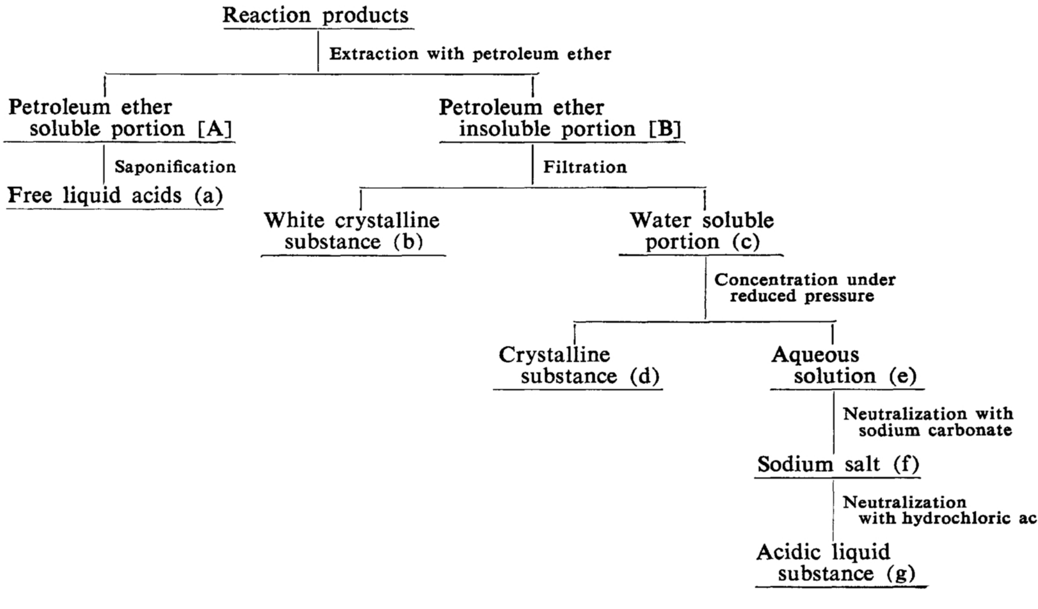

TABLE III. FRACTION (a). FREE ACID (Reaction No. 7, sample of fractional dist. 1.8 g.)

Fraction No.	Temp. of dist., °C/mmHg	Yield g.	N. v.	R_f value	Fatty acids detected
1	∼170	0.2	605.3	* 0.69, 0.82	C_3, C_4-monobasic
2	170∼210	0.3	461.9	* 0.82, 0.90, 0.96	C_4, C_6, C_8-monobasic
3	120∼140/15	0.6	365.6	* 0.90, 0.95 △ 0.59	C_6, C_8-monobasic C_9-monobasic
4	140∼160/15	0.4	305.3	△ 0.66, 0.59, 0.54	C_8, C_9, C_{10}-monobasic
5	160∼170/15	0.2	279.6	△ 0.54, 0.44	C_{10}, C_{12}-monobasic
6	Residue	0.1	—	△ 0.44	C_{12}-monobasic

Paper chromatography: * Monobasic C_2∼C_8-fatty acid, through the hydroxamic acid process³⁾.—One-dimensional ascending method; development solvent, butanol saturated with water; filter paper, Toyo. No. 2; development temperature, 30°C; coloring matter, 10% ferric chloride-ethanol solution. △ Members above monobasic C_8-fatty acid, through the 2,4-dinitrophenylhydrazide process⁴⁾.—One-dimensional ascending method; development solvent, methanol-acetic acid-tetraline; stationary phase, tetraline; filter paper, Toyo. No. 2; development temperature, 30°C; coloring matter, 0.5 N potassium hydroxide ethanol solution.

TABLE IV. FRACTION (d). CRYSTALLINE SUBSTANCE
(through fractional crystallization, sample 2.5 g.)

