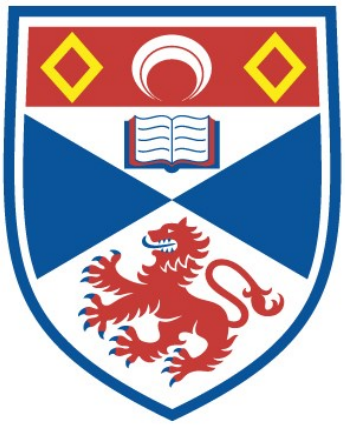
SOME REACTIONS OF METHYL OCTADECENOATES AND RELATED COMPOUNDS

Buvipali Srima Perera

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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Some Reactions of Methyl Octadecenoates and Related Compounds

A Thesis

presented by

Buvipali Srima Perera B Sc (Ceylon)

to the

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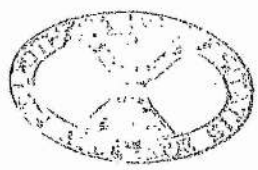

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Declaration

I hereby declare that this thesis is a record of the results of my own experiments, that it is my own composition and that it has not previously been presented in application for a higher degree.

The research work was carried out in the Department of Chemistry, University of St. Andrews, under the direction of Professor F.D. Gunstone, D Sc, FRIC.

Certificate

I hereby certify that (Mrs) Buvipali Srima Perera has spent twelve terms at research work under my supervision, has fulfilled the conditions of Ordinance 16 (St. Andrews) and that she is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Research Supervisor

Acknowledgements

I am deeply grateful to Professor F. D. Gunstone for the help and guidance he so readily gave me throughout this work.

I wish to thank Miss Zoe Backwell for her assistance during my final year and Mrs. W. Pogorzelec for typing this thesis.

Finally I must thank the Colombo Plan Authorities for enabling me to pursue this course and the Ceylon Institute of Scientific and Industrial Research for granting me study leave.

Contents

Abbreviations

ApL - Apiezon L grease

DEGS - Diethyleneglycolsuccinate polyester

DMF - Dimethylformamide

DMSO - Dimethylsulphoxide

IR - Infrared

LAH - Lithium aluminium hydride

MS - Mass spectra

NMR - Nuclear magnetic resonance

PE - Mixture of petroleum ether and ether

Ag^{+}TLC - Silver ion thin layer chromatography

TLC - Thin layer chromatography

TMS - Trimethylsilyl

DBU - 1,5-Diazobicyclo(5,4,0)undec-5-ene

SUMMARY

Part I The Methyl trans-Methyleneoctadecanoates

The sixteen isomeric methyl trans-methyleneoctadecanoates have been synthesised from the corresponding methyl trans alkenoates by the Simmons-Smith reaction, and some of their physical properties examined. Only one isomer (methyl trans-9,10-methyleneoctadecanoates) has previously been reported.

The gas liquid chromatographic data are interesting in that on both polar and non-polar columns the cis and trans isomers are well separated.

The methyl trans-methyleneoctadecanoates show diagnostic nuclear magnetic resonance signals around 9.8 to 9.6τ. The 2,3-; 3,4-; 5,6-; 16,17-; and 17,18- isomers differ from one another, but the remainder are very similar to each other.

The mass spectra of some of the isomers were examined but they do not provide much useful information.

Our data, along with that previously reported for the corresponding cis isomers (see ref 21), should assist in the recognition of these compounds. For complete identification, however it may be necessary, in addition to examine the mass spectrum of the hydrogenated ester.

Part II Halogenation of Unsaturated Long-chain Hydroxy Compounds

Neighbouring group participation in unsaturated hydroxy compounds occurring during reaction at the unsaturated centre has already been observed in appropriate long-chain compounds during various oxidation reactions and during oxymercuration. The halogenation of certain hydroxyalkenoates, octadecenols and octadecenoic acids has now been examined with a view to finding out if neighbouring group participation occurs during these reactions.

The halogenating agents employed were iodine monochloride, bromine and chlorine giving rise to the electrophilic reagents I^+, Br^+ and Cl^+ respectively.

In most reactions only the simple addition products (vic-dihalides) were observed and these were converted into ene-halides by dehydrohalogenation since the latter have been reported previously in only a few cases. The hydroxyl group was involved in halogenation in only a few instances - mainly in iodochlorination - to give substituted tetrahydrofurans (1,4-epoxides). Lactones were obtained during the halogenation of some unsaturated acids.

Attempts to obtain N-heterocyclic compounds by the reaction of long-chain amines were less successful but the conversion of methyl ricinoleate to methyl 12-amino-oleate was satisfactorily achieved.

PART I

The Methyl *trans*-Methyleneoctadecanoates

INTRODUCTION

1. Occurrence, biosynthesis and metabolism

The natural occurrence of long-chain acids containing cyclopropane or cyclopropene systems has been recognised since the discovery of lactobacillic acid (1), a metabolic product of *lactobacillus arabinosus*, and its recognition as *cis*-11,12-methyleneoctadecanoic acid. This and some related cyclopropane acids are present in many bacterial lipids.

$$CH_3(CH_2)_5\overset{\overset{CH_2}{\wedge}}{CH-CH}(CH_2)_9COOH \qquad (1)$$

Cyclopropene acids such as sterculic acid (2) are more common in fats of vegetable origin[1], but this acid is often accompanied by smaller amounts of dihydrosterculic acid.

$$CH_3(CH_2)_7\overset{\overset{CH_2}{\wedge}}{C=C}(CH_2)_7COOH \qquad (2)$$

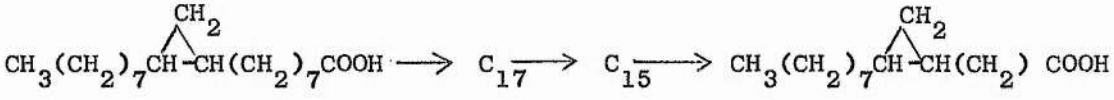
Dihydrosterculic acid is contained in the seed oil of many plants belonging to the order Malvales[2,3] and 2-hydroxysterculic is found in seeds of plants belonging to the family Bombaceae[4].

It seems likely that natural cyclopropane acids are derived from the corresponding unsaturated acids, and that the additional carbon atom is derived from methionine. Many bacteria synthesize lactobacillic acid from *cis* vaccenic acid.

Of the cyclopropane acid-containing phospholipids that have been examined it appears that this acid is esterified predominantly in 2-position.

When *cis*- and *trans*-9,10-methyleneoctadecanoic acids are fed to fat-deficient rats, *cis*- and *trans*-3,4-methylenedodecanoic acids accumulate. It is considered that the β-oxidation enzyme system of

mitochondria oxidises cyclopropane fatty acids only as far as the cyclopropane ring. No undesirable physiological effects are observed with the saturated compounds as have been observed with the cyclopropene fatty acids[5].



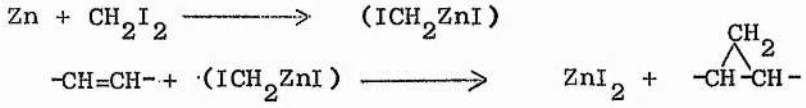
2. Syntheses

The formation of cyclopropanes from olefins usually occurs through a carbene intermediate. Carbene carbon is linked to two adjacent groups by covalent bonds and possesses two nonbonding electrons which may be in singlet or triplet states. Triplet carbenes may be considered as diradicals and singlet carbenes as electron-deficient species comparable to carbonium ions, but containing a nonbonding pair of electrons comparable to carbanions.

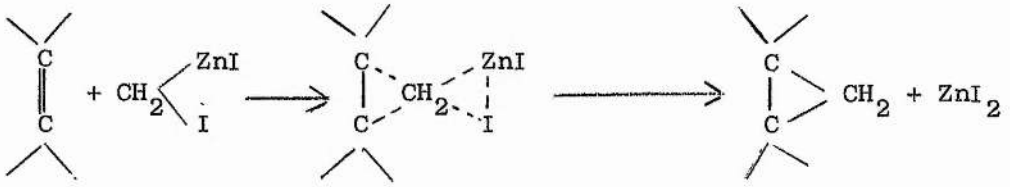
The two main reactions of singlet carbenes are methylene insertion into carbon hydrogen bonds and reaction with multiple bonds, both occurring through a concerted mechanism.

Carbenes have been produced in many ways[6-15]. But the procedure most widely employed is that described by Simmons and Smith[16-19].

In this reaction methylene addition is stereospecifically achieved by the reaction of olefin with Zn-Cu couple in ether containing di-iodo-methane.



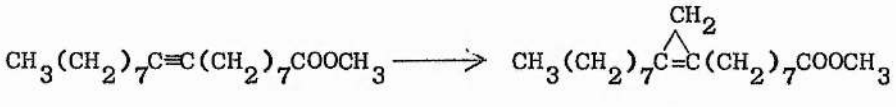
The active intermediate is possibly (ICH_2ZnI). The ether co-ordinates to the zinc and stabilises the reagent. The mechanism of cyclopropane formation by this method is not quite certain but a concerted cycloaddition process is probably in operation.



Studies on various olefins have shown that the intermediate behaves as an electrophile towards olefinic double bonds. This procedure was used for example by Christie and Holman[20] who prepared nineteen cyclopropane esters including methyl trans-9,10-methylene-octadecanoate and also by Christie and Gunstone et al[21] who converted all the methyl cis-octadecenoates to the cis-cyclopropane esters. Long-chain cyclopropane esters have also been produced by two interesting rearrangements of homo-allylic systems[22,23].

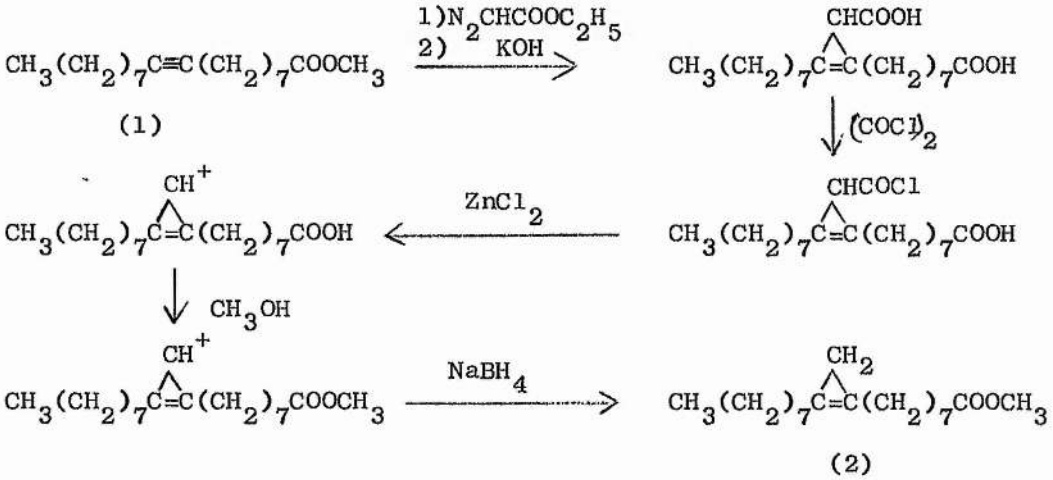
Useful procedures for converting acetylenic esters to cyclopropene derivatives such as methyl sterculate have recently been described.

Attenburger et al[24] has synthesised methyl sterculate (2) from methyl stearolate (1).



(1) (2) 10-11%

Gensler et al[25] used diazoacetic ester to generate the carbene and obtained methyl sterculate (2) from methyl stearolate (1).



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DISCUSSION

3. Synthesis of methyl trans-methyleneoctadecanoates

Several series of long-chain acids have been synthesised in these laboratories in order that their physical, chemical and biological properties can be examined. The acids prepared include all the isomeric cis-[26] and trans-[27] octadecenoates, octadecynoates[27], many diunsaturated octadecanoates[28], cyclopropanes[21] and epoxides[29] derived from the alkenoates and alkadienoates[30].

Particularly relevant to this investivation are the preparation of the complete series of methyl cis-methyleneoctadecanoates from the corresponding alkenoates[21], the study of their behaviour in the presence of phospholipid acyltransferases and a lysophosphatidyl ester as acceptor[31], and the preparation of several cis,cis-dimethyleneoctadecanoates[30].

The recent preparation of the methyl trans-alkenoates[27] made it possible to prepare the trans-methyleneoctadecanoates for comparison with their cis isomers. This was satisfactorily achieved by the Simmons-Smith reaction and yields were generally in the range 50-75% with the exception of the 2,3-isomer where it fell to 25%. This is probably the result of conjugation with the methoxycarbonyl group leading to some deactivation of the alkene system. A similar drop in yield was observed in the preparation of the cis isomer[21].

Table I Yield of trans-methyleneoctadecanoate from methyl trans-alkenoate

Isomer	Yield %
2,3	25
3,4	69
4,5	70
5,6	62
6,7	54
7,8	67
8,9	58
9,10	65
10,11	60
11,12	53
12,13	57
13,14	66
14,15	59
15,16	50
16,17	75
17,18	59

4. Thin Layer Chromatography

The thin layer chromatographic behaviour of several isomeric series has been examined including the methyl cis- and trans-alkenoates[32,33] on a silver ion system and the hydroxy and cis- and trans-epoxyoctadecanoates on silica[29]. Each isomeric series falls on a sinusoidal curve. Although the cis-methyleneoctadecanoates and some cis,cis-bismethyleneoctadecanoates[30] have been prepared and studied, there is no mention of relative Rf values. Our series of methyl trans-methyleneoctadecanoates, examined on silica impregnated with silver nitrate, showed no differential behaviour. All the spots lie on a straight line suggesting that there is little or no reaction between the trans-cyclopropane ring and the silver ions.

5. Gas Liquid Chromatography

The GLC behaviour of long-chain esters is usually expressed in terms of its ECL[35], and so many of these have been reported that they provide useful information about the structure of unknown esters[36,37].

It has been reported[21] that the isomeric methyl cis-methylene-octadecanoates behave similarly on polar and non-polar columns. Starting with the 2,3-isomer there is a gradual decrease in the retention time to the 5,6-isomer; this remains fairly constant until the 11,12-compound is reached and then increases quite rapidly up to the 17,18-isomer. Our trans series of compounds exhibited similar changes on both the phases examined (see table II).

Table II ECL of Methyl trans-Methyleneoctadecanoates

isomer	ECL[a]		Difference[b]		Difference[c]	
	DEGS	ApL	DEGS	ApL	DEGS	ApL
2,3	19.67	18.98	0.10	0.27	0.03	0.00
3,4	18.93	18.45	0.26	0.59	0.69	0.40
4,5	18.91	18.47	0.59	0.79	0.67	0.37
5,6	18.92	18.45	0.58	0.69	0.59	0.31
6,7	18.90	18.40	0.55	0.68	0.65	0.36
7,8	18.88	18.40	0.55	0.69	0.64	0.35
8,9	18.90	18.42	0.54	0.71	0.61	0.31
9,10	18.93	18.40	0.58	0.68	0.62	0.33
10,11	18.91	18.41	0.53	0.67	0.64	0.37
11,12	18.96	18.44	0.56	0.69	0.62	0.34
12,13	19.03	18.46	0.58	0.68	0.63	0.34
13,14	19.07	18.52	0.57	0.71	0.64	0.33
14,15	19.17	18.59	0.65	0.78	0.65	0.37
15,16	19.24	18.66	0.64	0.80	0.70	0.36
16,17	19.41	18.72	0.52	0.72	0.89	0.50
17,18	20.56	19.35	1.75	1.58	-	-

a Quoted values are based on two or more determinations which were carried out using appropriate saturated esters as internal standards

b ECL of trans-cyclopropane ester minus ECL of trans-alkenoate (the trans-alkenoate always has the lower ECL)

c ECL of cis-cyclopropane ester (taken from ref 21) minus ECL of trans-cyclopropane ester (the cis isomer always has the higher ECL)

On packed DEGS columns the minimum value (18.88) was obtained for the 7;8-isomer. The trans-cyclopropanes have shorter retention times than the corresponding cis isomers. The difference in ECL being about 0.6 for most isomeric pairs, and a mixture containing the cis- and trans-9,10-isomers was readily separated on our column. All the trans-cyclopropane esters examined also have higher ECL than the corresponding trans-alkenoates. This is about 0.6 for most pairs.

