# Ethylene Adduct of Conjugated Octadecadienoic Acids: II. Ozonization Products[1]

**E. J. DUFEK, J. C. COWAN and J. P. FRIEDRICH,**
**Northern Regional Research Laboratory,[2] Peoria, Illinois 61604**

## Abstract

Methyl 8-(4-*n*-hexylcyclohex-2-enyl)octanoate obtained by esterifying the adduct of ethylene and *trans,trans*-9,11-octadecadienoic acid was ozonized in methanol as a participating solvent. The resultant cyclic methoxyhemiperacetal was reduced with powdered zinc to the dialdehyde, methyl 9,12-diformylstearate, which was isolated as the tetramethyldiacetal. This dialdehyde readily air-oxidizes to give methyl 9,12-dicarboxystearate. Heating the cyclic methoxyhemiperacetal slowly from 25 to 100 C in vacuo results in an unusual decomposition reaction which gives hydrogen and methyl 9(12)-carbomethoxy-12(9)-carboxystearate as the primary products and methyl 9(12)-carbomethoxystearate as the major by-product. Treatment of the cyclic hemiperacetal with hydrogen peroxide in formic acid gave unexpectedly dihydroxystearic acid as one of the products.

## Introduction

The preceding paper (9) describes some peracid oxidation studies carried out on a $C_{20}$ cyclohexene fatty acid prepared by the Diels-Alder addition of ethylene to *trans,trans*-9,11-octadecadienoic acid. The $C_{20}$ adduct, 8-(4-*n*-hexylcyclohex-2-enyl)octanoic acid (CHA) (I) and ester (CHA-*me*), were oxidized in various media to give excellent yields of the desired epoxy, hydroxyformoxy and dihydroxylated products.

Although peracid oxidation reactions were carried out on CHA, a model compound, the commercial potential lies in the isomeric mixtures of $C_{20}$ fatty acids (ICHA) which are readily obtained when vegetable oils containing linoleic acid are treated with alkali and ethylene at 3000 psi and 260 C (14).

Work is being continued at the Northern Laboratory to prepare additional polyfunctional oxygenated derivatives of CHA. This paper describes the preparation of 9,12-dicarboxy- and 9,12-diformyl derivatives of stearic acid, which were obtained by ozonolysis and reductive ozonolysis of methyl 8-(4-*n*-hexylcyclohex-2-enyl)octanoate; see Scheme 1.

