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Oxidation of Methyl Conjugated Octadecadienoate with Monoperphthalic Acid

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Methyl *trans*-9-*trans*-11-octadecadienoate was oxidized with monoperphthalic acid under various conditions. The products obtained were separated into several fractions by washing them with an alkaline solution and then submitting them to column chromatography. The substance thus obtained from each fraction was studied by chemical and spectroscopic procedures. From the results of chemical tests, periodic acid cleavage, and spectroscopic observation in the infrared and ultraviolet regions, it is inferred that the oxidation products in all cases contain all the methyl *trans*-9,10-epoxy-*trans*-11- and methyl *trans*-11,12-epoxy-*trans*-9-octadecenoates, methyl dihydroxy-*trans*-octadecenoate, and methyl 9(10)-hydroxy-10(9)-(*o*-carboxy)benzoyloxy-*trans*-11- and methyl 11(12)-hydroxy-12(11)-(*o*-carboxy)benzoyloxy-*trans*-9-octadecenoates.

In the course of our studies of the oxidation of conjugated unsaturated fatty esters with organic peracids, it has been shown that the product obtained by treating methyl sorbate with monoperphthalic acid was methyl *trans*-4,5-epoxy-*trans*-2-hexenoate.[1] On the other hand, it has also been shown that no epoxy compounds were found in the oxidation products obtained by treating methyl β-eleostearate with peracetic, perbenzoic, and monoperphthalic acids.[2] Therefore, an investigation has been made to see what substances are obtained by the action of an organic peracid on methyl conjugated dienoate, which has the same number of carbon atoms as methyl eleostearate.

In the present study, methyl *trans*-9-*trans*-11-octadecadienoate was treated with monoperphthalic acid under various conditions. The oxidation product mixture thus obtained was then separated into several fractions, and the structures of the main components in each fraction were investigated.

Experimental*1

Materials. *Monoperphthalic Acid.* Monoperphthalic acid was prepared by the method described in a previous paper.[1]

Ricinelaidic Acid. Barium ricinoleate obtained from castor oil was purified by recrystallization from ethanol, and the ricinoleate was acidified to obtain pure ricinoleic acid. The ricinoleic acid was then isomerized with potassium nitrite and nitric acid at 60°C for 3 hr according to the procedure of McCutchon *et al.*[3] The crude product was recrystallized from 90% acetone to obtain pure ricinelaidic acid melting at 51.5—51.8°C (lit.[3] 51.0—51.5°C).

Methyl trans-9-trans-11-Octadecadienoate [$CH_3(CH_2)_5CH$=$CHCH$=$CH(CH_2)_7COOCH_3$]. According to the procedure of Schneider *et al.*,[4] pure ricinelaidic acid was heated at 235°C for 3 hr *in vacuo*, and then the temperature was increased until smooth distillation occurred. The distillate (bp 210—215°C at 4 mmHg) was recrystallized from 95% ethanol to obtain pure *trans*-9-*trans*-11-octadecadienoic acid melting at 54.5—55°C (lit.[5] 53—54°C). The dienoic acid was esterified by refluxing it with methanol, using sulfuric acid as a catalyst, under a nitrogen atmosphere. The GLC analysis of a polyester column of the methyl ester indicated the presence of a single component. The molar absorbance of the methyl ester was 33600 (lit.[5] 33400) at λ_{max} 231.5 mμ in a heptane solution.

Analysis. The monoperphthalic acid and oxirane oxygen contents were determined by the methods described in a previous paper.[1]

The other chemical characteristics were determined in the usual manner.

Spectroscopic Observation. The ultraviolet absorption was measured with a Beckman DU Spectrophotometer.

The infrared absorption was measured in a liquid film with a Perkin Elmer 337 Grating Infrared Spectrophotometer, a sodium chloride cell being used.

Oxidation. Methyl *trans*-9-*trans*-11-octadecadienoate (0.10 mol) was dissolved in 300 m*l* of ether, and then 0.10 mol of monoperphthalic acid was added to the

1) Y. Suhara and T. Minami, This Bulletin, **39**, 1968 (1966).