On an ApL column the variation in ECL within the series is similar to that observed on the DEGS column, with higher values when the ring is close to either end of the molecule. The trans-cyclopropanes again have higher retention times than the trans-alkenoates from which they are obtained and lower retention times than their cis-isomers.

Though most of the cis- and trans-alkenoates do not separate on DEGS or ApL packed columns the derived cyclopropanes produce different peaks, particularly on DEGS columns. The difficulty of preparing these compounds limits the value of this observation which has recently been exploited in the case of the epoxides[38].

Mixtures containing positional isomers differing in ECL by an amount greater than 0.2 could be separated on our packed column; the extent of separation depending on the difference in ECL (Table III).

Table III Separation of Positional Isomers

Isomers	Separation	Difference in ECL value
3,4 - 4,5	None	0.02
3,4 - 7,8	None	0.05
7,8 - 12,13	None	0.05
7,8 - 13,14	Slight	0.19
7,8 - 14,15	Fair	0.29
7,8 - 15,16	Good	0.36
7,8 - 16,17	Good	0.53

6. Infrared Spectra

Cyclopropane fatty esters give characteristic absorption bands at about 1020 cm^{-1} and 3050 cm^{-1} [3]. The C-H stretching vibrations in our trans-cyclopropane esters (3060 cm^{-1}) occur at slightly lower wavelengths than in the cis-esters (3050 cm^{-1}).

Table IV Infrared Absorptions

Isomer	ring CH stretching	>C=O stretching	ring methylene wagging
2,3	absent	1709,1735	1050
3,4	3085	1740	1028
4,5	3062	1740	1025
5,6	3060	1735	1020
6,7	3060	1735	1023
7,8	3060	1735	1023
8,9	3060	1735	1020
9,10	3060	1735	1020
10,11	3060	1735	1020
11,12	3060	1735	1020
12,13	3060	1735	1023
13,14	3060	1735	1020
14,15	3060	1735	1020
15,16	3060	1735	1020
16,17	3060	1738	1023
17,18	3068	1735	1015

7. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance in fatty acids and glycerides was reviewed by Hopkins in 1965[39], and this review was updated in 1970[40]. We now report the NMR spectra of all the methyl trans-methyleneoctadecanoates. We examined all the isomers using a 100 MHz instrument and four of them (3,4; 5,6; 14,15; and 17,18) with a 220 MHz instrument. Our results are summarised in Table V and commented on below.

Table V Principal features (τ values) of the NMR Spectra [100 Hz] of methyl trans-methyleneoctadecanoates

Isomer	OCH_3	αCH_2	$(CH_2)_n$	CH_3	ring protons*			
					Ha	Hb	Hc	Hd
2,3	6.41	7.74	8.75	9.15	see text			
3,4	6.35	7.83	8.74	9.12	9.74		9.25	9.50
4,5	6.37	7.66	8.74	9.18	9.79		9.60	
5,6	6.34	7.68	8.73	9.10	9.81		9.62	
6,7	6.38	7.66	8.73	9.10	9.83		9.64	
7,8	6.37	7.75	8.73	9.10	9.84		9.66	
8,9	6.37	7.74	8.72	9.11	9.84		9.65	
9,10	6.38	7.76	8.72	9.05	9.85		9.66	
10,11	6.38	7.75	8.70	9.10	9.82		9.66	
11,12	6.40	7.76	8.72	9.10	9.84		9.66	
12,13	6.37	7.74	8.71	9.10	9.84		9.66	
13,14	6.37	7.74	8.72	9.11	9.85		9.65	
14,15	6.38	7.76	8.72	9.10	9.84		9.65	
15,16	6.38	7.77	8.72	9.06	9.84		9.66	
16,17	6.38	7.74	8.74	9.00	9.86		9.66	
17,18	6.37	7.74	8.74	-	see text			

* see text

The ester methyl group ($-COOCH_3$)

The signal for these three protons occurs as a singlet between 6.34 and 6.41τ.

Methylene protons α and β to the ester group ($-CH_2CH_2COOCH_3$)

The protons on the C(2) carbon atom produce a triplet around 7.7τ. On the 220 MHz instrument the C(3) protons β to the ester group are also seen as a multiplet around 8.34τ.

Chain Methylene Groups $(CH_2)_n$

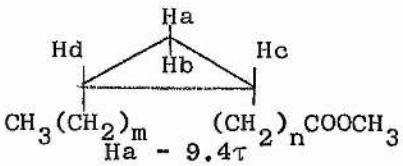
These protons give a signal which appears as a broad singlet around 8.7τ.

End methyl group ($CH_3(CH_2)_n$-)

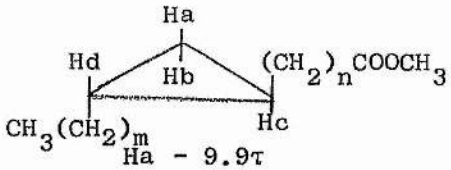
Except in the 16,17- and 17,18-isomers these protons give rise to an unresolved triplet around 9.10τ. In the 16,17-isomer it appears as a doublet at 9.06τ and in the 17,18-isomer it is part of the cyclopropane ring.

Ring protons

Greatest interest in these spectra centres on the signals arising from the various ring protons. Confusion over assignment of τ values to the various ring protons was clarified by Longone and Miller[41,42] who proposed the following assignments for the cis and trans cyclopropanes



Ha - 9.4τ
Hb - 10.3τ
Hc - 9.4τ
Hd - 9.4τ



Ha - 9.9τ
Hb - 9.9τ
Hc - 9.5τ
Hd - 9.5τ

Our values of 9.79-9.86 and 9.60-9.66 (except for the 2,3; 3,4; and 17,18 isomers) are very close to those predicted by Longone and Miller[41].

All four ring protons are non equivalent and the signals are complex due to overlap. The exact τ values and J values have not been worked out. The ring methylene signals of the 4,5- to 15,16-isomers appear as a doublet with satellite peaks but on the 220 MHz instrument this signal is somewhat simplified giving possibly a

symmetrical triplet (only the 5,6- and 15,16-isomers were examined on this instrument).

The Hc and Hd signals of the 4,5- to 15,16-isomers appear as a broad triplet but on the 220 MHz (5,6- and 15,16-isomers examined) this signal was resolved into a quintet.

In the 2,3-isomer the Hc signal is at about 7.74τ and there is a one-proton signal at 9.4τ, and the five-proton signal at 9.15τ arises from two ring protons and three end methyl protons.

In the 3,4-isomer the Hc proton at 9.25τ is more deshielded than the Hd proton at 9.5τ. The ring methylene protons give a signal at 9.74τ and the signal for the C(2) protons, normally a triplet, appears as two doublets.

In the 5,6-isomer a complex signal between 8.22τ and 8.46τ could not be assigned.

Five ring protons are present in the 17,18-isomer and our spectrum had five one-proton signals at 9.00, 9.10, 9.40, 9.60 and 10.10τ respectively which we were unable to allocate.

7. Mass Spectra

In recent reviews both Christie[3] and McCloskey[43] draw attention to the fact that mass spectra of long-chain cyclopropane esters are of little diagnostic value, except after hydrogenolysis of the cyclopropane system. This opinion is based largely on results obtained with cis-cyclopropane compounds but our present results show that the same is true for the trans-esters . Because of this we have confined our attention to only a few spectra (2,3- to 7,8- and 15,16-esters) run at 16 ev. The spectra of all seven isomers are very similar.

They all show significant peaks at m/e values corresponding to M and M-32. Campbell and Naweral[44] considered that cyclopropane

esters can be distinguished spectroscopically from the alkenoates from which they are prepared by the M/M-32 ratios, which lie between 10 and 40% for monoenes and between 5 and 11% for the corresponding cyclopropanes. For our trans-cyclopropane esters this ratio was considerably higher at 13-35% (average 27%).

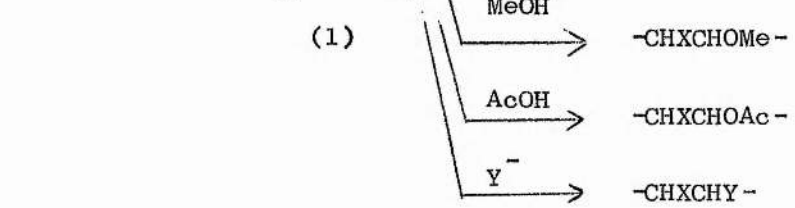
In addition to these ions the spectra are dominated by two series of peaks. These arise from the hydrocarbon ions $(C_nH_{2n})^+$, $(C_nH_{2n-1})^+$, $(C_nH_{2n-2})^+$ and $(C_nH_{2n-3})^+$ from n=5 to n=17 with $(C_nH_{2n-2})^+$ usually the largest, and from the less dominant series $(C_nH_{2n}COOCH_3)^+$ and $(CH_{n\,2n-2}COOCH_3)^+$. Fuller results are tabulated in the experimental section.

PART II

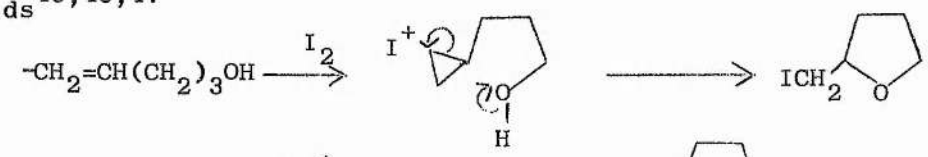
Halogenation of Unsaturated Long-Chain Hydroxy Compounds

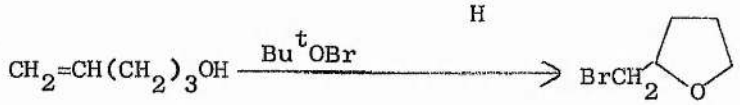
INTRODUCTION

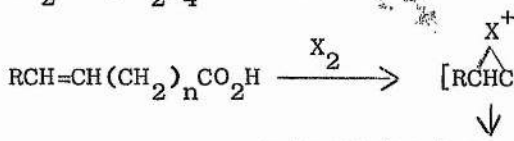
The commonly accepted mechanism for halogen addition involves an intermediate halonium ion (1). This mechanism accommodates the well known fact that the second stage of the addition process can be diverted by reaction with an alternative nucleophile present in the form of a solvent or an added anion.



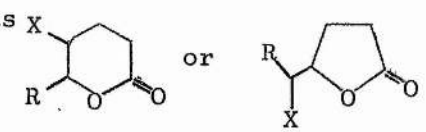
These proposals also provide a satisfactory explanation for intramolecular reactions in which the attacking nucleophilic species is part of the reacting alkene. There are many examples of reactions of this type though most of them involve short-chain alcohols and acids[45,46,47]



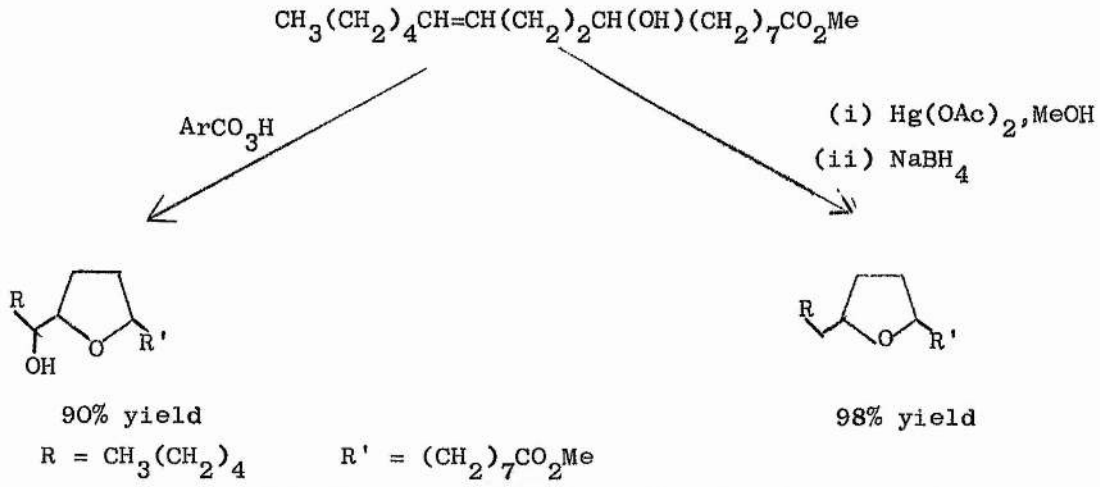




$RCHXCHX(CH_2)_nCO_2H$ + halogen-containing lactones such as



Recent work in this laboratory has provided examples of neighbouring group participation in the reaction of long-chain hydroxy alkenes, particularly with γ- and δ-hydroxyalkenes. The reactions most extensively studied include epoxidation and oxymercuration[48]



90% yield

98% yield

R = $CH_3(CH_2)_4$ R' = $(CH_2)_7CO_2Me$

The object of the present work was to study the halogenation of some long-chain hydroxyalkenes to see whether cyclic ethers would be formed. This would provide yet another route to the long-chain 1,4- and 1,5-epoxides via some new derivatives (halogenated cyclic ethers). We have examined the chlorination (in carbon tetrachloride solution), the bromination (mainly in carbon tetrachloride solution), and the iodochlorination (in acetic acid solution) reactions and have employed the following hydroxyalkenes as substrates: methyl ricinoleate (and its trans isomer), methyl 9-hydroxyoctadec-12-enoate (cis and trans isomers) and a number of octadecenoic acids and octadecenols with the double bond close to the functional group at C(1).

DISCUSSION

1. Halogenation of methyl oleate

The object of these studies was to investigate the possibility of neighbouring group participation in the reaction of appropriate unsaturated esters with halogens. Since the products were to be identified, in part, by NMR and MS it was considered useful to examine first the simpler reactions with methyl oleate.

When treated with iodine monochloride, bromine and chlorine, the ester is expected to give methyl 9(10)-chloro-10(9)-iodostearate, 9,10-dibromostearate and 9,10-dichlorostearate respectively. Since the addition occurs in a trans manner the product should be the threo isomers.

Each dihalide was subjected to partial dehydrohalogenation to give the ene-halides[49,50] by reaction with DBU or with sodium methoxide. Since these elimination reactions are also trans the products presumably have the Z-configuration.

$$-CH=CH- \longrightarrow -CHICHCl- \xrightarrow{-HI} -CH=CCl-$$

$$-CH=CH- \longrightarrow -CHBrCHBr- \xrightarrow{-HBr} -CH=CBr-$$

$$-CH=CH- \longrightarrow -CHClCHCl- \xrightarrow{-HCl} -CH=CCl-$$

threo- Z-isomers

The dihalides and ene-halides have similar polarity to methyl oleate and are not satisfactorily separated from the starting material by silica TLC. The ene-halides can however be satisfactorily chromatographed on DEGS column at 190°C (Table VI). From the NMR spectra of the dihalides and the ene-halides it is possible to make the assignments summarised in Table VI. For the discussion of the mass spectra see section 6.2 (spectra 1-5).