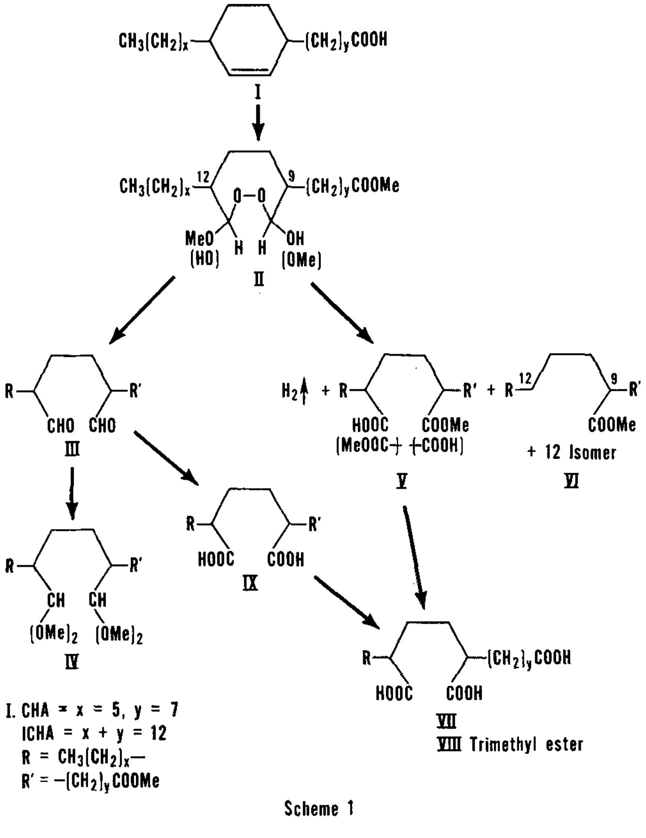
## Discussion

Ozonolysis by known procedures (1,17) of methyl 8-(4-*n*-hexylcyclohex-2-enyl)octanoate (CHA-*me*) (I) in methanol as a participating solvent yields an 8-membered cyclic methoxyhemiperacetal, methyl 8-(6-n-hexyl-2(5)-hydroxy-5(2)-methoxy-3,4-dioxacyclooctyl)octanoate (II). Data on II from elemental, methoxyl and active oxygen determinations agree closely with calculated values. Analysis for hydroperoxide (–OOH) with lead tetraacetate was negative (8). The cyclic structure proposed for II is similar to the structures described by Bailey (4,6) for the ozonolysis of phenanthrene in methanol, and later, by Warnell and Shriner (20) for the ozonolysis of indene in ethanol.

The hemiperacetal, II, is stable when stored at −25 C; however, when warmed to room temperature II decomposes slowly with evolution of a gas. Mass spectrometric analysis of the gaseous product showed its composition to be mainly hydrogen, a smaller amount of carbon monoxide and some carbon dioxide. Decomposition of II was carried out in vacuo by heating at 40 C for at least 8 hr, then at 50 C for at least 24 hr, and finally by increasing the temperature slowly to 100 C until completion of the decomposition. In this manner the decomposition of II could be controlled and the reaction followed by the periodic determination of the remaining active oxygen.

Attempts to shorten the time for decomposition of II by increasing the initial temperature above 60 C resulted in an extremely rapid evolution of gases. The acidic product formed was a complex mixture when it was analyzed, as methyl esters, by gas liquid chromatography (GLC). This method of decomposition was not considered further, and no attempt was made to interpret the complex gas liquid chromatogram.

When the crude acidic product (neutral equivalent 472) from the slow method of decomposition after esterification with diazomethane was analyzed by GLC (Fig. 1), the respective yields of methyl 9,12-dicarbomethoxystearate (VIII) and methyl 9(12)-carbomethoxystearate (VI) were 76% and 15–17%. The retention time of two minor components also



Scheme 1

---

[1] Presented in part at the AOCS-AACC Meeting, Washington, D.C., April 1968.

[2] No. Utiliz. Res. Dev. Div., ARS, USDA.

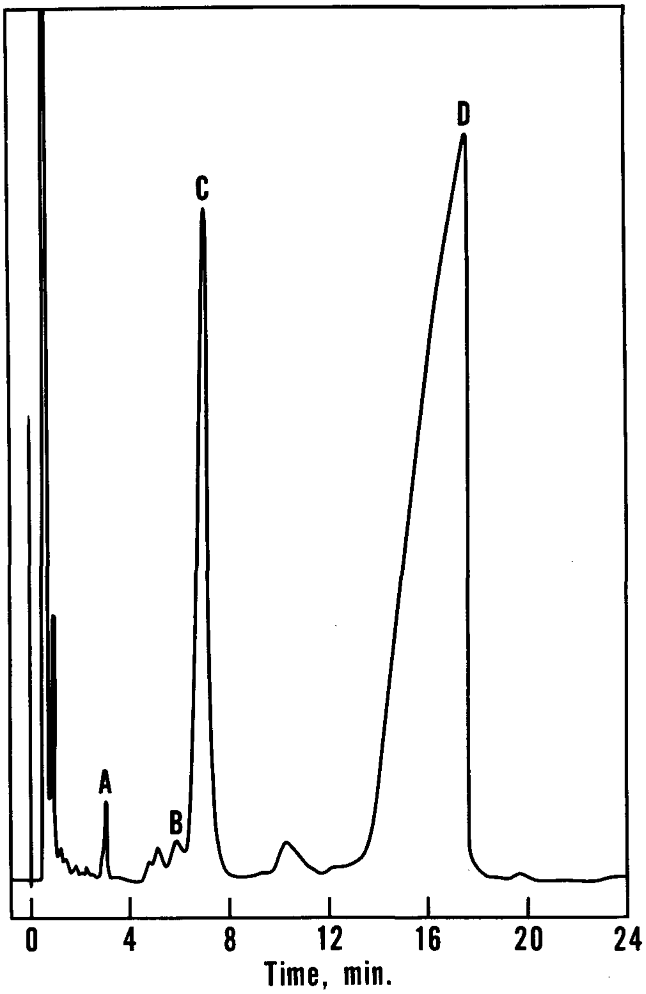
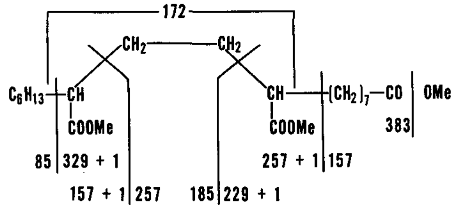