2) Y. Suhara and M. Nyui, *Yukagaku* (*J. Japan Oil Chemists' Soc.*), **13**, 590 (1964).

*1 All melting and boiling points are uncorrected.

3) M. A. McCutchon, R. T. O'Connor, E. F. DuPre, L. A. Goldblatt and W. G. Bickford, *J. Am. Oil Chemists' Soc.*, **36**, 115 (1959).

4) W. J. Schneider, L. E. Gast and H. M. Teeter, *ibid.*, **41**, 606 (1964).

5) H. P. Kaufmann, J. Baltes, F. Volbert and K. Brockhausen, *Fette, Seifen, Anstrichmittel*, **52**, 210 (1950).

solution under stirring. The mixture was stirred in the temperature range between 10 and 13°C. After 13 hr, 92.3% of monoperphthalic acid was consumed. The reaction mixture, containing the precipitate of *o*-phthalic acid[1] formed by the reaction, was then filtered off, and the filtrate was washed with water until free of acid. The ether solution was dried over anhydrous sodium sulfate, and then ether was distilled off *in vacuo* to measure the yield of the oxidation product mixture.

Separation of the Oxidation Product Mixture. The oxidation product mixture (28.4 g) was dissolved in 200 m*l* of ether again, and the ether solution was washed with 800 m*l* of a 5% aqueous potassium carbonate solution and then with water. The ether solution was dried over anhydrous sodium sulfate, and then the ether was distilled off *in vacuo*. The residue (14.6 g) was dissolved in 146 m*l* of petroleum ether, after which the solution was chromatographed over alumina. The inner diameter of the column was 20 mm, and the weight of alumina used was 365 g. The substances on the column were eluted with petroleum ether, ether, and glacial acetic acid successively. The volume of each solvent used was 600 m*l*. The solvent in the petroleum ether elution was distilled off *in vacuo*. The weight of the residue (I) was 2.0 g. The residue (II) obtained from the ether elution by the same procedure weighed 9.0 g. The glacial acetic acid elution was poured into water. The oil separated was extracted with ether, and then the ether solution was wahsed with water until free of acid. The ether solution was dried over anhydrous sodium sulfate, and then the ether was distilled off *in vacuo*. The weight of the residue (III) was 3.4 g.

On the other hand, the alkaline solution obtained by washing the ether solution of the reaction product mixture with potassium carbonate solution and water, was acidified with diluted sulfuric acid. In this case, hydrochloric acid was not used in order to avoid the opening of the oxirane ring which might be present in the solution. The oil separated was extracted with ether, and the ether solution was washed with water until free of acid. The ether solution was dried over anhydrous sodium sulfate, and then the ether was distilled off *in vacuo*. The weight of the residue (IV) was 13.6 g.

A part of IV (6.0 g) was saponified with potassium hydroxide in ethanol. The white precipitate formed during this procedure was filtered off, and then the saponified solution was acidified with diluted sulfuric acid. The oil separated was extracted with ether, and the ether solution was washed with water until free of acid. The ether solution was dried over anhydrous sodium sulfate, and then the ether was distilled off *in vacuo*. The weight of the residue (V) was 3.9 g.

The precipitate formed during the saponification procedure was acidified with hydrochloric acid in water, and then the water was evaporated *in vacuo*. The solid obtained was recrystallized from ethanol. This recrystallization gave white crystals melting at 208—209°C. A mixture of the crystals with *o*-phthalic acid (mp 210—211.5°C) melted at 199—202°C. The analytical characteristics of the crystals were as follows: Acid value: found, 680.3; calcd for phthalic acid, 675.4. Saponification value (found): 679.5. UV ε: 1260 at λ_{max} 274 mμ in an ethanol solution. (The λ_{max} of *o*-phthalic acid in a methanol solution is 272 mμ[6]).

6) Sadtler, 6272U, Samuel P. Sadtler & Son, Inc., Philadelphia (1960).

Therefore, the crystals are *o*-phthalic acid.