Table VI Halogenation and dehydrohalogenation of methyl oleate

Halogen	NMR Signals of dihalide and ene-halide			GLC
	-CHXCHX-	-CH=CX-	$-CH_2CH=CXCH_2-$	
ICl	6.12(CHCl)[a] 5.72(CHI)	4.62	7.90 and 7.68[c]	21.7
Br_2	5.83	4.44	7.90 and 7.62[c]	23.1
Cl_2	6.02[51,52b]	-	-	21.7

a Dehydrohalogenation of the chloroiodostearates gives chloro-octadecenoates

b ECL of methyl 9,10-dichlorostearate is 25.2 (DEGS)

c It is assumed that allylic protons adjacent to -CH= will have a higher τ value than allylic protons adjacent to -CX=

2.1 Bromination of methyl ricinoleate in carbon tetrachloride solution

When methyl ricinoleate is treated with bromine in carbon tetrachloride, there is no TLC evidence for any product less polar than methyl ricinoleate. The product is therefore considered to be methyl threo-9,10-dibromostearate and this conclusion is consistent with the following observations:-

(i) NMR Spectroscopy. The NMR spectrum was compared with those of authentic samples of the threo isomers of methyl 9,10-dibromostearate and methyl 9,10, 12,13-tetrabromostearate. Significant signals were observed in the 5-6τ region and are assigned as follows:-

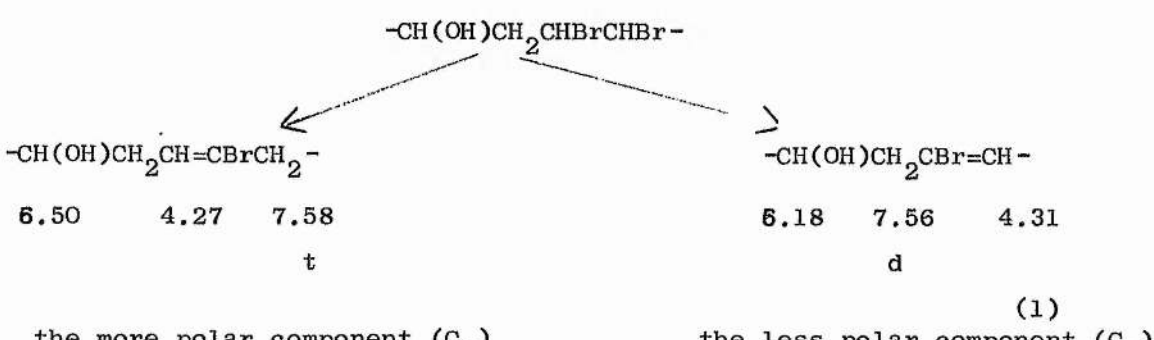
9,10-dibromostearate -CHBrCHBr-
5.83,5.83

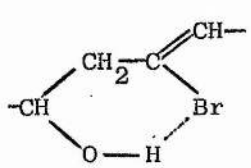
9,10,.12,13-tetrabromostearate $-CHBrCHBrCH_2CHBrCHBr-$
5.82 5.47 5.47 5.82

9,10-dibromo-12-hydroxystearate $-CH(OH)CH_2CHBrCHBr-$
5.45 5.80

(ii) Dehydrohalogenation (sodium methoxide) of methyl threo-9,10-dibromoricinoleate. The product of this reaction consists mainly

of two products, C_1 (35%, less polar) and C_2 (48%, more polar), which can be separated by careful TLC. The infrared spectra of both compounds show the presence of hydroxyl (3460 cm^{-1}) and of trisubstituted alkene (1660 cm^{-1}) groups. The two esters differed slightly in their GLC behaviour (C_1,23.60; C_2,23.55 as TMS ethers). These products are presumably the two possible ene-bromides. It seems likely that the 10-bromo-isomer (1) will be less polar because of the greater amount of intramolecular hydrogen bonding through the six membered formulation (2). The results is consistent with the NMR spectrum which shows a doublet at 7.56τ in the less polar isomer and a triplet at 7.58τ for the more polar isomer.





(2)

The mass spectra are discussed in section 6.2.

2.2 Bromination of methyl ricinoleate in other solvents

In carbon tetrachloride solution, bromination of methyl ricinoleate gives only methyl 9,10-dibromo-12-hydroxy-stearate and there is no evidence of any cyclic ether resulting from neighbouring group participation of the hydroxyl group in the bromination reaction occurring at the double bond. Using more polar solvents (DMF, DMSO, DMSO-CCl_4) there

was no change in the reaction product and TLC again showed little or no evidence of any product less polar than the hydroxy ester.

In acetic acid solution the dibromohydroxystearate (84%) was accompanied by a more polar product (16%) and that this is a mixture of the acetoxy bromides (3) and (4) is consistent with the NMR spectrum.

$$\underset{5.1}{-CH(OH)}\underset{}{CH_2}\underset{7.97}{CH(OCOCH_3)}\underset{6.0}{CHBr-} \qquad (3)$$

$$\underset{5.7}{-CH(OH)}\underset{}{CH_2}\underset{5.1}{CHBr}\underset{8.02}{CH(OCOCH_3)-} \qquad (4)$$

The separated singlets at 7.97τ and 8.02τ are particularly diagnostic for these structures.

The mass spectrum is detailed in section 6.2 (spectrum 8)

2.3 Bromination of methyl ricinelaidate

When methyl ricinelaidate is brominated the main product (88%) is the erythro dibromide. Separate signals (NMR) appear at 6.16τ and 5.80τ for the two -CHBr- protons. It is however not clear which signal belongs to which -CHBr- proton.

The MS is discussed in section 6.3 (spectrum 7)

Dehydrohalogenation of methyl erythro-9,10-dibromo-12-hydroxystearate

Removal of hydrogen bromide from the erythro-isomer gives two ene-bromides, which on GLC gave two close peaks of ECL values 23.9 and 24.2, and which could be separated on TLC into less polar (C_1, 17%) and more polar (C_2, 74%) fractions.

The proportion of the two ene-bromides is generally closer to 1:1 than was observed here. Though these two isomers are difficult

to separate by TLC the GLC behaviour of the separated components show that contamination is not serious and cannot account for the uneven amounts of the two ene-bromides. It is thus apparent that in the basic elimination of hydrogen bromide the hydrogen atom at C(9) is attacked in preference to the hydrogen atom at C(10).

In the NMR spectrum of the more polar isomer (C_2) the triplet at 7.59τ due to the C(8) protons shows it to be the 9-bromo-isomer. The CHOH proton signal and the olefinic proton signal are at 6.40τ and 4.13τ respectively.

The less polar component (C_1) is thought to be the 10-bromo-isomer, but no positive evidence is available for this. The C(11) proton signal is complex and cannot be interpreted. The CHOH proton is at 6.20τ and the olefinic proton signal at 4.06τ.

$-CH(OH)CH_2CH=CBrCH_2-$			$-CH(OH)CH_2CBr=CH-$		
6.40	4.13	7.59	6.20	7.6	4.06
more polar (C_2)			less polar (C_1)		

The MS is described in section 6.2 (spectra 11 and 13),

2.4 Iodochlorination of methyl ricinoleate

Iodochlorination of methyl ricinoleate produced mainly the two iodochlorides (88%). On GLC the TMS ether gives a peak of ECL 19.8 (the TMS ether of methyl ricinoleate also has an ECL of 19.8). The four signals in the NMR spectrum between 5 and 6τ are interpreted as shown:

$-CH(OH)CH_2\underline{CH}ICHCl$ - 5.29τ

$-CH(OH)CH_2CHCl\underline{CH}I$ - 5.40τ

$-CH(OH)CH_2\underline{CH}ClCHI$ - 5.70τ

$-CH(OH)CH_2CHI\underline{CH}Cl$ - 5.87τ

These mixed iodochlorides were treated with sodium methoxide and the product separated on TLC into two fractions (C_1 and C_2, the latter is more polar). The less polar isomer is probably the 10-chloro-isomer because of the doublet at 7.68τ due to the C(11) protons. The more polar component is possibly the 9-chloro-isomer.

The results are outlined in the partial structures shown:-

$-CH(OH)CH_2CCl=CHCH_2-$	$-CH(OH)CH_2CH=CClCH_2-$
6.4 7.68 4.53	6.4 4.48 7.78
less polar (C_1)	more polar (C_2)

The MS is discussed in section 6.2 (spectrum 14)

2.5 Chlorination of methyl ricinoleate

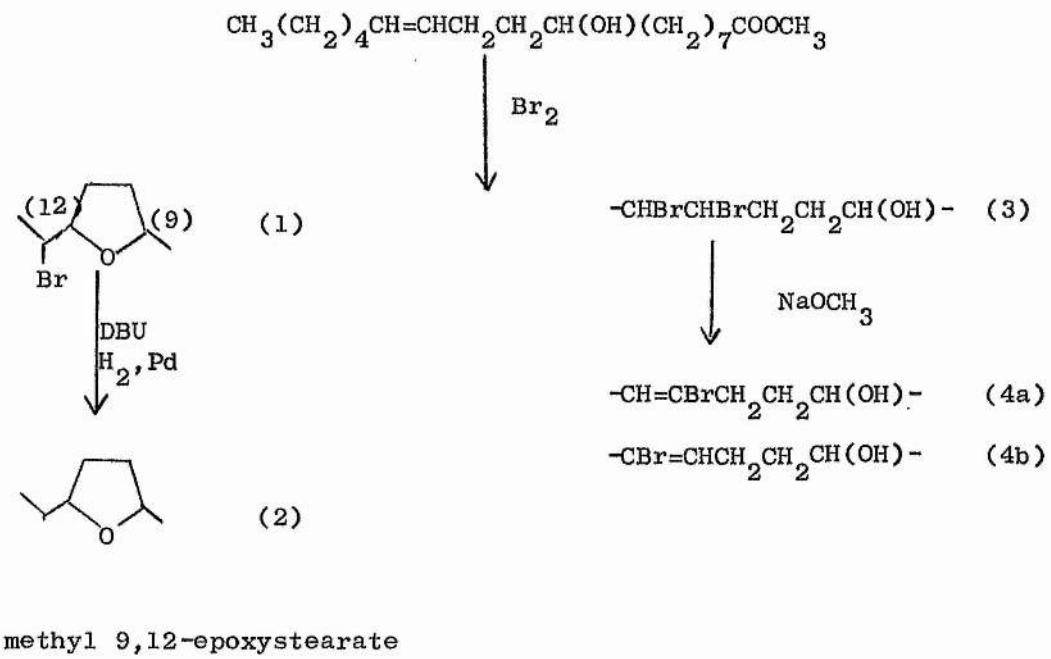
Chlorination of methyl ricinoleate gave mainly the dichloride. Its NMR spectrum showed a broad three-proton absorption band between 5.6τ and 6.2τ, due to the $-\underline{CH}Cl\underline{CH}Cl\underline{CH_2}\underline{CH}OH-$ protons in the molecule.

The MS is discussed in section 6.2 (spectrum 9)

The dichloride was dehydrohalogenated using DBU and the product behaved similarly to the ene-chlorides obtained from the iodochloride when examined on TLC and GLC.

3.1 Bromination of methyl 9-hydroxyoctadec-cis-12-enoate

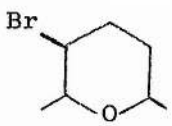
When methyl 9-hydroxyoctadec-cis-12-enoate (a γ -hydroxy-alkene) was reacted with bromine in carbon tetrachloride it gave two products which differed in polarity and were easily separated on TLC. These are shown to be the monobromo cyclic ether (1) which could be converted to the known methyl 9,12-epoxystearate (2) and the threo-dibromohydroxystearate (3) which was subsequently dehydrobrominated to give two ene-bromides (4a) and (4b).



methyl 9,12-epoxystearate

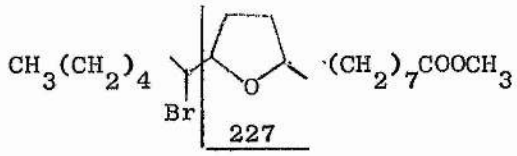
The less polar bromination product (40%) decomposed on GLC. It did not show the absorption associated with a hydroxyl group in its infrared spectrum and its NMR spectrum was readily interpreted in terms of structure (1). In particular a broad three-proton signal around 6.1τ was associated with the -CHBr- and the two >CHOCH< protons.

The presence of the five-membered ring structure (1) rather than the tetrahydropyran structure (5) was confirmed by comparison



(5)

of the debrominated product with methyl 9,12-epoxystearate which has been reported before[53,54], and by the MS of (6) which shows in particular a fragment of m/e 227 formed by the cleavage shown below:



(6)

Compound (6) was dehydrobrominated (DBU) and then hydrogenated to give methyl 9,12-epoxystearate identical in TLC and GLC behaviour (ECL 21.2 and 21.4) and in its NMR and MS with authentic samples of this cyclic ether prepared in other ways[53,54]. The double peak on GLC is considered to result from the cis and trans isomers of this ester.

The more polar bromination product (60%) is the expected addition product methyl threo-12,13-dibromo-9-hydroxyoctadecanoate. The NMR spectrum confirms the disappearance of olefinic protons and contains signals associated with the -CH(OH)- (6.4τ) and CHBr (5.79τ) protons.

After reaction with sodium methoxide the dibromide gave two ene-bromides (ECL of TMS ethers 23.9 and 24.0), which could only be imperfectly separated on TLC. The olefinic proton signal appeared as a triplet at 4.37τ.

Further discussion of the mass spectra is to be found in section 6.2 (spectra 22 and 25).

3.2 Bromination of methyl 9-hydroxyoctadec-cis-12-enoate in glacial acetic acid

When methyl 9-hydroxyoctadec-cis-12-enoate is brominated in glacial acetic acid, a slight increase in cyclic material is obtained (48%) over that obtained during the bromination of this alkenoate in carbon tetrachloride.

3.3 Bromination of methyl 9-acetoxyoctadec-cis-12-enoate

In this ester the lone pair of electrons on the oxygen atom is less available for cyclisation than in the corresponding hydroxy compound, also H^+ is a better leaving group than CH_3CO^+. This should result in smaller quantities of cyclic material being formed.

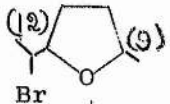
When methyl 9-acetoxyoctadec-cis-12-enoate is reacted with bromine the main product is the dibromide, which can be identified as the ene-bromide on GLC (TMS ether 23.9) after deacetylation and dehydrobromination.

3.4 Bromination of methyl 9-hydroxyoctadec-trans-12-enoate

Bromination of this trans alkenoate (γ-hydroxyalkene) in carbon tetrachloride gave less polar (7, 40%) and more polar fractions (8, 60%) which were separated on TLC.

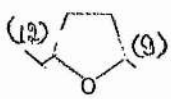
$CH_3(CH_2)_4CH{=}CHCH_2CH_2CH(OH)(CH_2)_7COOCH_3$

↓ Bromination



(7)

↓ DBU, H_2, Pd



(9)

methyl 9,12-epoxystearate

$-CHBrCHBrCH_2CH_2CH(OH)-$

↓ $NaOCH_3$ (8)

$-CH{=}CBrCH_2CH_2CH(OH)-$ (10a)

$-CBr{=}CHCH_2CH_2CH(OH)-$ (10b)

The less polar fraction was dehydrobrominated and hydrogenated. On GLC (ECL 21.2 and 21.4) and TLC it then had the same behaviour as the methyl 9,12-epoxystearate, obtained from the corresponding cis isomer. The structure of both compounds (7) and (9) is consistent with their mass spectra (section 6.2, 22 and 25) which confirm in particular the presence of the 9,12-epoxy function.

Bromination of this γ-hydroxy alkenoate in carbon tetrachloride results in 40% cyclic material, irrespective of the stereochemistry at the double bond. The more polar product is the erythro-dibromo ester (8). The two -CHBr- protons in this vicinal dibromide are slightly less shielded (5.89τ) than in the corresponding threo-isomer. When the dibromoester is dehydrohalogenated the resulting ene-bromides can be separated on TLC into a less polar fraction C_1 (10a) and a more polar fraction C_2 (10b). C_1 has an ECL of 23.8 (TMS ether) and C_2 has an ECL of 24.2 (TMS ether).

C_1 is the 12-bromo-isomer (10a) and C_2 the 13-bromo-isomer (10b). Evidence for this comes from a study of the C(11) and C(14) proton signals in the NMR spectrum of the two isomers.

$-CH=CBrCH_2CH_2CH(OH)-$			$-CH_2CBr=CHCH_2CH_2CH(OH)-$		
4.21	7.49		7.59	4.21	
(t)	(t)	(10a)	(t)	(t)	(10b)
less polar (C_1)			more polar (C_2)		

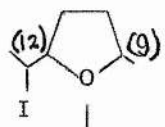
The C(11) proton signal is more deshielded in (10a) than the C(14) proton signal in (10b).

3.5 Iodochlorination of methyl 9-hydroxyoctadec-cis-12-enoate

This hydroxy ester when treated with iodine monochloride in acetic acid yields a high proportion (84%) of cyclic material (11)

which does not show hydroxyl group absorption in the infrared spectrum. The iodo cyclic ether can easily be converted to the iodine-free compound (13) by treatment with sodium borohydride. The resulting methyl 9,12-epoxystearate had an ECL (21.2 and 21.4) identical to that obtained in the previous experiment and also behaves similarly on TLC. The presence of the tetrahydrofuran unit was confirmed in the MS of the epoxide (13) and of the iodinated compound (11) from which it was formed.