FIG. 1. Gas chromatogram of crude products (methyl esters) from heat-decomposed methoxyperoxyhemiacetal (II). (A) Methyl stearate (?) (B) Methyl 8-(4-*n*-Hexylcyclohex-2-enyl)octanoate (?). (C) Methyl 9(12)-carbomethoxystearate (VI). (D) Methyl 9,12-dicarbomethoxystearate. F&M gas chromatograph Model 5750, 6 ft × ¼ in. column packed with 3% JXR and programmed at 225 C and 30 cc/min.

in the mixture (total less than 2%) indicates the presence of CHA methyl ester (unreacted starting material) and methyl stearate. The presence of methyl stearate indicates that a small amount of double decarboxylation occurs. The remaining oxidation products are unidentified. GLC analysis of the crude acidic products before esterification with diazomethane showed that VI was present, at least in part, as the carbomethoxystearate. The acid ester of VI (a carboxystearate) may also be present since it would probably be held up on the column, but there is no evidence for its presence. The acidity in the decomposition product was due mainly to methyl 9(12)-carboxy-12(9)-carbomethyoxystearate (V). Attempts to isolate V by recrystallization from hexane, ethyl acetate, or acetone failed. Saponification of the crude acidic products containing V followed by crystallization from benzene gave a 73.4% yield (based on CHA-*me*) of 9,12-dicarboxystearic acid (VII).

Treatment of VII with diazomethane gave VIII, whose structure was confirmed by mass spectrometric analysis as a $C_{20}$ tribasic acid (trimethyl ester). The expected molecular ion peak at m/e = 414 was not present. The loss of $CH_3O$– from the molecular ion gave rise to the expected peak at m/e = 383. Other



Scheme 2

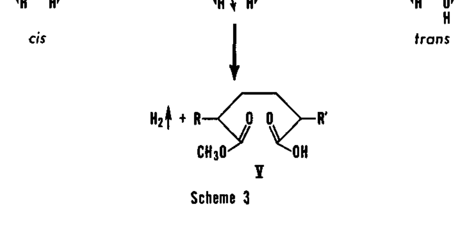
fragmentation peaks also present at m/e = 198, 226, 266, 291, 298, 323 and 354 are the result of multiple fragmentations of $H_2O$, $CH_3OH$, $CH_3O\text{–}\overset{O}{\overset{\|}{C}}\text{–}$, and $CH_3O\text{–}\overset{+OH}{\overset{\|}{C}}\text{–}CH_2\text{–}$ (the m/e = 74 peak) found in all methyl esters; see Scheme 2. Since the mass spectrum also had a strong peak at m/e = 174, $CH_3O\text{–}\underset{OH}{\underset{|}{C}}= CHCH_2CH_2\overset{/}{C}H\text{–}\underset{+OH}{\underset{\|}{C}}\text{–}OCH_3$ is proposed as a possible structure. This structure, however, should be doubly charged because it has two rearranged hydrogens giving rise to the peak at m/e = 87.

Mass spectrometric analysis also confirmed the composition of VI as a mixture of methyl 9- and 12-carbomethoxystearates. Major peaks at m/e = 127, 157, 199+1, 229+1 and 325 occurred in the spectrum for the 9-isomer and peaks at m/e = 85, 157+1, 199, 271+1 and 325, for the 12-isomer. These data agree with the fragmentation patterns reported by Frankel et al. (13) for the quantitative mass spectrometric analysis of methyl carbomethoxystearates.

The hydrogen-yielding decomposition of II is an unusual reaction but mechanistically feasible via a 6-membered cyclic transition state which can be formed from the *cis*-isomer of the hemiperacetal, II. The decomposition is similar to that reported by Briner and Meier (7) for the product obtained by ozonolysis of butene-1 with water as the participating solvent. Their product, a dihydroxyperoxide, yielded propionic and formic acids as well as hydrogen. Scheme 3 shows reaction for II.