Cryst., No.	Yield, g.	N. v.	M. p., °C	R_f value	Fatty acids detected
1	0.8	943.9	180∼183	□ 0.67	C_4-dibasic
2	1.2	763.5	150∼153	□ 0.88	C_6-dibasic
3	0.4	651.0	110∼131	□ 0.88 ○ 0.48	C_6-dibasic C_9-dibasic
4	0.1	—	—	□ 0.89 ○ 0.48	C_6-dibasic C_9-dibasic

Paper chromatography: □ Dibasic C_2∼C_6-fatty acid, through the chloroform-acetic acid-water process⁵⁾.—One-dimensional ascending method; development solvent, chloroform-acetic acid-water; filter paper, Toyo. No. 2; development temperature, 20°C; coloring matter, 0.1% bromocresolgreen-ethanol solution. ○ Members above dibasic C_6-fatty acid, through the petroleum ether-chloroform-acetic acid process⁶⁾.—One-dimensional ascending method; development solvent, petroleum ether-chloroform-acetic acid; filter paper, Toyo. No. 2; development temperature, 20°C; coloring matter, 0.1% bromocresolgreen-ethanol solution.

was saponified to convert it into free fatty acids (a).

The petroleum ether insoluble portion [B] was spontaneously separated to a white crystalline substance (b) and a water-soluble portion (c). The crystalline substance b, which was filtered out from c, was washed with distilled water several times and the washing water used was added to c. The whole of c was concentrated under 20 mmHg pressure. In this case c was separated into an aqueous solution (e) and the crystalline substance (d). The aqueous solution (e) showing itself to be acidic was neutralized by the use of a 1% aqueous solution of sodium carbonate. By concentrating this solution, a solid sodium salt (f) was obtained. The salt f was acidified with hydrochloric acid, and then extracted with a large amount of ether. After removing the ether by distillation, an acidic liquid substance (g) was obtained. Examination was made about the substances separated through the process mentioned above respectively. In Table II, the treating procedure of the reaction products are represented.

Petroleum Ether Soluble Portion [A].—This portion is a rather viscous oily substance and is fragrant. It being presumable that pelargonic aldehyde produced by the breakage between the positions of 9 and 10 may exist in the portion A, this portion was tested to see whether it may form an adduct of sodium bisulfite by the ordinary process or not. However, this test did not give any positive result. Then, a 2 N hydrochloric acid solution of 2,4-dinitrophenylhydrazine was added to the portion A. In this case, a very small amount of yellowish orange precipitates was obtained, the amount of which was not sufficient for identification.

This portion A was next converted to the free acid by saponification with a 5% alcoholic potassium hydroxide solution. The free acid thus obtained was subjected to fractional distillation and the constants of the distillates were measured. The result of Reaction No. 7 is given in Table III.

Each of the portion A obtained in Reactions No. 1—No. 6 was similarly subjected to fractional distillation. Almost the same result as that of Reaction No. 7 was obtained. Moreover, as the hydroxyl value of the portion A was all zero, this portion has no hydroxy compound.

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3) Y. Inoue and M. Noda, *J. Japan Oil Chemist's Soc.* (*Yukagaku*), **1**, 136 (1952).

4) Y. Inoue and M. Noda, *Bull. Agr. Chem. Soc. Japan*, **19**, 214 (1955).

5) M. Kobayashi, *J. Japan Oil Chemist's Soc.* (*Yukagaku*), **4**, 53 (1955).

6) M. Kobayashi, ibid., 5, 85 (1956).

TABLE V. FRACTION (g). ACIDIC LIQUID SUBSTANCE
(sample of the fractional distillation, 1.5 g.)

Fraction No.	Temp. of dist., °C	Yield g.	N. v.	R_f value	Fatty acids detected
1	~120	0.5	930.6	* 0.50	C_2-monobasic
2	120~145	0.4	759.6	* 0.50, 0.68	C_2, C_3-monobasic
3	145~165	0.4	633.0	* 0.68, 0.82	C_3, C_4-monobasic
4	Residue	0.2	595.1	* 0.82	C_4-monobasic

Paper chromatography: * Hydroxamic acid process[3].

Petroleum Ether Insoluble Portion [B].—*Crystalline Substance (d) Contained in the Water Soluble Portion (c).*—The substance is assumed to be dibasic acid from its good solubility in water, and good crystallizable property. This crystalline substance was fractionally crystallized from a 10% ethanol solution, and the crystals shown in Table IV were obtained in the case of Reaction No. 7.

The fraction d obtained in Reactions No. 1—No. 6 was similarly subjected to the fractional crystallization with almost the same result as that mentioned above. In cases of the oxidizing conditions as in Reactions No. 1, No. 3 and No. 6, the formation of low members of dibasic acid such as C_2 and C_3 was observed.