$CH_3(CH_2)_4CH{=}CHCH_2CH_2CH(OH)(CH_2)_7COOCH_3$



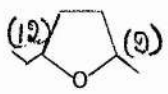
(11)

$-CHClCHI(CH_2)_2CH(OH)-$ (12a)

$-CHICHCl(CH_2)_2CH(OH)-$ (12b)

$NaBH_4$

$NaOCH_3$



(13)

$-CCl{=}CH(CH_2)_2CH(OH)$ (14a)

$-CH{=}CCl(CH_2)_2CH(OH)$ (14b)

methyl 9,12-epoxystearate

The more polar fraction is the mixed iodochlorides (12a) and (12b). The broad signal 6.3τ arise by protons -CH(OH)- and -CHCl-. The signal at 5.64τ is due to proton -CHI- .

$\underline{b}\ \ \underline{a}\ \ \underline{b}$
$-CHClCHICH_2CH(OH)-$

$\underline{a}\ \ \underline{b}\ \ \ \ \underline{b}$
$-CHICHClCH_2CH_2CH(OH)-$

a signal at 5.64τ

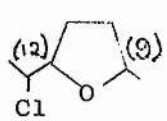
b signal at 6.3τ

When treated with sodium methoxide the iodochlorides dehydroiodinate giving the ene-chlorides (14a) and (14b). The NMR spectrum indicates the presence of one vinylic proton at 4.22τ.

3.6 Chlorination of methyl 9-hydroxyoctadec-cis-12-enoate

Chlorinating methyl 9-hydroxyoctadec-cis-12-enoate gave 32% of less polar material (TLC) which is probably methyl 13-chloro-9,12-epoxystearate (15). It had an ECL of 24.5 and 24.9 on DEGS and the infrared spectrum does not show absorption associated with the hydroxyl group.

$CH_3(CH_2)_4CH{=}CHCH_2CH_2CH(OH)(CH_2)_7COOCH_3$



(15)

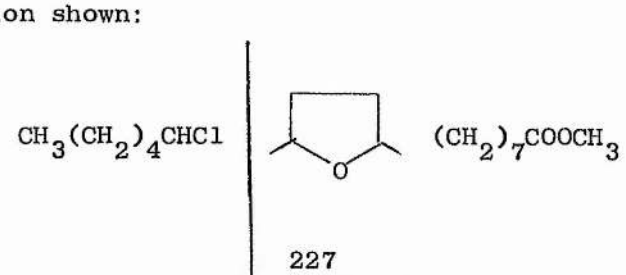
$-CHClCHClCH_2CH_2CH(OH)-$ (16)

DBU

$-CH{=}CClCH_2CH_2CH(OH)-$ (17a)

$-CCl{=}CHCH_2CH_2CH(OH)-$ (17b)

The peak in the MS at m/e 227 is probably due to the fragmentation shown:



In contrast to the iodo and bromocyclic ethers we could not convert (15) to methyl 9,12-epoxystearate. The more polar component is the dichloride (16). The two -CHCl- protons (NMR) gave a signal at 6.00τ.

The dichlorides, when treated with DBU, dehydrochlorinate giving the two ene-chlorides. This product is found to be

identical on GLC (TMS 22.8) and TLC to the product obtained by dehydroiodination of the corresponding iodochloride.

4. Octadecenols

Study of the halogenation of unsaturated hydroxy esters is restricted because of the limited number of available compounds, and the limited range of structural types represented by these compounds. A more systematic study is possible using isomeric octadecenols obtained by lithium aluminium hydride reduction of the isomeric methyl octadecenoates. These were available through previous synthetic studies[26].

4.1 Bromination

Bromination of the cis-6-, 5-, and 3-octadecenols gave the following products.

	Dibromide (%)	Cyclic ether (%)
6c	100	-
5c	88	12
3c	100	-

It is clear that under the reaction conditions employed by us bromination occurs mainly in the expected fashion to furnish the dibromo alcohol, and other products resulting from involvement of the OH group are either not formed or present only as minor components.

The dibromo alcohols have the same polarity on TLC as the unreacted alcohols. The NMR spectra shows the absence of the

olefinic proton signal and the presence of the vicinal dibromide signal as a multiplet of 5.8τ. In the 3,4-dibromo alcohol the C(3) proton is more deshielded and gives a signal at 5.55τ. The infrared and MS were not very helpful in establishing the structure.

The dibromide can be converted to ene-bromides by sodium methoxide treatment. The following ECL values were obtained on GLC.

	DEGS (TMS ether)
Δ6	18.4 (20.2 ApL)
Δ5	18.0
Δ3	18.6

The ene-bromides from the 5,6-dibromo alcohol were accompanied by 15% of a component ECL 14.7. This is the ECL of the octadecenol. A weak olefinic proton is present in the NMR spectrum of the ene-bromides. This signal was absent in the NMR spectrum of the dibromide.

In the NMR spectra of the ene-bromides the olefinic proton signal appeared at the following τ values.

Δ6	Δ5	Δ3
4.42	4.42	4.26

The lower τ value of the olefinic proton in the Δ3 ene-bromides could be due to the proximity to the alcohol function.

The MS are discussed in section 6.2 (spectra 26, 29, 32, 34, and 36).

4.2 Iodochlorination Studies

When unsaturated alcohols with the double bond close to the hydroxyl function were treated with Wij's reagent the following products were obtained

	Dihalogeno alcohol (%)	Dihalogeno acetate (%)	Haldgeno cyclic ether (%)	Unidentified (%)
6c	89	11	-	-
5c	78	6	16	-
4c	-	6	83	11

The Δ4 alcohol gave a good yield of cyclic ether. Since the dihalide is a mixed one, two signals were obtained for hydrogen attached to the halogen-carrying carbons in the NMR spectrum.

	CHI (τ)	CHCl (τ)
6c	5.71	6.24
5c	5.70	6.22

The iodochlorides were converted to the ene-chlorides which were stable on GLC and had NMR signals around 4.6τ for the olefinic protons.

	DEGS (TMS)	NMR (CH=Cl)τ
6c	17.7*	4.62
5c	17.6*	4.60

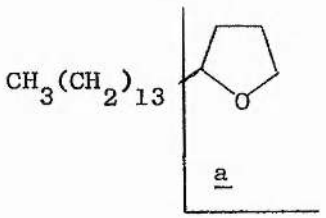
* accompanied by a peak at 14.8 (15%)

The MS are discussed in section 6.2 (spectra 27, 30, 31, and 35).

The cyclic material obtained from octadec-cis-4-enol is less polar than the alcohol on TLC. The infrared spectrum does not show the presence of the OH group and the NMR spectrum does not have a significant signal at 6.4τ for $-CH_2OH$ protons.

The MS is discussed in section 6.2 (spectrum 39).

The iodo cyclic ether was reduced with sodium borohydride. On GLC the product had an ECL 15.9 and is identical (on GLC and TLC) with the cyclic ether obtained by oxymercuration-demercuration[53] of the same octadecenol. The base peak in the MS (section 6.2, spectrum 40) at m/e 71 is due to fragment (a).



This is consistent with the structure 2-tetradecyltetrahydrofuran and the iodine-containing compound is presumably 2(1'-iodotetradecyl)tetrahydrofuran (or 1,4-epoxy-5-iodo-octadecane).

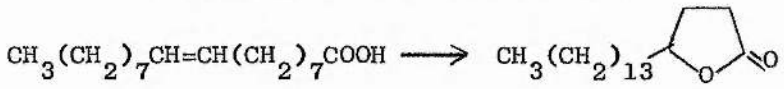
Results quoted by others on the halogenation of short-chain unsaturated alcohols[45,46] are given below.

	cyclic ether (%)	
	Br_2/CH_3OH	I_2
$CH_2=CH(CH_2)_2OH$	None	None
$CH_2=CH(CH_2)_3OH$	50-60	100
$CH_2=CH(CH_2)_4OH$	5-10	Not given

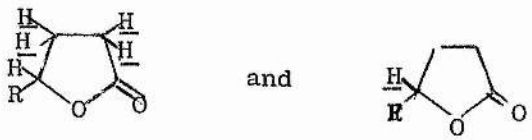
We did not examine the bromination of the Δ4 alcohol, but with I^+ we got 83% of cyclic material, which resembles the value quoted above for the short-chain Δ4-enol.

5.1 Preparation of Stearolactones

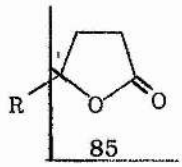
The acid-catalysed isomerisation of oleic acid to give γ-stearolactone has been investigated by several workers and most recently by Swern[55]. This is accomplished by protonation followed by double bond migration and lactonisation.



We used this method to synthesize an authentic sample of γ-stearolactone which is easily recognised by its infrared spectrum (absorption of carbonyl group at 1780 cm^{-1}), GLC behaviour(ApL 19.6, DEGS 26.4), NMR spectrum[56], and by the peak m/e 85 in the MS.



7.5τ 5.8τ

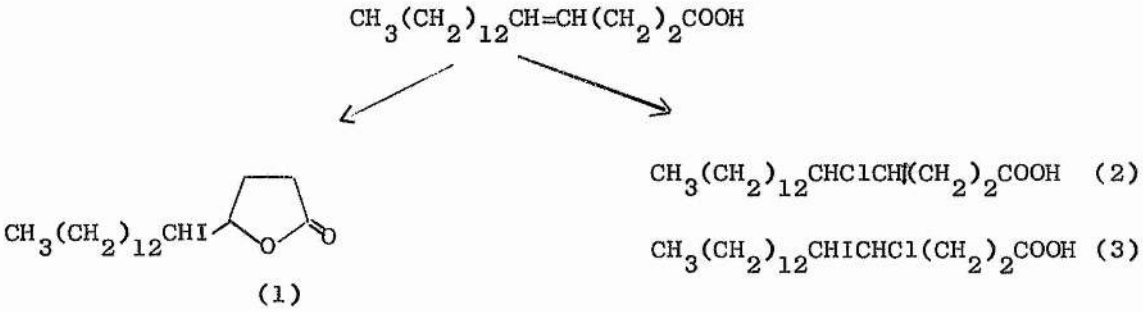


An attempt to prepare δ-stearolactone was less successful. Methyl octadec-cis-4-enoate was submitted to acetoxymercuration-demercuration[53] to give a mixture of methyl 5- and 4-acetoxyoctadecanoates. When hydrolysed and heated the product was probably a 1:1 mixture of the γ- and δ-stearolactones (ECL 26.4 and 27.1) but these were not separated from each other. This reaction was patterned on the methoxymercuration-demercuration of the ester

which gave the 5- and 4-methoxy-esters in a more useful 4:1 ratio.

5.2 Iodochlorination of octadec-cis-4-enoic acid

When octadec-cis-4-enoic acid is treated with Wij's reagent the possible products are (1), (2) and (3)



(1)

The product contained the iodolactone (1) to the extent of 61%. On TLC using PE10 as developing solvent the lactone (Rf = 0) was not separated from the acid, but by using acetic acid in the developing solvent the lactone could be moved up the plate. Even in this solvent it still has a lower Rf than oleic acid.

The NMR signals at 7.5τ and 5.8τ are those expected of a γ -lactone[56] and were also present in the NMR spectrum of our authentic sample of γ -stearolactone.

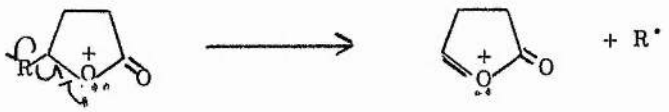
Tulloch[57] studied the GLC behaviour of methyl hydroxyoctadecanoates on polar and non-polar columns and observed that methyl 4-hydroxyoctadecanoate had a similar ECL value to γ -stearolactone (27.15 on a polar column and 19.85 on a non-polar column). He concluded that the hydroxy ester was converted to the lactone at the moment of injection.

We observed ECL 19.6 (ApL) and 26.4 (DEGS) for our authentic γ-stearolactones. The iodolactone gave similar peaks after

reaction with sodium borohydride.

The IR spectra of lactones are important since they enable us to differentiate between the various ring sizes. The acid absorbs at 1710 cm^{-1}, a δ-lactone at 1740 cm^{-1}, a γ -lactone at 1780 cm^{-1}, and a β-lactone at 1840 cm^{-1} [58].

The most important feature in the MS of a lactone is the fragment arising by loss of the alkyl chain[59,60].



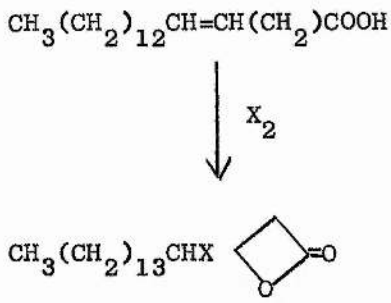
m/e 85

The base peak of our authentic lactone was at m/e 85 and the iodolactone also had a peak m/e 85. See section 6.

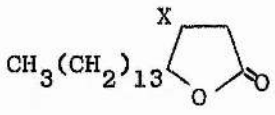
The other component is possibly chloro-iodo acid. Its IR spectrum showed absorption at 1710 cm^{-1}. When heated with DBU and esterified the product could be separated into four components on TLC but there was insufficient of each for complete identification.

5.3 Bromination of octadec-cis-3-enoic acid

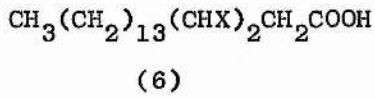
Halogenation of this acid could give rise to the lactone(s) (4) and (5) and the dibromide (6).



(4)



(5)

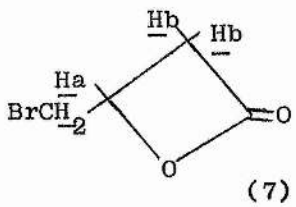


(6)

Recently published papers[61,62] reveal that during iodination both (4) and (5) form under different conditions.

Bromination of octadec-cis-3-enoic acid in sodium bicarbonate solution gave 36% of the β-lactone which was recognized from the appearance of the IR band at 1840 cm^{-1} [63].

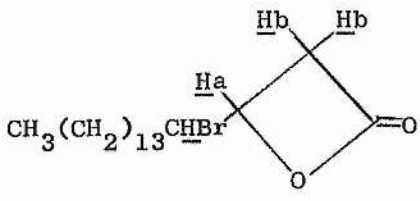
The significant NMR signals given below (8) resemble those previously reported for the simpler β-lactone (7).



(7)

Ha = 5.2-5.5τ

Hb = 6.2-6.7τ



(8)

Ha CHBr	5.8 to 5.9τ
Hb	6.4τ

6 Discussion of Results

6.1 NMR spectra

These studies have provided useful information about the NMR spectra of long-chain halogen-containing compounds and about the influence of the neighbouring halogen and hydroxyl group on chemical shifts. This is summarised in Tables VII and VIII.

The dihalides

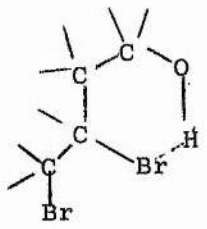
The -CHX- signals of the vicinal dihalides examined are fairly constant except when close to the hydroxyl group, where the signal is often split or spread out. In all cases it appears as a multiplet.

Philaja and Ketola[70] have examined the NMR spectrum of 9,10-dichloro-octadecanoic acid and report that the -CHCl- protons give a signal at 6.07τ. We have examined the dichloro product of three alkenoates, see table VII, and where the double bond is isolated our τ values for the -CHCl- protons agree with those of Philaja and Ketola. The product obtained by chlorination of methyl ricinoleate has a broad absorption band from 5.4τ to 6.4τ possibly due to the proximity to the hydroxyl group. The -CHBr- signals in methyl threo-dibromostearate are at 5.83τ and this value is hardly changed (5.79-5.82) in a range of hydroxy dibromides when n = 2, 3, and 4. When n = 1, however, two separate -CHBr- signals are observed at

$$-CHBrCHBr(CH_2)_nCH(OH)-$$

5.52 and 5.82τ in the dibromide from methyl ricinoleate and at 5.45 and 5.80τ in the dibromide from octadec-cis-3-enol. This change could arise from the closeness of the hydroxyl group to

one of the -CHBr- groups and/or to the possibility of hydrogen bonding as shown in the accompanying structure. We propose (tentatively) that the -CHBr- closer to the hydroxyl group is responsible for the signal of lower τ value.



The erythro-dibromide from methyl ricinelaidate gave -CHBr- signals at 5.80 and 6.16τ but with no other information about erythro-dibromides we are not able to comment further on these values.

Signals from the chloro-iodo compounds are uniform in all the compounds (CHCl, 6.1 to 6.3τ and CHI, 5.6 to 5.7τ) except in methyl ricinoleate (see table VII).