The spatial arrangement of the molecules at the time of formation of II should give rise to both *cis*- and *trans*-isomers. The *trans*-isomer can also form a 6-membered cyclic transition state yielding an ester aldehyde under these conditions (16); however, none was present as indicated by the dinitrophenyl hydrazone test.

A reasonable mechanism for the formation of VI cannot be given at this time other than a radical decomposition or a rearrangement of the Criegee



Scheme 3

zwitterions (5,19) before addition to the aldehyde and stabilization by addition of methanol. Attempts to increase the yield of VI by prolonged heating of II → V + VI in vacuo or heating VII for three days in vacuo failed to produce VI.

Oxidative cleavage of II (isomeric mixture prepared from ICHA) with hydrogen peroxide in formic acid, followed by saponification, yielded VII and an isomeric mixture of dihydroxystearic acids in 59.3% and 21.3% yields (GLC analysis), respectively. Compound VI was not formed in this reaction. The dihydroxystearic acids, which were isolated by crystallization, had a neutral equivalent of 317 (calcd 316.5). Correct microanalytical data were obtained on both the acid and its methyl ester. Mass spectrometric analysis of the methyl esters showed them to be a mixture of dihydroxystearates with hydroxyl groups on carbons 6 through 15. These methyl dihydroxystearates were compared with a mixture of methyl 9,12- and 10,12-dihydroxystearate prepared from methyl ricinoleate by epoxidation (10,11) and catalytic reduction (12,15). The retention times (GLC) of the dihydroxystearates prepared from ICHA and methyl ricinoleate were identical.

Reductive ozonolysis of CHA-*me* in methanol and acetic acid with activated powdered zinc (3) gave methyl 9,12-diformylstearate (III). Some of the impurities, believed to be dimethyl acetals, were removed by recrystallization. Although hydrolysis in acidic aqueous acetone removed most of the acetals, other unidentified byproducts were formed that were not removed by recrystallization. Reductive ozonolysis of CHA-*me* with hydrogen and 10% palladium on carbon (17) yielded a complex mixture of products. No attempt was made to separate this mixture. Treatment of the dialdehyde III (prepared from ICHA-*me*) with methanol and dimethoxypropane under acidic conditions gave the dimethyldiacetal, methyl 9,12-bis(dimethoxymethyl)stearate (IV).

Air-oxidation of the dialdehyde (III) gave a 70% yield (GLC) of methyl 9,12-dicarboxystearate (IX). Attempts to prepare IX directly from CHA-*me* by ozonolysis in methylene chloride and water at 0 to 10 C followed by decomposition of the cyclic peroxide, methyl 8-(6-*n*-hexyl-2,5-dihydroxy-3,4-dioxacyclooctyl)octanoate, (similar to II → V) resulted in a product that gave a complex gas liquid chromatogram containing 36.4% IX, 12.1% VI and 10.6% III. The other peaks were not identified. Correct microanalytical data were obtained on the cyclic dihydroxyperoxide.

## Experimental Procedures

All melting points were taken on a Kofler hot stage and are uncorrected.

Samples (ca. 1 mg) for GLC analysis were treated with diazomethane and run at 225 C or programmed from 180 to 300 C at 4°/min, 30 cc/min on an F&M model 5750 equipped with a 6 ft × 1/4 in., 3% JXR column.

### 8-(4-n-Hexylcyclohex-2-enyl)octanoic acid (CHA) (I)

This compound plus the isomeric mixture of I (ICHA), which differs from I only in the position of the cyclohexene ring and the methyl esters (CHA-*me* and ICHA-*me*), were prepared as previously described (9,14).

### Methyl 8-(6-n-Hexyl-2-hydroxy-5-methoxy-3,4-dioxacyclooctyl) octanoate (II)

CHA-*me* (6 g) in methanol (50 ml) was ozonized at 0–10 C according to the procedure described by Pryde et al. (18). Removal of the solvent in vacuo at room temperature gave 7.4 g of viscous water-white oil, which was stored at −25 C. The product slowly decomposed at room temperature. Test for hydroperoxide with lead tetraacetate was negative (8).