Each acid thus separated has nearly an equal neutralization value to the corresponding pure acid. Furthermore, no depression of the melting point was observed when each acid was subjected to the mixed melting point determination.

The Sodium Salt (f) and the Acidic Liquid Substance (g). — The substance g obtained from the salt f was fractionally distilled, and inquiries were made about the respective fractions. The result of Reaction No. 7 is shown in Table V.

In the result shown above, the neutralization values of fractions No. 1, No. 2 and No. 3 were nearly equal to those of acetic, propionic and butyric acids, 934.5, 757.4 and 637.1, respectively. Accordingly it may be confirmed that the main components of these fractions are acetic, propionic and butyric acids. The results of the fractional distillation of g obtained in Reactions No. 1—No. 6 were almost the same as the above. Furthermore, from the result of paper chromatography[3] (hydroxamic acid process: R_f value 0.90) it was observed that small quantities of monobasic C_6 fatty acid were contained in g obtained in Reactions No. 1—No. 3.

White Crystalline Substance (b).—This substance is insoluble in water and petroleum ether. From its saponification value, hydroxyl value and melting point in addition to the insolubility nature mentioned above, this substance seemed to be nonoxidized methyl 9,10-dihydroxy stearate (Table VI). Furthermore, because of its slightly higher acid value and the considerably wide range of its melting point, the formation of free 9,10-dihydroxystearic acid due to the partial hydrolysis of the ester is presumable. Accordingly, this was saponified, and the melting point of 130~132°C and the neutralization value of 175~176 were obtained for the resulting acid. No depression of the melting point was observed when mixed with 9,10-dihydroxystearic acid. Moreover, the substance b was subjected to paper chromatography[5,6]. No existence of dibasic acid in it, however, was observed.

Results

The yields and constants of the separated substances, and the results concerning them in paper chromatography are summarized in Table VI.

As shown in Table VI, lower members of monobasic acid were mainly detected in the portion A. Water soluble lower members of monobasic and dibasic acid and unchanged methyl 9, 10-dihydroxystearate were detected in the portion B. Further, it was found that under the reaction conditions as in Reactions No. 3, No. 4 and No. 5, more than 80% of the methyl 9, 10-dihydroxystearate used was oxidized.

Discussion

In the present experiments, the reaction products, except the nonoxidized substance, had no hydroxyl value. This fact indicates that the hydroxyl group of the initial sample was removed during the oxidation with hydrogen peroxide.

Furthermore, from the fact that monobasic C_9-acid and dibasic C_9-acid were present in the portion A and also in the fraction d, it is clear that the positions of 9 and 10 where the hydroxyl group was initially located are oxidized. The production of the only small quantity of C_9-compounds by breakage at this position is probably explained by the consideration that this position is first attacked by oxygen and C_9-compounds are produced, but the resulting substances are immediately oxidized, and the compounds of smaller carbon numbers are formed. It is evident that lower monobasic acids than C_{10} are liable to be oxidized with hydrogen peroxide[7]. Alternatively, it is considered that other positions of the carbon chain are simultaneously split by the oxidation. This fact is clearly found from the formation of C_{12}, C_{10}-acids and/or lower acids. In case

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[7] H. Kameoka, ibid., 9, 351 (1960).