The ene-halides

The more important signals arising from these compounds are derived from the vinylic and allylic protons. The vinylic proton signal appear between 4.22τ and 4.62τ.

Allylic protons. Prior to the examination of the spectra of ene-halides from the hydroxy alkenoates we examined those derived from methyl oleate and observed that allylic protons in the latter could give rise to signals having the τ values given below.

$$-CH_2CH{=}CXCH_2-$$

$$7.90 \qquad \begin{matrix} 7.68\ (X{=}Br) \\ 7.62\ (X{=}Cl) \end{matrix}$$

Both ene-halides have signals at 7.90τ. Based on this fact

we assumed it could result from protons adjacent to vinylic proton. This signal is not clearly seen in all the spectra examined, and we did not lay much importance to it when assigning tentative structures to some of the separated hydroxy ene-halides. Our discussion is limited to the allylic protons adjacent to the halogen atom.

The ene-bromides from methyl ricinoleate could be separated into two isomers on TLC. The less polar isomer has a doublet at 7.56τ for the C(11) protons and hence is the 10-bromo-isomer. The more polar isomer has a triplet at 7.58τ arising possibly from the C(8) protons and is the 9-bromo-isomer. The ene-bromides from methyl 12-hydroxyoctadec-trans-9-enoate were scraped off as two bands on TLC. The more polar isomer has a triplet at 7.59τ (C(8) protons) is possibly the 9-bromo-isomer. The C(11) proton in the other isomer is complex (not a doublet) and is around 7.62τ. The ene-halides derived from methyl threo-12,13-dibromo-9-hydroxy-stearates could not be satisfactorily separated on TLC into the two isomers. The multiplet in the spectrum around 7.55τ could probably be from the allylic ($-CH_2CX=-$) protons of both isomers. The ene-bromides from the corresponding erythro isomer were separated into two components on TLC. The two isomers have NMR signals at 7.49τ (the less polar isomer) and at 7.59τ (the more polar isomer) and if this difference arises from the proximity of the OH group then these must be the 12- and 13-bromo compounds respectively.

The ene-bromides from the octadecenols were not separated into the two isomers on TLC. The 6(7), 5(6), bromo-octadecenols had signals at 7.61τ in their spectra for these allylic protons ($-CH_2CX=-$). In the 3(4)-bromo compound two triplets for these

Table VII τ values of the NMR spectra of dihalides

-CHXCHY-	X=Y=Cl	X=Y=Br	X=Cl, Y=I[a]
threo-dihalogeno adducts of			
methyl oleate	6.03	5.83	6.12,5.72
octadec-cis-6-enol	-	5.82	6.24,5.71
octadec-cis-5-enol	-	5.81	6.22,5.70
octadec-cis-3-enol	-	5.55,5.82[b]	-
methyl ricinoleate	5.4-6.4	5.45,5.80[c]	5.70,5.43[d] 5.87,5.29
methyl 9-hydroxy 18:1 (12c)	6.0	5.79[e]	6.3[f],5.64

a CHCl is quoted before -CHI-

b these refer to the protons C(3) and C(4) respectively

c these values refer to C(10) and C(9) respectively,
Values for the erythro-isomer are 5.80 and 6.16

d these refer to the 10-chloro-9-iodo- and 9-chloro-10-iodo-isomers

e erythro-isomer 5.86

f unresolved from -CH(OH)- signal

Table VIII τ values of the NMR spectra of ene-halides

	-CH=CX-	-CH$_2$CH=CX-	-CH=CXCH$_2$-
methyl esters (Z-isomers)			
9(10)-bromo Δ9	4.44	7.91	7.62
9-bromo-12-hydroxy Δ9[a]	4.27	7.78	7.58
10-bromo-12-hydroxy Δ9[b]	4.31	7.78[d]	7.56
12(13)-bromo-9-hydroxy Δ12[c]	4.37	7.90	7.50,7.62
9(10)-chloro Δ9	4.62	7.90	7.68
9-chloro-12-hydroxy Δ9	4.48	7.78[d]	7.78[d]
10-chloro-12-hydroxy Δ9	4.53		7.68
12(13)-chloro-9-hydroxy Δ12	4.22	7.96	7.54
Octadec-1-enols (Z-isomers)			
6(7)-bromo-octadec-6-enol	4.42	7.88	7.61
5(6)-bromo-octadec-5-enol	4.42	7.88	7.61
3(4)-bromo-octadec-3-enol	4.26	7.86	7.59,7.40
6(7)-chloro-octadec-6-enol	4.62	8.00	8.00
5(6)-chloro-octadec-5-enol	4.60	7.6 to 8.4	7.6 to 8.4

a corresponding values for E-isomer, 4.13, 7.78, 7.59

b corresponding values for E-isomer, 4.06, 7.78, possibly 7.62

c corresponding values for E-isomer, 12-bromo-, 4.21, 7.95, 7.49
13-bromo-, 4.21, 7.88, 7.59

d included in C(2) signal

protons were observed, one at 7.40τ (3-bromo-isomer) and the other at 7.59 (4-bromo-isomer).

Methyl 9(10)-chloro-12-hydroxy-10(9)-iodostearate gave two ene-chlorides which could be separated into less polar and more polar components on TLC. The less polar component has a doublet at 7.68τ for its C(11) protons (possibly) and hence is the 10-chloro-isomer. In the more polar product this signal merges with the C(2) proton signal. Methyl 12(13)-chloro-9-hydroxyoctadec-12-enoates had a multiplet at 7.54τ arising from the C(11) protons of the 12-chloro compound and C(14) protons of the 13-chloro compound.

6.2 Mass Spectra

Fuller details of the mass spectra are collected together in the experimental section. Since they resemble one another in many ways it is convenient to discuss them all together. Many of the spectra provide information about the gross structure of the products but do not reveal the position of the halogen atoms. Points of particular structural value have already been made earlier in the discussion.

Most of the spectra contain fragments frequently associated with long-chain compounds arising from ions belonging to the series $[C_nH_{2n \pm x}]^+$ and $[(CH_2)_nCO_2Me]^+$. These are so common that they are excluded from the following discussion.

(i) Methyl dihalogenostearates and the ene-halides derived from them (Spectra 1-5) With the exception of the ene-chloride (spectrum 5) these compounds do not produce a molecular ion peak

even at 16 ev. The fragments of high mass number result from loss of X and X_2H from the dihalogeno esters and loss of X and XH from the monohalogeno esters. Fragments containing the ester function may lose a further 32 mass units (CH_3OH).

(ii) Derivatives of methyl ricinoleate (and ricinelaidate) (spectra 6-14). The methyl dihalogenohydroxystearates give similar mass spectra with peaks arising from loss of X and X_2H. The latter fragment (311) also gives rise to other ions at 293 and 279 from further loss of 18 (H_2O) and 32 (CH_3OH) mass units respectively. Also present are fragments resulting from the loss of 85 or 86 mass units. Since these are only present in the compounds derived from methyl ricinoleate it is assumed that they result from cleavage between C(12) and C(13).

$$CH_3(CH_2)_5\left|\begin{matrix}CH(OH)CH_2CHXCHX(CH_2)_7CO_2Me\\ M-85\end{matrix}\right.$$

$[O{\equiv}CCH_2CH{=}CH(CH_2)_7CO_2Me]^+$ P(225) $C_{13}H_{21}O_3$ $\qquad$ $[CH_2CH{=}CH(CH_2)_7CO_2Me]^+$ Q(197) $C_{12}H_{21}O_2$

Two additional fragments of mass number 225 (P) and 197 (Q) occur in most of these spectra, frequently as dominant peaks, which sometimes also lose a further 32 mass units. These may have the structure shown above or be some closely related isomer.

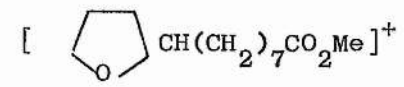
The ene-halides derived from the dihalogenohydroxystearates give similar spectral fragments resulting from loss of one or more X, XY, 85, 32, 18. The fragment Q and ions based on it are frequently dominant and fragment P is also sometimes present.

These results indicate that the hydroxyl group remains attached

to C(12) as expected but do not indicate the position of the halogen atom or double bond beyond confirming that they remain between the hydroxyl and ester function.

(iii) Derivatives of methyl 9-hydroxyoctadec-12-enoate (spectra 15-25) These derivatives are of three types: the dihalogeno-hydroxy esters, the ene-halides derived from them, and cyclic esters.

In the dihalogenohydroxy esters a fragment at 311 (resulting from loss X_2H) again appears along with ions resulting from further loss of water (293) and methanol (279) and these are accompanied by ions (frequently dominant) at 227 (R) 187 (S) and 155 (T). Fragments R and S (but not T) lose 32 mass units. It is tentatively proposed that these have the structures shown below:



or $[C_3H_4CH(OH)(CH_2)_7CO_2Me]^+$

$C_{13}H_{23}O_3$

R(227)

$[CH(OH)(CH_2)_7CO_2Me]^+$

S(187) $C_{10}H_{19}O_3$

$[CH_3(CH_2)_4CH=CH(CH_2)_2CH(OH)]^+$

T(155) $C_{10}H_{19}O$

The peak at 155 could be due to fragment T and/or the ion S after loss of 32 mass units. The peak at 227 is dominant in the spectra of the cyclic ethers (see below), in the hydroxy

compounds the cyclic ion may be formed in the mass spectrometer or the fragment may exist in some acyclic isomeric form.

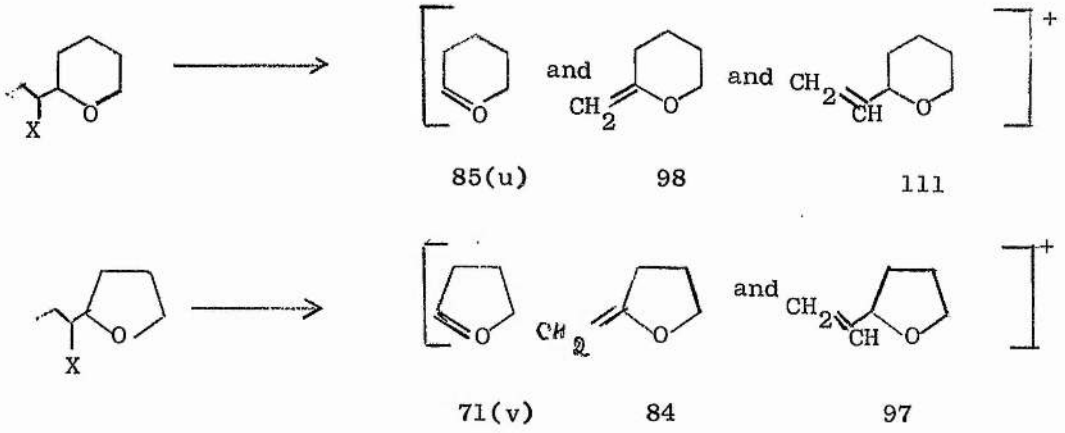
The ene-halides have spectra resembling those of their dihalogeno precursors with peaks at 311 (M-X), 227 (R), 187 (S), 155 (T) and at other m/e values derived from these by further loss of the usual fragments. There is also evidence for the loss of 57 mass units, probably C_4H_9, by cleavage between C(14) and C(15).

The cyclic ethers give more informative mass spectra. In addition to loss of X and XH followed by further loss of 18 and 32 mass units, there are strong peaks at 227 and 209 (loss of water). These latter have previously been reported[54] to be characteristic of 9,12-epoxystearates and provide additional evidence that cyclic ethers linked to C(9) and C(12) are formed during the halogenation reactions.

(iv) Derivatives of Octadecenols (spectra 26-40) The spectra of the dihalogeno-octadecenols are dominated by peaks at M-X, $M-X_2$ (268) and $M-X_2H$ (267) and also at 250 and 249 resulting from loss of water from the two previous peaks.

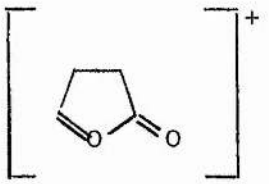
The ene-halides have peaks at 267 (M-X) and at 18 units less than both the molecular ion peak and the M-X peak.

The mass spectra of the cyclic ethers produced in some of these reactions are of greater diagnostic value. The halogenated cyclic ethers show peaks at 267 (M-X) and at 85, 98, and 111 for tetrahydropyrans and at 71, 84 and 97 for tetrahydrofurans. These probably arise from the structures shown below or from a related isomeric form.



The halogen-free tetrahydrofuran had its base peak at m/e 71, but the peak at m/e 84 was not present. The fragment of m/e 97 was present but probably arose from $[C_7H_{13}]^+$.

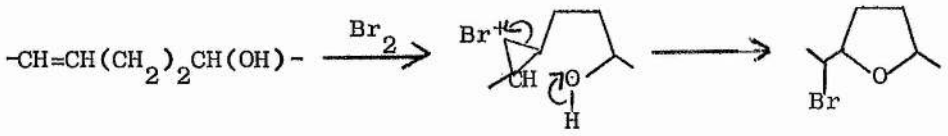
(v) Derivatives of stearolactones (spectra 41 and 42) Our sample of a γ-stearolactone had its base peak at m/e 85 and the 5-iodo- - stearolactone also had a dominant peak at m/e 85 which is probably due to the C_4 fragment.



6.3 Halogenation Products

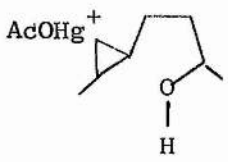
This study was concerned with the halogenation of unsaturated long-chain compounds containing a hydroxyl (or carboxyl) group which might conceivably become involved in the halogenation process as in the example shown below which leads to a tetrahydrofuran derivative

(a 1,4-epoxide). Six-membered cyclic compounds might also be formed.

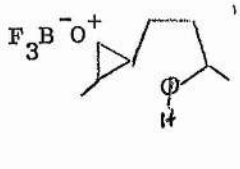


(1)

Previous studies in this department have shown that reactions of this type occur during oxymercuration and in acid-catalysed epoxide rearrangements[48] where the intermediates (2) and (3) have some resemblance to that depicted above (1) for the halogenation reaction



(2)



(3)

Halogenations which might produce the simple addition product (dihalide) or halogenated cyclic ether may be affected by several factors including: (i) the halogenating agent, (ii) the reaction solvent, (iii) the nature of the hydroxy alkene (in particular the number of methylene groups between the double bond and the hydroxyl group) and (iv) the configuration of the double bond.

Our general procedure involved separating the halogenated product into its components by prep TLC. In particular, the cyclic ethers are much less polar than the hydroxy compounds and

Table IX Halogenation Products

Hydroxy alkene -CH=CH(CH_2)$_n$CH(OH)-	n	halogenating agent and solvent		Cyclic ether (%)	Dihalide (%)
methyl ricinoleate	1	Br_2	CCl_4	0	100
methyl ricinoleate	1	Br_2	AcOH	0	84[a]
methyl ricinelaidate	1	Br_2	CCl_4	10[b]	90
methyl ricinoleate	1	ICl	AcOH	12[b]	88
methyl ricinoleate	1	Cl_2	CCl_4	0	100
9OH 12c	2	Br_2	CCl_4	40	60
9OH 12c	2	Br_2	AcOH	48	45[c]
9OAc 12c	2	Br_2	CCl_4	0	100
9OH 12t	2	Br_2	CCl_4	40	60
9OH 12c	2	ICl	AcOH	84	16
9OH 12c	2	Cl_2	CCl_4	32	68
Octadecenols					
6c	4	Br_2	CCl_4	0	100
5c	3	Br_2	CCl_4	6[b]	88
3c	1	Br_2	CCl_4	0	100
6c	4	ICl	AcOH	0	89[d]
5c	3	ICl	AcOH	16	78[e]
4c	2	ICl	AcOH	83	11[f]
Octadecenoic acids					
4c	2	ICl	AcOH	61	39?
3c	1	Br_2	Aq. $NaHCO_3$	36 and 64?	

a acetoxy bromo esters, 16%

b less polar material (TLC)

c acetoxy bromo esters, 16%

d acetoxy dihalide, 11%

e acetoxy dihalide, 6%

f acetoxy dihalide, 6%

are therefore readily separated. Methods of converting dihalides to ene-halides have recently been reported[49] and we took this opportunity of preparing such compounds from our dihalides since most of these ene-halides have not been prepared before.

$$RCHXCHXR' \longrightarrow RCH=CXR' + RCX=CHR'$$

Two isomeric forms of the ene-halides are obtained and in some cases we were able to separate these (TLC) and to identify each component on the basis of its polarity and its NMR spectra.