*Analysis.* Calculated for $C_{22}H_{42}O_6$: C, 65.63; H, 10.52; $CH_3O$, 15.42. Found: C, 65.54; H, 10.41; $CH_3O$, 15.35. Active oxygen (20) calculated: 3.98; found: 3.3.

One drop of the ozonized product (II) was converted to the bis-dinitrophenylhydrazone melting at 166–167 C (from ethyl acetate).

*Analysis.* Calculated for $C_{33}H_{46}N_8O_{10}$: C, 55.44; H, 6.48, N, 15.67. Found: C, 55.71; H, 6.66; N, 16.09.

### Methyl 9,12-Diformylstearate (III)

A solution of CHA-*me* (6.0 g) in glacial acetic acid (40 ml) and methanol (50 ml) at 0–10 C was treated with oxygen containing 2–3% ozone. After the reaction was complete, the solution was warmed to 20–25 C and powdered zinc (5 g) (3) was added portionwise at such a rate as to maintain the temperature at 20–25 C. The solution was stirred for 2 hr and gave a negative test for peroxide with acidified potassium iodide. After filtration the solution was poured into ice water and extracted with ether. The ether solution was washed with 5% sodium bicarbonate and water, and then dried. Evaporation of the ether gave 6.5 g of product. GLC analysis indicated that 85% of the product was a mixture of III and its dimethyl acetals. Carbonyl by hydroxylamine hydrochloride was 12.3% (81.2% of theoretical). Methoxyl calcd. for III: 8.75; found: 12.61. This product was purified partially by recrystallization from hexane, ethyl acetate and acetone. The melting point was 33–37 C.

*Analysis.* Calculated for III, $C_{21}H_{38}O_4$: C, 71.14; H, 10.80; $CH_3O$, 8.75. Found: C, 70.77; H, 10.90; $CH_3O$, 9.88.

The 2,4-dinitrophenylhydrazone melted at 165–167 C. Hydrolysis of 1 g of impure dialdehyde in water (10 ml) and acetone (40 ml) containing hydrochloric acid (2 drops) for 2 hr yielded a product with decreased amount of methyl acetals and increased amounts of unidentified by-products. Carbonyl by hydroxylamine hydrochloride for III was 11.28 (71.4%). Found $CH_3O$: 10.68.

ICHA-*me* (50 g) in acetic acid (50 ml) and methanol (50 ml) were ozonized, reduced and isolated as described above. The oil (56.6 g) was analyzed by IR for carbonyl (73%) (2). Carbonyl analysis by hydroxylamine, which includes both free aldehyde and dimethyl acetals, was 13% (85% of theoretical).

### Methyl 9,12-Bis(dimethoxymethyl)stearate (IV) (Isomeric Mixture)

The isomeric diformyl derivative (VI) (50 g) was added to a solution of dimethoxypropane (100 ml), methanol (200 ml), and 5% hydrogen chloride in methanol (20 ml). After standing at room temperature for 24 hr the solution was passed through alumina (25 g). Removal of the solvent and distillation of the product gave a water-white oil (49 g, 77.8%) boiling at 190–200 C (0.040 mm).

*Analysis.* Calculated for $C_{25}H_{50}O_6$: C, 67.22; H, 11.28; $CH_3O$, 34.73; carbonyl, 12.5%. Found: C, 68.10; H, 11.28; $CH_3O$, 32.5; carbonyl, 10.25% (82% of theoretical).

### Methyl 9(12)-Carbomethoxy-12(9)-carboxystearate (V)

CHA-*me* (5 g) was converted to II by ozonolysis in methanol. After removal of the methanol in vacuo, II was decomposed by heating slowly in vacuo to 40 C for 10 hr, at 50 C for 36 hr, and then heated slowly to 100 C. This temperature was maintained for 10 hr at which time the active oxygen was less than 0.1% (20).

*Analysis.* Calculated for $C_{22}H_{40}O_6$: C, 65.95; H, 10.07; $CH_3O$, 15.50. Found: C, 67.08; H, 10.44; $CH_3O$, 13.95.