Determination of the Positions of Epoxy and Hydroxyl Groups. In the Results and Discussion section of this paper, it will be inferred that II is an epoxy compound, while III and V will be inferred to be dihydroxy compounds. Therefore, the positions of epoxy and hydroxyl groups on them were investigated. For this purpose, II, III, and V were converted to the corresponding dihydroxyoctadecanoic acids according to the procedure of Maerker *et al.*[7] The vicinal hydroxyl group content of the dihydroxy acid was determined according to the procedure of the A.O.C.S. method[8] for the determination of the α-monoglyceride content.

In the case of the dihydroxyoctadecanoic acid, which has vicinal hydroxyl groups, the dihydroxy acid was cleaved into aldehyde and aldoacid with periodic acid according to the procedure of Maerker *et al.*[7] The aldehyde and aldoacid thus obtained were then both oxidized to give mono- and dicarboxylic acid with silver oxide according to the procedure of Bumpus *et al.*[9] After the resultant mono- and dicarboxylic acids had been esterified with diazomethane, the esters obtained were analyzed by gas-liquid chromatography. The instrument used was a Hitachi Gas Chromatograph KGL-2B with an Apiezon M column.

Results and Discussion

The peroxide values of the residues I—V were in the range between 40.1 and 49.3 meq/kg. Such values may be due to the presence of traces of monoperphthalic acid. If any peroxides at all are formed during the oxidation reaction, the amounts of these peroxides as calculated from the peroxide values are all negligible.

The structures of the main components in the residues I—V will be discussed below.

I. The saponification value was 191.6; this value agrees with the theoretical value for the starting material (190.5). The molar absorbance was 33500 at λ_{max} 231.5 mμ in a heptane solution. The intense absorption at this wavelength arises from the conjugated *trans,trans* diene.[5] Moreover, the infrared spectrum exhibited the band at 988 cm^{-1} assigned to the conjugated *trans,trans* diene;[10] its spectrum was nearly the same as that of the starting material.

From these facts, I may be said to be the unreacted starting material.

II. II was purified by recrystallization from methanol at the temperature of −30°C. The saponification and iodine values and the oxirane oxygen content of the purified product (II′) were 181.7, 80.0 and 5.03% respectively; these values agree with the theoretical values for methyl epoxyoctadecenoate (saponification value, 180.7; iodine value,

7) G. Maerker, E. T. Haeberer and W. C. Ault, *J. Am. Oil Chemists' Soc.*, **43**, 100 (1966).
8) A. O. C. S. Tentative Method, Cd 11-57.
9) F. M. Bumpus, W. R. Taylor and F. M. Strong, *J. Am. Chem. Soc.*, **72**, 2116 (1950).
10) D. Chapman, *J. Am. Oil Chemists' Soc.*, **42**, 353 (1965).

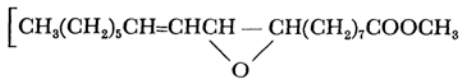
81.7; oxirane oxygen content, 5.15%). In the ultraviolet observation, no peak appeared in the wavelength region between 220 and 400 mμ in a heptane solution. The infrared spectrum exhibited the band at 968 cm^{-1} assigned to the isolated *trans* double bond.[10] The band at 890 cm^{-1} is due to the *trans* oxirane group.[11] Neither of the two bands assigned to the *cis* oxirane group (near 830 cm^{-1})[11] and the larger ring of cyclic ether (1140—1070 cm^{-1})[11] were present in the spectrum.

From these facts, II′ may be inferred to be methyl *trans*-epoxy-*trans*-octadecenoate.

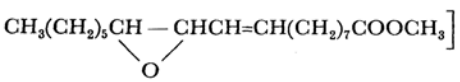
In order to determine the position of the oxirane ring on the hydrocarbon chain, II′ was converted to dihydroxyoctadecanoic acid. The vicinal hydroxyl groups content of the dihydroxy acid was 10.33%; the content is similar to the theoretical content for vicinal dihydroxyoctadecanoic acid (10.75%).

The cleavage product mixture obtained by treating the dihydroxy acid with periodic acid, followed by oxidation and esterification, was an almost equimolar mixture of methyl esters of heptanoic, nonanoic, nonanedioic, and undecanedioic acids.