The halogeno cyclic ethers were less polar than the hydroxy dihalides. Some of their physical characteristics were determined and these were in most cases converted to halogen-free compounds for comparison with samples prepared in other ways.

Some of the results are summarised in Table IX and from these it is possible to draw the following conclusions.

i) Halogenation of methyl ricinoleate (a β-hydroxy alkene) gave mainly the dihalide with chlorine, bromine and iodine monochloride and we found little or no evidence for participation of the OH group in the reaction leading to the production of a cyclic ether. This was also true for the bromination of the trans isomer. In contrast to this, oxymercuration-demercuration[64] gave 10% of cyclic ether from methyl ricinoleate and 99% of cyclic ether from its trans isomer.

ii) Halogenation of methyl 9-hydroxyoctadec-cis-12-enoate gave cyclic ether in moderate yield. The yield of ether depends on the halogen involved and increased in the series chlorination (32% ether), bromination (40% ether) and iodochlorination (84% ether).

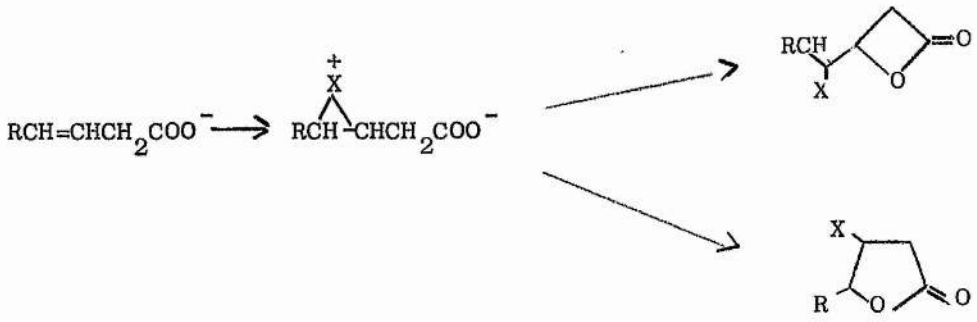
This, presumably, reflects stability of the intermediate halonium ion. The yield of bromo ether was marginally increased (to 48%) by conducting the reaction in acetic acid rather than carbon tetrachloride. Bromination of the cis and trans esters gave the same yield of cyclic ether but this compound was not formed from the corresponding acetoxy alkenoate. Oxymercuration of both the cis and trans esters gave cyclic ethers in high yield (> 90%).

This unsaturated hydroxy acid and its ester are known to give unexpectedly high iodine values although they give satisfactory values after acetylation[65,66]. This effect is not apparent with ricinoleic acid and its esters so that in this respect (as in many others) β- and γ-hydroxy alkenes behave differently. It is clear from our present studies that reaction with iodine monochloride converts most of the hydroxy alkenoate to an iodo cyclic ether. This, however, like normal halogen addition, requires one mole of reagent and the discrepancy in the iodine value must result from further reaction between Wijs reagent and cyclic ether. We have not examined this question.

iii) Among the cis-octadecenols examined, cyclic ethers predominate from the Δ4 compound (this, like methyl 9-hydroxyoctadec-12-enoate, is a γ-hydroxy alkene) and are minor products from the Δ5 alcohol. The 3c alcohol, like its analogue, methyl ricinoleate, did not furnish any cyclic ether.

iv) Halogenation of appropriate alkenoic acids is reported to give lactones and we have confirmed this for two members of the octadecenoic acid series. The 4c acid gives the γ-lactone in

high yield and the 3c acid gives a mixture of β- and γ-lactones.



EXPERIMENTAL

EXPERIMENTAL

General Procedures

Purification of Solvents

All solvents were reagent grade unless otherwise stated. Dimethylformamide was dried first by the addition of benzene and the removal of water as an azeotrope (bp 78°C) and then distilled (bp 153°C) and stored over molecular sieves. Diethyl ether was dried by standing over calcium chloride. After decantation and distillation it was stored over sodium wire. Methanol and ethanol were dried by reaction with magnesium and iodine according to Vogel's procedure. Pyridine was distilled from potassium hydroxide pellets.

Spectroscopic Analysis

Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrometer. Samples were examined as 1% solutions in spectroscopic grade (BDH) carbon disulphide or carbon tetrachloride or as a liquid film.

Mass Spectra

The spectra were obtained at 16 or 70 ev on an AEI MS902 mass spectrometer.

Nuclear Magnetic Resonance

Spectra were recorded on 15% solutions in carbon tetrachloride using a Perkin Elmer R-10 spectrometer or a Varian HA-100 operating at 100 MHz. Chemical shifts are reported in τ values in the thesis.

Chromatographic Techniques

Analytical TLC was carried out on glass plates (20 x 5 cm) with a layer of silica gel G (0.25 mm thickness) or with silica gel G containing 10-20% silver nitrate.

Preparative TLC was carried out on glass plates (20 x 20 cm) with a silica layer 1 mm in thickness. Except in a few instances ether-petroleum mixtures were used as developing solvents. These are indicated by symbols such as PE20 which indicates a mixture of 20% ether and 80% petroleum by volume. In the text, TLC bands are named A,B,C and D starting with the least polar (i.e. the band with highest Rf value).

Analytical plates were sprayed with a 10% solution of phosphomolybdic acid in ethanol and heated at 120^{o}C to make the separated components visible.

Components on preparative plates fluoresced under UV light after the plates had been sprayed with a methanol solution of 2,7-dichlorofluorescein (0.2%). Bands were scraped off, slurried with a mixture containing ether and methanol, filtered and evaporated. Residual dichlorofluorescein was removed either by percolation through a florisil column or by washing with sodium bicarbonate.

Gas Liquid Chromatography (GLC)

A Pye 104 model chromatograph with a flame ionisation detector was used throughout. Columns used were 20% diethylene glycol succinate (DEGS) packed on HMDS Chromosorb W or 3% Apiezon L packed on AW DMCS Chromosorb G.

Saturated straight-chain methyl esters were used as internal or external standards.

General Chemical Procedures

Esterification

Small scale esterifications were carried out by refluxing the acid (up to 200 mg) for 20 min with 14% boron trifluoride[67] methanol complex (5 ml) diluted with dry methanol (20 ml). The ester was poured into sodium bicarbonate and recovered.

Larger quantities of acids (10 g) were esterified by refluxing for one hr with methanolic sulphuric acid (0.25M, 50 ml).

Methanolysis

Glycerides (25 g) were converted to methyl esters at room temperature by shaking overnight, or by refluxing (30 min) with dry methanolic sodium methoxide (200 ml, 0.1M).

Trimethylsilylation[68]

Long-chain hydroxy compounds were converted into their trimethylsilyl ethers (TMS ethers) to facilitate examination by GLC. To a small quantity of the material (5 mg) in pyridine (1 ml) was added hexamethyldisilazane (0.2 ml) and trimethylchlorosilane (0.1 ml). After 5 min the pyridine was removed under vacuum and the TMS ethers dissolved in ether.

Lithium aluminium hydride reduction

To a stirred suspension of LAH (20 mg) in dry ether was added dropwise a solution of the ester (100 mg) in dry ether (2 to 5 ml). After stirring for 10 min at room temperature, excess hydride was destroyed by the cautious addition of wet ether followed by water.

The product was acidified and extracted in ether.

Hydrogenation

Samples (10 mg) in methanol (5 ml) were shaken with 10% palladium/charcoal (10 mg) as catalyst in a hydrogen atmosphere for one hour at room temperature. The catalyst was removed by filtration and the product recovered.

von Rudloff oxidation[69]

Oxidative cleavage was used to determine the position of unsaturated centres in long-chain compounds.

An oxidising solution of potassium periodate (22.4 g) and potassium permanganate (0.4 g) in one litre of water was used.

The unsaturated material (5 mg) in distilled t-butanol (7 ml) and water (1 ml) was shaken overnight with 5% aqueous potassium carbonate (1 ml) and oxidising solution (2 ml). Excess oxidising agent was destroyed with sulphur dioxide and the solution made alkaline (KOH). The solvent was blown off with nitrogen, the residue acidified, and the oxidative products were extracted and esterified.

Methyl 12-Hydroxyoctadec-cis-9-enoate

This was prepared from castor oil. Oil was neutralised by percolation through a short alumina column (80-120 mesh) using chloroform as solvent and the neutralised oil was converted to methyl esters by methanolysis. Pure methyl ricinoleate was obtained by chromatography on silica gel (Sorbsil M60) using

petroleum with increasing amounts of ether as developing solvent.

Methyl 9-Hydroxyoctadec-cis-12-enoate[65]

This was isolated from Strophanthus courmontii seed oil by partition of the mixed acids between 20% aqueous methanol and petroleum to give a concentrate of the required hydroxy acid in the methanol layer. This concentrate was esterified and further purified by column chromatography.

Chlorination

Chlorination was carried out as suggested by Pihlaja and Ketola[70]. An ice cold solution of chlorine in carbon tetrachloride (2.5 to 3M) was added dropwise to the alkene, also in carbon tetrachloride, and cooled to -25°C. Addition was at such a rate as to maintain a temperature of -20°C. When the solution assumed a permanent yellow colour the addition was stopped and the reaction mixture was stirred at -30°C for a further hour. The solution was finally washed with sodium thiosulphate (0.3M) and the product recovered.

Bromination

Bromination was effected at 0-20°C by the dropwise addition of bromine solution (2 drops in 5 ml carbon tetrachloride) to the alkenoate (100 mg in 5 ml carbon tetrachloride) until the solution assumed an orange colour. After stirring for a further half hour the solution was washed with sodium thiosulphate (0.3M) and the bromo ester recovered.

Iodochlorination[71]

Wijs solution (0.1M) was prepared by dissolving iodine (1.90 g) and iodine trichloride (1.75 g) in warm glacial acetic acid (225 ml). A mixture of the alkene (150 mg) in chloroform or carbon tetrachloride (10 ml) and Wijs reagent (15 ml) was kept in the dark for 30 min. Excess iodine monochloride was then destroyed by the addition of potassium iodide solution (5 ml, 0.6M) and after washing with sodium thiosulphate (0.3M) the product was recovered.

Halogen Removal Procedures

(i) Sodium Methoxide[49]

The dihalide (100 mg) in dry benzene (15 ml) was refluxed for 1 hour with a solution of sodium in anhydrous methanol (30 ml, 0.4M). The reaction mixture was diluted with water, acidified and extracted with ether.

(ii) 1,5-Diazobicyclo(5,4,0)undec-5-ene (DBU)

The dihalide was heated with DBU on a steam bath for an appropriate time (see text). Water was added and the product~~ed~~ extracted in ether.

(iii) Sodium Borohydride Reduction[72]

A solution of the iodo compound (50 mg) and sodium borohydride (15 mg) in dry dimethylformamide (5 ml) was heated at 85°C for 1 hr. The product was acidified and extracted with ether.

Oxymercuration-demercuration[53]

Excess mercuric acetate (100 mg) and methyl oleate (50 mg) in methanol (10 ml) were left in a stoppered flask at room temperature for 2 to 4 days. Sodium borohydride (20 mg) in water (10 ml) was added dropwise with stirring to the oxymercuration reaction mixture at $0^{o}C$. The reaction mixture was stirred at room temperature for 30 min, saturated with sodium chloride and extracted with ether.

Part I

Starting Materials

Samples of most of the isomeric methyl trans-octadecenoates were available from a previous synthetic programme. Methyl trans-octadec-3- and 16-enoates were obtained by stereomutation of the corresponding cis esters by reaction with 3-mercaptopropionic acid[73].

Methyl octadec-trans-2-enoate was obtained from octadec-2-ynoic acid by the following procedure. The octadec-2-ynoic acid was esterified by refluxing it with methanolic sulphuric acid (0.25M) for half an hour and the methyl ester (585 mg) in methanol (28 ml) was partially reduced with hydrogen and Lindlar's catalyst in the presence of quinoline (1 drop). This cis methyl ester was allowed to react with mercuric acetate (770 mg) at room temperature for two days. Hydrochloric acid (3M) in methanol (15 ml) was added to the ice-cooled stirred solution and after stirring for a further half hour at room temperature the trans ester was extracted and examined on GLC (19.57, DEGS).

Preparation of methyl trans-methyleneoctadecanoates

In a typical experiment the zinc copper couple was prepared as recommended by Christie[20]. Zinc dust was added to a vigorously stirred and nearly boiling solution of glacial acetic acid (10 ml). After one minute cupric acetate monohydrate (0.4 g) in hot glacial acetic acid (10 ml) was added and the mixture stirred for one further minute. The supernatant liquid was then decanted and the zinc copper couple washed with glacial acetic acid (5 x 20 ml) and with anhydrous ether (5 x 20 ml).

To the zinc copper couple in anhydrous ether (10 ml), was added dropwise a solution of methyl trans-octadecenoate (0.4 g) in di-iodomethane (4 ml) and anhydrous ether (5 ml), and this was refluxed overnight. The solution was decanted, washed with hydrochloric acid (1M) and the excess di-iodomethane was removed under reduced pressure on a steam bath. The more polar impurities remained on a florisil column when the cyclopropane esters were eluted with a mixture (70:30) of petroleum ether and ether. The cyclopropane esters were finally purified on Ag^{+}TLC using petroleum ether and ether (90:10) as developing solvent. The yields are given in table 1.

Mass spectra

The mass spectra of some methyl trans-methyleneoctadecanoates are given in Table X.

Table X Mass spectra (16 ev) of methyl trans-methyleneoctadecanoates

m/e	Intensity of peak relative to base peak (=100) [Values below 2 are ignored and m/e values with no significant peak are omitted] isomeric methyl trans-methyleneoctadecanoates						
	2,3	3,4	4,5	5,6	6,7	7,8	15,16
54*	4	3	7	7	6	9	4
55*	5	3	12	7	6	15	8
56*	8	6	20	10	15	27	7
57	17	10	0	18	22	29	15
67	0	3	6	9	6	14	6
68*	10	13	31	34	46	36	14
69*	13	9	19	16	26	40	24
70*	10	7	16	14	21	34	33
71	14	7	14	13	15	21	11
73	11	3	8	7	5	7	1
74	68	100	93	42	67	85	58
75	16	30	24	11	15	19	15
79	0	0	0	5	2	3	1
80	2	1	6	7	6	6	3
81	8	5	14	18	12	22	10
82*	15	10	49	46	39	50	24
83*	22	18	46	40	42	70	38
84*	23	22	90	81	100	95	77
85	11	7	16	14	16	19	12
87†	100	47	65	57	60	55	38
88	10	13	7	5	5	5	4
93	2	0	3	5	2	4	1
94	3	3	10	14	10	10	6
95	10	5	17	22	15	23	13
96*	22	27	96	100	92	100	58
97*	25	25	66	68	64	77	50
98*	18	22	66	73	78	72	59
99	4	7	10	11	10	10	7
101†	10	54	11	14	13	13	8
102	2	4	4	33	2	0	2
105	2	2	8	13	13	7	2

m/e	2,3	3,4	4,5	5,6	6,7	7,8	15,16
107	2	0	0	6	3	4	2
108	3	2	8	13	7	9	5
109	7	4	12	16	11	17	12
110*	13	14	58	57	67	75	31
111*	17	16	45	44	50	55	30
112	3	7	18	20	21	21	16
113	15	3	8	6	5	6	4
114	34	8	100	21	12	13	6
115	18	8	61	16	19	22	10
116	2	1	6	8	3	3	2
119	6	0	6	10	6	5	2
120	0	0	20	46	39	6	1
121	2	0	7	14	8	6	4
122	3	6	4	13	4	6	5
123*	8	6	20	25	25	27	16
124*	17	7	24	40	25	36	18
125*	9	8	25	26	23	44	18
126	3	3	7	7	6	10	5
127	8	4	10	10	10	8	5
128†	10	23	66	68	67	16	10
129†	12	11	18	27	27	15	10
130	2	2	4	5	6	4	4
133	2	0	4	8	3	5	2
134	0	1	10	33	13	8	4
135	2	1	6	13	5	6	4
137*	6	4	14	21	19	21	12
138*	5	5	16	22	26	28	18
139*	5	5	15	16	13	15	13
140	2	1	4	5	4	4	3
141†	8	5	26	22	18	17	13
142†	2	4	22	21	11	14	4
143†	10	15	12	13	22	24	13
147	0	0	0	6	2	4	1
148	0	0	4	17	5	4	3
149	3	0	4	8	3	4	3

m/e	2,3	3,4	4,5	5,6	6,7	7,8	15,16
151*	4	2	10	16	12	13	9
152*	3	3	14	24	15	23	16
153*	3	3	10	11	7	14	8
155†	3	2	9	40	6	5	3
156†	0	0	4	12	7	0	1
157†	3	4	4	6	5	12	5
165*	3	1	6	12	7	8	7
166*	3	3	9	15	8	9	9
167*	2	1	5	7	4	6	5
169	2	2	4	7	6	4	2
171	3	2	4	10	4	5	4
179*	2	0	4	4	5	5	5
180*	3	4	11	14	11	10	15
181*	0	1	4	6	4	4	5
183	2	1	6	4	7	6	4
185†	3	3	0	3	3	3	4
193	0	0	0	5	3	3	3
194*	6	6	28	33	33	26	23
195*	2	0	7	9	10	8	7
196*	0	0	0	0	3	0	44
197*	0	0	4	5	4	4	7
199†	4	4	0	0	2	0	3
207	0	0	0	6	3	3	4
208*	2	2	0	7	6	5	6
213†	4	8	4	3	2	0	3
221	0	0	0	6	3	2	4
222	0	2	4	5	3	3	11
227†	4	3	0	3	2	0	5
234	4	5	17	24	16	12	8
235	2	2	6	12	7	7	7
236	12	30	63	46	46	32	30
237	3	10	26	10	11	7	7
249	0	0	0	6	0	4	5
250	3	4	5	11	4	6	1
278	14	20	70	52	92	75	100

m/e	2,3	3,4	4,5	5,6	6,7	7,8	15,16
279	7	4	22	15	28	30	44
310	3	6	16	16	22	10	12
311	0	1	4	6	5	1	2

* Signals from hydrocarbon peaks (see text)

† Oxygen containing peaks (see text)

1.1 Bromination of methyl oleate

Methyl oleate (235 mg) in carbon tetrachloride (5 ml) gave a brominated ester (360 mg) with the same polarity (TLC) as methyl oleate. The product decomposed on GLC (DEGS, 190°C).