The neutral equivalent of the water-white oil (5.9 g) was 472. The calculated neutral equivalent is 400.5. Attempts to purify this product by crystallization from hexane, ethyl acetate, or acetone failed. A sample of the crude decomposition product was treated with diazomethane and analyzed by GLC (Fig. 1): Trimethyl ester (VIII), 76%; dimethyl ester (VI), 15–17%; plus minor unidentified peaks believed to include CHA and methyl stearate.

In a second experiment the gases evolved from the decomposition of II were collected in an apparatus that was first flushed with helium and then evacuated. Mass spectrometric analysis of the gases collected showed qualitatively the presence of a trace amount of helium, a large quantity of hydrogen, a lesser amount of carbon monoxide, and a small amount of carbon dioxide.

### 9,12-Dicarboxystearic Acid (VII) and Methyl 9,12-Dicarbomethoxystearate (VIII)

The oil (5.1 g) containing V was saponified [potassium hydroxide (5 g), water (5 ml), and ethanol (50 ml)]. Acidification and three recrystallizations from benzene (25 ml)-ether (2–3 ml) yielded 3.65 g (73.4% based on starting material I) of VII melting at 117–118 C.

*Analysis.* Calculated for $C_{20}H_{36}O_6$: C, 64.48; H, 9.74; neutral equivalent, 124.1. Found: C, 64.70; H, 9.74; neutral equivalent, 125.5.

The triacid (VII) was treated with diazomethane and the trimethyl ester (VIII) filtered through Celite.

*Analysis.* Calculated for $C_{23}H_{42}O_6$: C, 66.62; H, 10.21; $CH_3O$, 22.46. Found: C, 66.72; H, 10.21; $CH_3O$, 22.33.

### Methyl 9(12)-Carbomethoxystearate (VI)

The benzene filtrates from the crystallization of VII which contained the major by-product (VI) were evaporated to remove benzene. The residue (1 g) was dissolved in a small quantity of benzene and placed on a silicic acid column (1 × 3 cm). The column was eluted with benzene and 50 ml fractions were collected. Each fraction was analyzed by GLC and the fraction containing VI was evaporated to dryness in vacuo at 100 C.

*Analysis.* Calculated for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31; $CH_3O$; 17.41. Found: C, 69.98; H, 11.16; $CH_3O$, 16.65.

### Methyl 9,12-Dicarboxystearate (IX)

Air was bubbled slowly through III (1 g) in toluene for two weeks. A sample treated with diazomethane and analyzed by GLC indicated a 70.2% yield of dicarboxy ester (IX). Three recrystallizations from ethyl acetate-methanol (9:1) gave IX melting at 116–118 C.

*Analysis.* Calculated for $C_{21}H_{38}O_6$: C, 65.25; H, 9.91; $CH_3O$, 8.03; N.E., 193.2. Found: C, 64.69; H, 9.88; $CH_3O$, 8.04; N.E., 203.1.

### Oxidative Cleavage of II

A solution of II (7 g, isomeric mixture prepared from ICHA-*me*), formic acid (100 ml), and 28% hydrogen peroxide (20 ml) was heated carefully until the solution became homogeneous. The reaction was exothermic and required external cooling. After the reaction subsided, the solution was refluxed for 1 hr, poured into water, and extracted with ether. The ether solution was washed with 5% sodium bicarbonate and then with water until neutral. The yield was 5.8 g. Saponification of 3 g of product with ethanolic potassium hydroxide followed by acidification gave a product containing 21.3% dihydroxystearic acid and 59.3% VII (GLC analysis as methyl esters). One recrystallization each from acetone and ethyl acetate gave 0.58 g of dihydroxystearic acid, mp 92–95 C.

*Analysis.* Calculated for $C_{18}H_{36}O_4$: C, 68.31; H, 11.47; N.E., 316.5. Found: C, 68.14; H, 11.32; N.E., 317.

The dihydroxy acid was treated with diazomethane and this mixture of isomeric methyl dihydroxystearates melted at 69–73 C.

*Analysis.* Calculated for $C_{19}H_{38}O_4$: C, 69.04; H, 11.58; $CH_3O$, 9.38. Found: C, 68.70; H, 11.50; $CH_3O$, 9.04.