From the results of the chemical tests, the periodic acid cleavage, and the infrared and ultraviolet spectrophotometry described above, II′ may be inferred to be an almost equimolar mixture of methyl *trans*-9,10-epoxy-*trans*-11- and methyl *trans*-11,12-epoxy-*trans*-9-octadecenoates



and

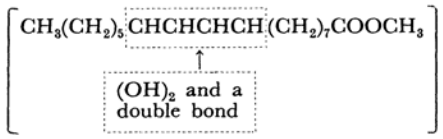


III. The saponification, iodine, and hydroxyl values were 174.1, 75.2, and 338.3 respectively; these values agree with the theoretical values for methyl dihydroxyoctadecenoate (saponification value, 170.8; iodine value, 77.3; hydroxyl value, 341.6). In the ultraviolet observation, no peak appeared in the wavelength region between 220 and 400 mμ in a heptane solution. The infrared spectrum exhibited the band at 968 cm^{-1} assigned to the isolated *trans* double bond.[10] The bands at 3418 and 1072 cm^{-1} are due to the hydroxyl group[12] and to the secondary alcohol, which has α-unsaturation[13] respectively.

From these facts, III may be inferred to be methyl dihydroxy-*trans*-octadecenoate.

In order to determine the positions of hydroxyl groups, III was converted to dihydroxyoctadecanoic acid. The vicinal hydroxyl group content of the dihydroxy acid was only 0.46%. This fact shows that the positions of hydroxyl groups on the dihydroxy acid are not vicinal.

From the results of the chemical tests, and the infrared and ultraviolet spectrophotometry, it may be inferred that III is methyl dihydroxy-*trans*-octadecenoate, on which the positions of hydroxyl groups are not vicinal



IV and V. The acid, saponification, iodine, and hydroxyl values of IV were 116.4, 351.8, 53.0, and 116.7 respectively; these values agree with the theoretical values for methyl hydroxy-(carboxy)benzoyloxyoctadecenoate (acid value, 117.2; saponification value, 353.2; iodine value, 53.3; hydroxyl value, 117.2). If IV is a mixture of phthalic acid and methyl hydroxyoctadecenoate, the phthalic acid content as calculated with the found acid value of IV is 34.5%, and hence, that of methyl hydroxyoctadecenoate is 65.5%. In this case, the acid, iodine, and hydroxyl values of the mixture are 116.4, 53.3, and 117.8 respectively; these values agrees with the found values of IV. The saponification value of the mixture, however, is only 234.0, in contrast to the found value of IV, 351.8. Therefore, IV is not the mixture described above. Since the ether solution containing IV was washed with water until it was acid free, IV does not contain free phthalic acid. Free *o*-phthalic acid, however, was liberated from IV by the saponification procedure.

In the ultraviolet observation of IV, a very weak peak appeared at 274 mμ in a heptane solution; this peak suggests the presence of the phenyl group.[6] The infrared spectrum exhibited the band at 968 cm^{-1} assigned to the isolated *trans* double bond.[10] The bands at 3450 and 1072 cm^{-1} are due to the hydroxyl group[12] and to the secondary alcohol, which has α-unsaturation,[13] respectively. In addition, the spectrum showed the three bands at 1602, 1580, and 1490 cm^{-1}; all of them are due to aromatic hydrocarbons.[14] These results are in harmony with the results of ultraviolet observation. The band at 1740 cm^{-1} due to the ester carbonyl group[15] was broarder than that of the starting material; this suggests the possibility of the presence of acid carbonyl.

From these facts, IV may be inferred to be methyl hydroxy-(*o*-carboxy)benzoyloxy-*trans*-octadecenoate.

The acid, saponification, iodine, and hydroxyl values of V were 175.8, 176.3, 78.7, and 354.3 respectively; these values agree with the theoretical

11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London (1958), p. 114.
12) L. J. Bellamy, *ibid.*, p. 95.
13) L. J. Bellamy, *ibid.*, p. 109.
14) L. J. Bellamy, *ibid.*, p. 64.
15) L. J. Bellamy, *ibid.*, p. 178.

values, 178.4; iodine value, 80.7; hydroxyl value, 356.8). In the ultraviolet observation, no peak appeared in the wavelength region between 220 and 400 mμ in a heptane solution. The infrared spectrum exhibited the band at 968 cm^{-1} assigned to the isolated *trans* double bond.[10] The bands at 3380 and 1072 cm^{-1} are due to the hydroxyl group[12] and to the secondary alcohol, which has α-unsaturation,[13] respectively. The strong band at 1708 cm^{-1} is due to the acid carbonyl group.[16]

From these facts, V may be inferred to be dihydroxy-*trans*-octadecenoic acid.