(i) NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$CH_3(CH_2)_n$-
8.70	singlet	-$(CH_2)_n$
8.20	broad	-$CH_2CHBrCHBrCH_2$-
7.78(2H)	triplet	-CH_2COOCH_3
6.43(3H)	singlet	-$COOCH_3$
5.83(2H)	multiplet	-CHBrCHBr-

(ii) MS See section 6 (spectrum 1)

(iii) the dibromide (145 mg) was converted to the ene-bromides (98 mg, ECL 23.1 on DEGS) with sodium methoxide. This gave the NMR signals listed below. The mass spectrum (number 4) is given in section 6.

NMR Spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$CH_3(CH_2)_n$-
8.70	singlet	-$(CH_2)_n$-
7.91		-CH_2CH=CBr-,
7.78	multiplet	-CH_2COOCH_3,
7.62		and -CH_2CH=CBrCH_2-
6.42(3H)	singlet	-$COOCH_3$
4.44(1H)	triplet	-CH=CBr-

1.2 Iodochlorination of methyl oleate

The methyl esters of olive oil (207 mg)* were treated with iodine monochloride to give a product (283 mg) which on preparative TLC gave three bands. The major band (88%, ECL 18.6) is methyl 9(10)-chloro-10(9)-iodostearate on the basis of the following evidence.

(i) NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.70	singlet	-$(\underline{CH}_2)_n$-
7.78(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.41(3H)	singlet	-$COOCH_3$
6.12(1H)	multiplet	-$\underline{CH}Cl$-
5.72(1H)	multiplet	-$\underline{CH}I$-

(ii) For MS see section 6 (spectrum 3)

(iii) When dehydroiodinated with sodium methoxide, the iodochlorides (125 mg) gave methyl 9(10)-chloro-octadec-9-enoate (61 mg, ECL 21.7) which had the same polarity on TLC as starting material and showed the NMR signals (100 MHz) given below. Its MS (spectrum 5) is reported in section 6.

* This was used as an impure sample of methyl oleate.

τ value and no. of protons	Appearance	Assignment
9.12(3H)	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.70	singlet	-$(\underline{CH}_2)_n$-
7.90		-$\underline{CH}_2CH=CXCH_2$-,
7.78	multiplet	-$\underline{CH}_2COOCH_3$, and
7.68		-$CH_2CH=CX\underline{CH}_2$-
6.40(3H)	singlet	-$COO\underline{CH}_3$
4.62(1H)	triplet	-$\underline{CH}$=CCl-

1.3 Chlorination of methyl oleate

The product (1.5 g) obtained by chlorination of olive oil methyl esters (1.5 g) was separated by preparative TLC into four bands (A-D) of which only the major band (C, 82%, gives a poorly resolved peak of ECL 26.2 on a DEGS column) was examined. Spectroscopic and chromatographic studies and comparison of its dehydrochlorinated product with that obtained from methyl 9(10)-chloro-10(9)-iodostearate show it to be methyl 9,10-dichlorostearate.

(i) NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11(3H)	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.70	singlet	-$(\underline{CH}_2)_n$-
7.74(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.42(3H)	singlet	-$COO\underline{CH}_3$
6.03(2H)	multiplet	-$\underline{CH}Cl\underline{CH}Cl$-

(ii) Dehydrochlorination (50 mg) with DBU (6 hr) gave a product (30 mg) which had the same TLC and GLC (ECL 21.70) behaviour as the methyl 9(10)-chloro-octadec-9-enoate obtained from the iodochloride.

2.1 Bromination of methyl ricinoleate in carbon tetrachloride

Bromine in carbon tetrachloride was added to methyl ricinoleate (222 mg) at 0°C. The solution was stirred for half an hour, washed with sodium thiosulphate and the product (300 mg) recovered. The Rf value of the product was unchanged on TLC and its TMS ether decomposed on GLC. The IR spectrum showed hydroxyl group absorption at 3460 cm^{-1}.

(i) NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$-\underline{CH}_3(CH_2)_n-$
8.64	singlet	$-(\underline{CH}_2)_n-$
8.20	multiplet	$-CH(OH)\underline{CH}_2CHBr-$
7.78(2H)	triplet	$-\underline{CH}_2COOCH_3$
6.40(3H)	singlet	$-COOC\underline{H}_3$
6.2	broad	$-\underline{CH}(OH)-$
5.80(1H)	multiplet	$-CH(OH)CH_2CHBrC\underline{H}Br-$
5.45(1H)	multiplet	$-CH(OH)CH_2\underline{CH}BrCHBr-$

(ii) MS See section 6 (spectrum 6)

(iii) Dehydrobromination. The dibromide (80 mg) was refluxed with sodium methoxide for an hour, and after acidification the product (62 mg) was extracted with ether. Two major fragments, C_1 (35%, less polar) and C_2 (48%, slightly more polar), were separated on TLC (PE20).

Fraction C_1

In its IR spectrum C_1 showed absorption bands at 3460 cm^{-1} and 1660 cm^{-1} due to hydroxyl group and trisubstituted alkene absorption respectively. There is no absorption band at 970 cm^{-1}. The TMS ether of this ene-bromide had an ECL of 23.6 and was identified as methyl 10-bromo-12-hydroxy-octadec-9-enoate. Its mass spectrum is given in section 6 (spectrum 12).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$CH_3(CH_2)_n$-
8.66	singlet	-$(CH_2)_n$-
7.78	multiplet	-CH(OH)CH CBr=CHCH_2- and CH_2COOCH_3
7.56(2H)	doublet	-CH(OH)CH_2CBr=CH-
6.40(3H)	singlet	-$COOCH_3$
6.2(1H)	broad	-CH(OH)-
4.31(1H)	triplet	-CH=CBr-

Fraction C_2

The slightly more polar product C_2 (ECL of TMS ether 23.55), had an IR spectrum similar to that of C_1 and is thought to be methyl 9-bromo-12-hydroxy-octadec-9-enoate on the basis of its NMR spectrum.

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.69	singlet	-$(\underline{CH}_2)_n$-
7.78	multiplet	-$\underline{CH}_2COOCH_3$ and -$CH(OH)\underline{CH}_2CH{=}CBrCH_2$-
7.58	triplet	-$CH(OH)CH_2CH{=}CBr\underline{CH}_2$-
6.6(1H)	broad	-$\underline{CH}(OH)$-
6.40(3H)	singlet	-$COOCH_3$
4.27(1H)	triplet	-$CH(OH)CH_2\underline{CH}{=}CBr$-

2.2 Bromination of methyl ricinoleate in other solvents

Methyl ricinoleate was brominated in the usual manner in dimethylformamide, in dimethylsulphoxide and in a mixture of dimethylsulphoxide and carbon tetrachloride. From the polarity of the major product on TLC it was concluded that the product did not contain cyclic material.

When brominated in acetic acid solution, methyl ricinoleate (264 mg) gave a product (326 mg), isolated after neutralisation (sodium bicarbonate) and sodium thiosulphate treatment, which separated into two bands on TLC.

Band A (84%) with the same polarity on TLC as methyl ricinoleate was identified as methyl 9,10-dibromo-12-hydroxystearate on the basis of its ready conversion to the two ene-bromides (ECL of TMS ether 23.60) with sodium methoxide.

Band B (16%) was more polar (TLC) and was shown by its infrared spectrum to contain an OH group (3440 cm^{-1}). Its mass spectrum is reported in section 6 (spectrum 8).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.66	singlet	-$(\underline{CH}_2)_n$-
8.02	singlet	-$CH(OH)CH_2CHBrCH(OCOC\underline{H}_3)$-
7.97	singlet	-$CH(OH)CH_2CH(OCOC\underline{H}_3)CHBr$-
7.78(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.5	broad	-$\underline{CH}(OH)$-
6.41(3H)	singlet	-$COOC\underline{H}_3$-

[Three ill-defined signals at about 6.0, 5.7 and 5.1 probably arise from the $CH(OH)CH_2CH(OCOCH_3)C\underline{H}Br$, -$CH(OH)CH_2C\underline{H}BrCH(OCOCH_3)$ and -$C\underline{H}OCOCH_3$- protons respectively.]

2.3 Bromination of methyl ricinelaidate

When methyl ricinelaidate (30 mg) was treated with bromine in carbon tetrachloride the product (50 mg) consisted mainly of polar material (90%), which was examined in the usual way. From previous experience and by a study of its spectra it is thought to be methyl erytrho-9,10-dibromo-12-hydroxystearate. Its mass spectrum is recorded in section 6 (spectrum 7).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.65	singlet	-$(\underline{CH}_2)_n$-
7.91 to 8.1	broad	-CH(OH)$\underline{CH}_2$CHBrCHBr-
7.78	triplet	-$\underline{CH}_2COOCH_3$
6.40(3H)	singlet	-$COO\underline{CH}_3$
6.16(2H) and 5.80(1H)	multiplet	-$\underline{CH}$(OH)$CH_2\underline{CH}Br\underline{CH}$Br-

The erythro-dibromide (50 mg) was refluxed with sodium methoxide and the product (40 mg) recovered. Its TMS ether gave two peaks on GLC (23.9 and 24.2). The ene-bromides were separated by TLC into less polar (C_1, 17%, ECL 23.9) and more polar (C_2, 74%, ECL 24.2) components and each was examined by IR, NMR and MS.

Fraction C_2

This fraction showed hydroxyl group (3460 cm^{-1}) and trisubstituted alkene absorption (1645 cm^{-1}) in the infrared spectrum and is methyl 9-bromo-12-hydroxyoctadec-9-enoate. Its MS is recorded in section 6 (spectrum 13).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.66	singlet	-$(\underline{CH}_2)_n$-
7.82 7.78	multiplet	-CH(OH)$\underline{CH}_2$CH=CBrCH$_2$- and -$\underline{CH}_2$COOCH$_3$
7.59(2H)	triplet	-CH(OH)CH$_2$CH=CBr$\underline{CH}_2$-
6.5(1H)	broad	-$\underline{CH}$(OH)-
6.40(3H)	singlet	-COO$\underline{CH}_3$
4.13	triplet	-$\underline{CH}$=CBr-

Fraction C_1

This component had an IR spectrum similar to fraction C_2. However, it could not be completely identified as methyl 10-bromo-12-hydroxyoctadec-9-enoate. Its MS is reported in section 6 (spectrum 12)

NMR spectrum

τ value and no. of protons		Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.68	singlet	-$(\underline{CH}_2)_n$-
7.95 7.78	multiplet	-CH(OH)CH$_2$CBr=CH$\underline{CH}_2$- and -$\underline{CH}_2$COOCH$_3$
7.62	doublet	-CH(OH)$\underline{CH}_2$CBr=CH-
6.40(3H)	singlet	-COO$\underline{CH}_3$
6.2	broad	-$\underline{CH}$(OH)-
4.06	triplet	-CBr=$\underline{CH}$-

2.4 Iodochlorination of methyl ricinoleate

When methyl ricinoleate (200 mg) was treated with Wijs solution the major component (88% of 310 mg, ECL of TMS ether 19.8) was similar to methyl ricinoleate in its behaviour on TLC. Its NMR and mass spectra were recorded and the dihalide was submitted to dehydrohalogenation. The MS is detailed in section 6 (spectrum 10).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.66	singlet	-$(\underline{CH}_2)_n$-
8.16	multiplet	-CH(OH)$\underline{CH}_2$CHClCHI-
7.96	multiplet	-CH(OH)$\underline{CH}_2$CHICHCl-
7.76(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.40(3H)	singlet	-$COOCH_3$
6.2(1H)	broad	-$\underline{CH}$(OH)-
5.87*	broad	-CH(OH)CH_2CHI$\underline{CH}$Cl-
5.70*	broad	-CH(OH)$CH_2\underline{CH}$ClCHI-
5.40*	broad	-CH(OH)CH_2CHCl$\underline{CH}$I-
5.29*	broad	-CH(OH)$CH_2\underline{CH}$ICHCl-

* weak signals

Methyl 9(10)-chloro-12-hydroxy-10(9)-iodostearate (220 mg) was refluxed with sodium methoxide for one hour. The product (150 mg) showed hydroxyl group absorption (3400 cm^{-1}) and trisubstituted alkene absorption (1650 cm^{-1}) in its IR spectrum. The MS is in section 6.2 (spectrum 14).

Its TMS ether gave a single peak on GLC (22.5) but the ene-chloride gave two bands of very similar polarity (C_1, 35% and C_2, 53%) on TLC. The NMR spectra of each of these was recorded.

Band C_1

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.12	triplet (unresolved)	$CH_3(CH_2)_n$-
8.68	singlet	$-(CH_2)_n-$
7.78	triplet	$-CH_2COOCH_3$
7.68	doublet	$-CH(OH)CH_2CCl=CH-$
6.42(3H)	singlet	$-COOCH_3$
6.4	broad	$-CH(OH)-$
4.53	triplet	$-CH(OH)CH_2CCl=CH-$

Band C_2

This fraction (probably the 9-chloro isomer) has an ECL of 22.6 for its TMS ether.

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$CH_3(CH_2)_n$-
8.68	singlet	$-(CH_2)_n-$
7.78	multiplet	$-CH_2COOCH_3$, $-CH(OH)CH_2CH=CCl-$ and $-CH(OH)CH_2CH=CClCH_2-$
6.4	broad	$-CH(OH)-$
4.48	triplet	$-CH(OH)CH_2CH=CCl-$

2.5 Chlorination of methyl ricinoleate

When methyl ricinoleate (455 mg) was chlorinated in carbon tetrachloride the product (579 mg) contained no material less polar (TLC) than the starting material. Its NMR and IR spectrum (OH group absorption) were recorded and the dihalide was submitted to dehydrohalogenation. The MS is given in section 6 (spectrum 9).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.66	singlet	-$(\underline{CH}_2)_n$-
7.76(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.40(3H)	singlet	-$COO\underline{CH}_3$
5.40 to 6.40 (3H)	broad	-$\underline{CH}(OH)CH_2\underline{CH}Cl\underline{CH}Cl$-

The dichloride (40 mg) was heated with DBU for 5 hours and the product (29 mg) was identical in its GLC (ECL 22.6 TMS) and TLC behaviour with the ene-chlorides obtained from the iodochlorides.