A mixture of methyl 9,12- and 10,12-dihydroxystearate was prepared from methyl ricinoleate by epoxidation (10,11) followed by catalytic reduction (12,15). The epoxide contained 3.86% oxirane oxygen. Reduction of methyl 9,10-epoxy-12-hydroxystearate (8.6 g) in glacial acetic acid (100 ml) with 1 g of 5% palladium on charcoal at 60 psi and 25 C gave a crystalline product. One recrystallization from acetone and two from hexane gave methyl 9,12- and 10,12-dihydroxystearate, mp 70–72 C. No depression in the melting point was observed when mixed with the sample obtained from oxidative cleavage. The dihydroxystearates had the same retention time when analyzed by GLC.

### Methyl 8-(6-n-Hexyl-2,5-dihydroxy-3,4-dioxacyclooctyl) octanoate

A mixture of CHA-*me,* methylene chloride, and water (1:1:1) at 0–10 C was treated with ozone. After completion of the reaction, additional methylene chloride was added and the mixture cooled at −25 C. Decantation from the ice crystals and removal of the solvent in vacuo gave a water-white oily product.

*Analysis.* Calculated for $C_{21}H_{40}O_6$: C, 64.92; H, 10.37; $CH_3O$, 7.99. Found: C, 65.30; H, 10.14; $CH_3O$, 7.96. Active oxygen calculated: 4.12. Found: 4.39.

Decomposition of the dihydroxyperoxide in vacuo, as described in the preparation of V, gave a complex mixture of products as indicated by GLC. Based only on retention times, the mixture contained 36.4% IX, 12.1% VI, and 10.6% III.

ACKNOWLEDGMENTS

Mrs. Clara McGrew, Mrs. Bonita Heaton and Mrs. Karen Jones performed the microanalyses; George McManis, the infrared analyses; Edward Selke and William Rohwedder, the mass spectrometric analyses; and Robert Beal and Roger Eisenhauer prepared the isomeric cyclohexene acid and methyl esters.

## REFERENCES

1. Ackman, R. G., M. E. Retson, L. R. Gallay and F. A. Vandenheuvel, Can. J. Chem. *39*, 1956–1963 (1961).
2. Anders, D. E., and E. H. Pryde, JAOCS *43*, 305–306 (1966).
3. Awl, R. A., and E. H. Pryde, Ibid. *43*, 35–37 (1966).
4. Bailey, P. S., J. Am. Chem. Soc. *78*, 3811–3816 (1956).
5. Bailey, P. S., Chem. Rev. *58*, 925–1010 (1958).
6. Bailey, P. S., and S. B. Mainthia, J. Org. Chem. *23*, 1089–1092 (1958).
7. Briner, E., and R. Meier, Helv. Chim. Acta *12*, 529–553 (1929).
8. Criegee, R., H. Pilz and H. Flygare, Chem. Ber. *72*, 1799 (1939).
9. Dufek, E. J., L. E. Gast and J. P. Friedrich, JAOCS *47*, 000–000 (1970).
10. Findley, T. W., and D. Swern, U.S. Patent 2,567,930 (1951).
11. Findley, T. W., D. Swern and J. T. Scanlan, J. Am. Chem. Soc. *67*, 412–414 (1945).
12. Fore, S. P., and W. G. Bickford, J. Org. Chem. *26*, 2104–2105 (1961).
13. Frankel, E. N., S. Metlin, W. K. Rohwedder and I. Wender, JAOCS *46*, 133–138 (1969).
14. Friedrich, J. P., E. W. Bell and R. E. Beal, Ibid. *39*, 420 (1962).
15. Mack, C. H., W. G. Bickford and K. S. Markley, U.S. Patent 2,727,048 (1955).
16. Milas, N. A., P. Davis and J. T. Nolan, Jr., J. Am. Chem. Soc. *77*, 2536–2541 (1955).
17. Moore, D. J., E. H. Pryde and J. C. Cowan, JAOCS *42*, 894–898 (1965).
18. Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, J. Org. Chem. *25*, 618–621 (1960).
19. Story, P. R., and J. R. Burgess, Tetrahedron Letters *11*, 1287–1292 (1968).
20. Warnell, J. L., and R. L. Shriner, J. Am. Chem. Soc. *79*, 3165–3167 (1957).

[Received August 25, 1969]