TABLE VI. REACTION PRODUCTS

Reaction No.	Petroleum ether soluble portion [A]			Petroleum ether insoluble portion [B]											
				Water soluble portion (c)							White crystalline substance (b)				
				Crystalline substance (d)			Aqueous solution (e)								
								Acidic liquid substance, g.							
	Yield g.	N. v.	Fatty acids detected *, △	Yield g.	N. v.	Acids detected □, ○	Na-salt (f) g.	Yield g.	N. v.	Acids detected, *	Weight g.	A. v.	S. v.	M. p., °C	Acids detected
1	1.5	235.7	C_{18}, C_{12}, C_{10}, C_9, C_8, C_6, C_4-monobasic	0.6	589.3	C_2, C_3, C_4, C_6, C_9-dibasic	1.3	0.3	320.9	C_2, C_3, C_4, C_6-monobasic	2.5	72.1	177.6	110~119	Methyl 9,10-dihydroxy-stearate
2	1.0	307.1	C_{18}, C_{12}, C_{10}, C_9, C_8, C_6, C_4-monobasic	1.1	659.9	C_4, C_6, C_9-dibasic	1.9	1.0	559.7	C_2, C_3, C_4, C_6-monobasic	1.7	55.8	188.4	89~ 96	〃
3	1.2	346.1	C_{12}, C_{10}, C_9, C_8, C_4, C_3, C_2-monobasic	1.8	603.2	C_2, C_3, C_4, C_6, C_9-dibasic	2.8	1.4	735.2	C_2, C_3, C_4, C_6-monobasic	0.5	43.0	186.8	94~104	〃
4	1.2	306.6	C_{12}, C_{10}, C_9, C_8, C_4, C_3, C_2-monobasic	1.7	594.8	C_4, C_6, C_9-dibasic	1.9	0.9	783.6	C_2, C_3, C_4-monobasic	1.0	47.1	180.6	88~104	〃
5	1.7	321.5	C_{12}, C_{10}, C_9, C_8, C_6, C_4, C_3-monobasic	2.1	615.0	C_4, C_6, C_9-dibasic	2.8	1.4	755.0	C_2, C_3, C_4-monobasic	1.4	39.8	176.5	92~104	〃
6	1.9	331.2	C_{12}, C_{10}, C_9, C_8, C_6, C_4-monobasic	2.0	605.1	C_3, C_4, C_6, C_9-dibasic	3.4	1.7	743.0	C_2, C_3, C_4-monobasic	4.3	40.5	179.8	93~104	〃
7	2.3	332.4	C_{12}, C_{10}, C_9, C_8, C_6, C_4, C_3-monobasic	3.2	590.6	C_4, C_8, C_9-dibasic	3.8	1.8	780.6	C_2, C_3, C_4-monobasic	2.5	43.6	181.5	89~104	〃

Paper chromatography: * hydroxamic acid process[3)]; △ 2,4-dinitrophenylhydrazide process[4)]; □ chloroform-acetic acid-water process[5)]; ○ petroleum ether-chloroform-acetic acid process[6)].

of the formation of C_{12}, C_{10}-acids, hydroxy acids were not obtained. The mechanism concerning no formation of hydroxy acid has not yet been available.

The formation of considerably large amount of C_4- and C_6-dibasic acids was observed. These products should result from (i) the further oxidation of the substances produced by the breakage of the bond between 9 and 10, and (ii) the secondary oxidation of monobasic C_{12}- and C_{10}-acids which are produced by the direct oxidation of methyl 9, 10-dihydroxystearate. The formation of considerably quantities of dibasic acids will be ascribed to the oxidation of the methyl group of the lower monobasic acids produced by the direct oxidation mentioned above. Moreover, in case of the oxidizing conditions as in Reactions No. 1, No. 3 and No. 6, the formation of lower members of dibasic acid such as C_2 and C_3 was recognized. These C_2- and C_3-dibasic acids may probably be formed under other conditions of reaction. Because of the easy decomposition of these dibasic acids, however, they will be decomposed when the reaction conditions are intense. Furthermore, it is considered that the formation of various lower homologues of fatty acid is due to the same oxidation course as that of the saturated fatty acid methyl ester(2) irrespective of the hydroxyl groups present in the sample molecule.

In short, in the oxidation of methyl 9, 10-dihydroxystearate with hydrogen peroxide, the following reactions will be presumed. That is, the positions 9, 10 containing hydroxyl groups are first oxidized, and the products of such oxidation are subjected to the secondary oxidation, and also there occurs the other reaction following the course of the oxidation similar to that of the saturated acid.

Summary

Methyl 9, 10-dihydroxystearate is oxidized with a 30% hydrogen peroxide solution, under such conditions as the mole ratio of methyl 9, 10-dihydroxystearate to hydrogen peroxide is one to fifteen or more, the reaction time 2 hr., the temperature 138~155°C, and the pressure 110~145 kg./cm^2. Also, it was recognized that 80% or more of methyl 9, 10-dihydroxystearate was oxidized.

As the oxidation products, acetic, propionic, butyric, caproic, caprilic, pelargonic, caprinic and lauric acids were obtained as monobasic acids, and oxalic, malonic, succinic, adipic and azelaic acids were also produced as dibasic acids. Especially, succinic and adipic acids were obtained with good yield.

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