Three and nine-tenth grams of V were obtained from 6.0 g of IV; this yield agrees with the theoretical yield of dihydroxyoctadecenoic acid based on the weight of methyl hydroxy-(carboxy)benzoyloxy-octadecenoate. This fact also supports the inferrences that IV is methyl hydroxy-(carboxy)benzoyloxyoctadecenoate and that V is dihydroxyoctadecenoic acid.

In order to determine the positions of the hydroxyl groups, V was converted to dihydroxyoctadecanoic acid. The vicinal hydroxyl group content of the dihydroxy acid was 10.54%; the content agrees with the theoretical content for vicinal dihydroxyoctadecanoic acid (10.75%).

The cleavage product mixture obtained by treating the dihydroxy acid with periodic acid, followed by oxidation and esterification, was an almost equimolar mixture of methyl esters of heptanoic, nonanoic, nonanedioic, and undecanedioic acids.

From the results of the chemical tests, the periodic acid cleavage, and the infrared and ultraviolet spectrophotometry described above, V may be inferred to be an almost equimolar mixture of 9,10-dihydroxy-*trans*-11- and 11,12-dihydroxy-*trans*-9-octadecenoic acids

$$\left[CH_3(CH_2)_5CH{=}CHCH(OH){-}CH(OH)(CH_2)_7COOH\right.$$

and

$$\left.CH_3(CH_2)_5CH(OH){-}CHCH{=}CH(CH_2)_7COOH\right]$$

Therefore, IV may be inferred to be an almost equimolar mixture of methyl 9-(10)-hydroxy-10(9)-(*o*-carboxy)benzoyloxy-*trans*-11- and methyl 11(12)-hydroxy-12(11)-(*o*-carboxy) benzoyloxy-*trans*-9-octadecenoates

$$\left[CH_3(CH_2)CH{=}CHCH(OR){-}CH(OH)(CH_2)_7COOCH_3\right.$$

and

$$\left.CH_3(CH_2)_5CH(OR){-}CHCH{=}CH(CH_2)_7COOCH_3\right];$$

R: $-CO-C_6H_3(COOH)-$

16) L. J. Bellamy, *ibid.*, p. 161.

Table 1. Conditions of oxidation
Methyl *trans*-9-*trans*-11-octadecadienoate
29.4 g (0.10 mol)
Ether as solvent 300 ml

Expt. No.*	Monoperphthalic acid mol	Reaction temp. °C	Reaction time hr	Consumption of peracid %
1	0.10	7— 9	13	87.8
2	0.10	7— 9 10—13	13 3	91.8
4	0.10	16—18	7	85.8
5	0.16	10—13	13	69·4
6	0.20	10—13	10	59.4

* Expt. No. 3 was described in the section of Experimental.

The other conditions of oxidation are shown in Table 1. The weights of substances obtained from similar fractions described in the Experimental section are presented in Table 2. The chemical characteristics and the ultraviolet and infrared spectra of the substances are nearly the same as those of substances described above. The weight of the oxidation products of Expt. Nos. 5 and 6 are considerably higher than those of the others. These higher weights are caused by the increased we ight of their alkaline soluble substances.

Table 2. Weights of substances obtained from fractions

A

Expt. No.	Oxidation product g	Alkaline insoluble substance g	Alkaline soluble substance g
1	28.0	17.6	10.0
2	28.6	16.2	12.0
4	28.8	12.4	15.6
5	33.6	13.8	19.0
6	39.6	10.4	28.2

B

Expt. No.	Substance from petroleum ether elution g	Substance from ether elution g	Substance from AcOH elution g
1	4.6	9.2	3.4
2	3.2	9.4	3.4
4	1.4	7.2	3.6
5	1.4	8.0	4.2
6	0.8	6.0	3.4