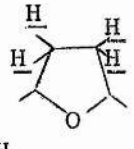
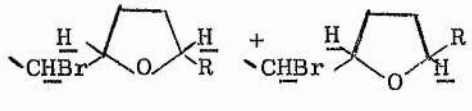
3.1 Bromination of methyl 9-hydroxyoctadec-cis-12-enoate

Methyl 9-hydroxyoctadec-cis-12-enoate (300 mg) was treated with bromine in carbon tetrachloride and the product (448 mg) recovered. The brominated ester separated on TLC into a less polar (A, 40%) and more polar (B, 60%) fractions.

Fraction A

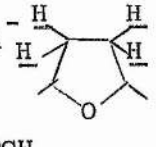
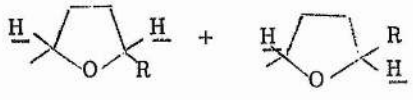
This fraction does not show hydroxyl group absorption in its IR spectrum and is thought to be a cyclic ether. The MS is given in section 6 (spectrum 22).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.09	triplet (unresolved)	$CH_3(CH_2)_n$-
8.67	singlet	$-(CH_2)_n-$ 
8.15	broad	
7.78(2H)	triplet	$-CH_2COOCH_3$
6.40(3H)	singlet	$-COOCH_3$
6.10(3H)	broad	

The bromine-containing cyclic ether (100 mg) was heated with DBU (6 hr, 100°C) and the recovered product (60 mg) was hydrogenated and purified on TLC. It was examined by GLC (ECL 21.2 and 21.4 on DEGS) and by NMR and MS (section 6, spectrum 25).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.12	triplet (unresolved)	$CH_3(CH_2)_n$-
8.68	singlet	$-(CH_2)_n-$ 
8.2	broad	
7.79(2H)	triplet	$-CH_2COOCH_3$
6.40	singlet	$-COOCH_3$
6.3	broad	

The more polar fraction is considered to be the threo-dibromo ester. The MS is given in section 6 (spectrum 15).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.08	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.65	singlet	-$(\underline{CH}_2)_n$-
7.77(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.4	broad	-$\underline{CH}$(OH)-
6.40	singlet	-$COO\underline{CH}_3$
5.79	multiplet	-$\underline{CH}BrC\underline{H}Br$-

The dibromide (150 mg) was treated with sodium methoxide and the product (139 mg) recovered. On GLC it had ECL (as TMS ethers) of 23.9 and 24.0. No clear separation of the two isomers was observed on TLC.

The ene-bromides show hydroxyl group absorption and trisubstituted alkene absorption at 3450 cm^{-1} and 1650 cm^{-1} respectively. The MS is detailed in section 6 (spectrum 20).

NMR spectrum

τ value and no. or protons	Appearance	Assignment
9.10	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.70	singlet	-$(\underline{CH}_2)_n$-
7.90	unresolved	-$\underline{CH}_2CH=CBrCH_2CH_2CH(OH)$- and -$CBr=CH\underline{CH}_2CH_2CH(OH)$-
7.78	triplet	-$\underline{CH}_2COOCH_3$
7.62 7.50	multiplet	-$\underline{CH}_2CBr=CHCH_2CH_2CH(OH)$- and -$CH=CBr\underline{CH}_2CH_2CH(OH)$-
6.5	broad	-$\underline{CH}(OH)$-
6.40	singlet	-$COO\underline{CH}_3$
4.37	multiplet	-$\underline{CH}=CBr(CH_2)_2CH(OH)$- and -$CBr=\underline{CH}(CH_2)_2CH(OH)$-

3.2 Bromination of methyl 9-hydroxyoctadec-cis-12-enoate in glacial acetic acid

Methyl 9-hydroxyoctadec-cis-12-enoate (156 mg) was brominated in glacial acetic acid and the product (204 mg) was separated by TLC into 3 main fractions: A (48%), B (45%) and C (6%).

Fraction A

This fraction is thought to be the bromine-containing cyclic ether and was identified after dehydrobromination (DBU) and hydrogenation by its GLC behaviour (ECL 21.2 and 21.4).

Fraction B

Fraction B is the threo dibromo ester, since on dehydrobromination with sodium methoxide it gave the same ene-bromides

(ECL 23.9 and 24.0 as TMS ether) as did the previous sample of *threo* dibromo ester.

Fraction C

The small more polar product (6%) was not examined, but is thought to be an acetoxy bromo hydroxy ester.

3.3 Bromination of methyl 9-acetoxyoctadec-*cis*-12-enoate

The acetoxy ester (100 mg) was treated with bromine in carbon tetrachloride and the product gave one main spot on TLC. No less polar material was observed.

After dehydrobromination (sodium methoxide) and trans-esterification (methanolic sodium methoxide), the bromo ester (20 mg) gave a product (15 mg) with ECL 23.9 and 24.0 as TMS ethers.

3.4 Bromination of methyl 9-hydroxyoctadec-*trans*-12-enoate

Methyl 9-hydroxyoctadec-*trans*-12-enoate was prepared from the *cis* isomer as follows. The *cis* isomer (1 g) was refluxed for 1 hour with acetic anhydride (15-20 ml) and anhydrous sodium acetate (1-2 g). The acetoxy compound was stereomutated using β-mercaptopropionic acid[73] (4 g) and the *cis* and *trans* isomers separated on Ag^+TLC. The *trans* alkenoate was deacetylated by allowing it to stand overnight in methanol (10 ml) containing sodium (0.15 g), and the hydroxy *trans*-alkenoate recovered.

The less polar product (50 mg) was dehydrobrominated (DBU) and the recovered product (30 mg), after hydrogenation, showed the same TLC behaviour as did the material before dehydrohalogenation. On GLC it had ECL of 21.2 and 21.4 and is thought to be methyl 9,12-epoxystearate, identical on TLC and GLC to that obtained in the previous experiment.

The more polar fraction is the erythro dibromo ester.

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.08	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.66	singlet	-$(\underline{CH}_2)_n$-
7.76(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.4	broad	-$\underline{CH}$(OH)-
6.40(3H)	singlet	-$COOCH_3$
5.86(2H)	multiplet	-$\underline{CH}Br\underline{CH}Br$-

The erythro dibromide (200 mg) was refluxed with sodium methoxide and the product (160 mg) recovered. On GLC its TMS ethers gave two peaks (23.8 and 24.2) and it could be separated on TLC into a less polar fraction (C_1, 41%) and a slightly more polar fraction (C_2, 59%).

Fraction C_1

This fraction showed hydroxyl group and trisubstituted alkene absorption at 3460 cm^{-1} and 1635 cm^{-1} respectively and on GLC had an ECL of 23.8 as a TMS ether. Its MS is recorded in section 6 (spectrum 18).

NMR spectrum

τ value and no. or protons	Appearance	Assignment
9.10	triplet (unresolved)	$CH_3(CH_2)_n$-
8.66	singlet	-$(CH_2)_n$-
7.95	unresolved signal	-$CH_2CH{=}CBr(CH_2)_2CH(OH)$-
7.78(2H)	triplet	-CH_2COOCH_3
7.49(2H)	triplet	-$CH{=}CBrCH_2CH_2CH(OH)$-
6.5	broad	-CH(OH)-
6.40(3H)	singlet	-$COOCH_3$
4.21(1H)	triplet	-CBr=CH-

Fraction C_2

Fraction C_2 shows hydroxyl group absorption at 3410 cm^{-1} and trisubstituted alkene absorption at 1635 cm^{-1}. On GLC it has an ECL of 24.2 as TMS ether. The MS is detailed in section 6 (spectrum 19).

NMR spectrum

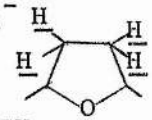
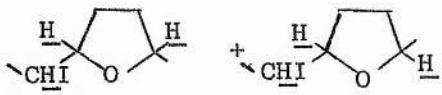
τ value and no. of protons	Appearance	Assignment
9.09	triplet (unresolved)	$CH_3(CH_2)_n$-
8.67	singlet	-$(CH_2)_n$-
7.88	unresolved	-$CBr{=}CHCH_2CH_2CH(OH)$-
7.78	triplet	-CH_2COOCH_3
7.59	triplet	-$CH(OH)CH_2CH_2CH{=}CBrCH_2$-
6.5	broad	-CH(OH)-
6.40	singlet	-$COOCH_3$
4.21	triplet	-$CBr{=}CHCH_2CH_2CH(OH)$-

3.5 Iodochlorination of methyl 9-hydroxyoctadec-cis-12-enoate

When the 9-hydroxy ester was treated with Wijs reagent the product (216 mg) was predominantly the less polar component (84%) and was separated by TLC from the small amount of polar material (16%).

The less polar product did not show hydroxyl group absorption in its IR spectrum and is thought to be the monoiodo cyclic ether. Its MS is reported in section 6 (spectrum 23).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.09	triplet (unresolved)	$CH_3(CH_2)_n$-
8.68	singlet	$-(CH_2)_n-$
8.2	broad	
7.78(2H)	triplet	$-CH_2COOCH_3$
6.40(3H)	singlet	$-COOCH_3$
6.20(1H) 5.99(2H)	multiplet	

The iodine-containing ether (131 mg) was deiodinated by heating for an hour (85°C) with sodium borohydride in dry DMF (10 ml). The product (98 mg) had the same behaviour on GLC (21.2 and 21.4) as the methyl 9,12-epoxystearate previously identified.

The more polar product seems to be a mixture of the two possible iodochlorides. The MS is recorded in section 6 (spectrum 17).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.08	triplet (unresolved)	$CH_3(CH_2)_n$-
8.64	singlet	$-(CH_2)_n-$
7.78(2H)	triplet	$-CH_2COOCH_3$
6.40	singlet	$-COOCH_3$
6.3	broad	-CH(OH) and two CHCl [C(12) and C(13)]
5.64(2H)	broad	two CHI [C(12) and C(13)]

Treated with sodium methoxide the iodochlorides (48 mg) gave the ene-chlorides (31 mg, ECL TMS ether 22.8) which showed infrared absorption for a hydroxyl group and a trisubstituted alkene at 3420 cm^{-1} and 1650 cm^{-1} respectively. The MS is given in section 6 (spectrum 21)

NMR spectrum

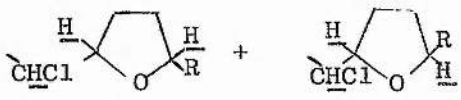
τ value and no. of protons	Appearance	Assignment
9.09	triplet (unresolved)	$CH_3(CH_2)_n$-
8.60	singlet	$-(CH_2)_n-$
7.96	unresolved	possibly $-CH(OH)CH_2CH_2CH=CClCH_2-$ and $CH(OH)CH_2CH_2CCl=CHCH_2-$
7.78	triplet	$-CH_2COOCH_3$
7.54	multiplet	possibly $CH(OH)(CH_2)_2CH=CClCH_2-$ and $CH(OH)CH_2CH_2CCl=CH-$
6.5	broad	-CH(OH)-
6.40(3H)	singlet	$-COOCH_3$
4.22(1H)	triplet	-CH=CCl-

3.6 Chlorination of methyl 9-hydroxyoctadec-cis-12-enoate

When chlorinated this hydroxy ester (370 mg) gave a product (380 mg) which could be separated into a less polar (32%) and a more polar band (68%) on TLC.

The less polar component did not show hydroxyl group absorption in the infrared spectrum and had ECL 24.5 and 24.9. Its MS is given in section 6 (spectrum 24).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.67	singlet	-$(\underline{CH}_2)_n$-
7.78(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.40	singlet	-$COOCH_3$
6.2 6.0	broad	

On the basis of GLC evidence this material (50 mg) remained unchanged after treatment with DBU (6 hr, 100°C).

The TLC behaviour and infrared absorption at 3460 cm^{-1} indicated that the more polar product contained a hydroxyl group. Its MS is reported in section 6 (spectrum 16).

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.10	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.65	singlet	-$(\underline{CH}_2)_n$-
8.2	multiplet	-$\underline{CH}_2CHClCHClCH_2$-
7.78(2H)	triplet	-$\underline{CH}_2COOCH_3$
6.5	broad	-$\underline{CH}$(OH)-
6.40	singlet	-$COO\underline{CH}_3$
6.00	multiplet	-$\underline{CH}Cl\underline{CH}Cl$-

The dichloride, heated with DBU(6 hr, 100°C) gave a product identical in its TLC and GLC (ECL TMS ether, 22.8) behaviour with that obtained by reaction with sodium methoxide.

4. The Octadec-cis-enols

The Δ6 to Δ3 alcohols were prepared from the corresponding esters by reduction with lithium aluminium hydride and the products were purified by TLC. They had ECL of 20.2 (Δ6), 20.4 (Δ5), 20.2 (Δ4) and 20.2 (Δ3) on a DEGS column. The TMS ether of the Δ6 alcohol was also examined on ApL (18.0) and DEGS (14.8) columns.

Significant peaks in their NMR spectra are indicated below.

8.0 4.73 8.0 6.49
$-CH_2CH=CHCH_2CH_2CH_2CH_2CH_2OH$

8.0 4.70 8.0 6.46
$-CH_2CH=CHCH_2CH_2CH_2CH_2OH$

7.96 4.69 7.96 6.45
$-CH_2CH=CHCH_2CH_2CH_2OH$
7.98 4.63 7.76 6.48
$-CH_2CH=CHCH_2CH_2OH$

4.1 Bromination Studies

The unsaturated alcohols were brominated and the products purified by TLC. Dibromides were subsequently dehydrobrominated by reaction with sodium methoxide. The products were examined by NMR and MS and sometimes also by infrared spectroscopy.

(i) Octadec-cis-6-enol

The alcohol (131 mg) gave the threo-dibromide (180 mg) with TLC behaviour similar to that of the unsaturated alcohol. The (122 mg) ene-bromides still contained an OH group (infrared absorption at 3440 cm^{-1}) and had an ECL of 20.2 (ApL) as the alcohol and 18.4 (DEGS) as the TMS ether. The NMR spectra contained the following significant peaks.

threo-6,7-dibromo-octadecanol

5.82
8.0 8.0 6.43
$-CH_2CHBrCHBrCH_2CH_2CH_2CH_2CH_2OH$

ene-bromides

7.88 4.42 7.61 6.45
$*-CH_2CH=CBrCH_2CH_2CH_2CH_2CH_2OH$

The mass spectra are detailed in section 6.2 (spectra 27 and 32).

(ii) Octadec-cis-5-enol

Bromination of this alcohol (217 mg) gave a product (334 mg)

* two isomers

which separated into three bands by TLC. The major component (88%, the threo dibromide) was accompanied by two less polar minor components (each 6%). The least polar with an ECL of 16.1 on DEGS (probably a decomposition product) did not contain a hydroxyl group (infrared spectrum) and was probably a brominated cyclic ether. The product of intermediate polarity was not identified.

The dibromide (118 mg) was dehydrobrominated by reaction with sodium methoxide. The product (85 mg, ECL of TMS ether 18.0 (DEGS) with a minor peak (15%) at 14.8) was a mixture of ene-bromides. The MS are recorded in section 6 (spectra 29 and 34).

NMR spectra

threo-5,6-dibromo-octadecanol

$$\overset{a}{-CH_2}\overset{5.81}{CHBrCHBr}\overset{a}{CH_2}-$$

ene-bromides

$$\overset{7.88}{-CH_2}\overset{4.42}{CH=CBr}\overset{7.61}{CH_2}-$$

a - 8.00τ

(iii) Octadec-cis-3-enol

The majority of the bromination product (141 mg) from octadec-cis-3-enol (98 mg) had the same polarity on TLC as the original alcohol and was the threo-dibromo alcohol. After dehydrobromination the dibromide gave ene-bromides (68 mg, IR, 3620 cm^{-1}, ECL TMS ether 18.6 on DEGS, MS in section 6, spectrum 36).

NMR spectra

threo-3,4-dibromo-octadecanol

$-CH_2CHBrCHBrCH_2CH_2OH$

5.82 5.55 6.22

ene-bromides

$CH_2CH=CBrCH_2CH_2OH$

4.26 7.40 6.29

and

$-CH_2CBr=CHCH_2CH_2OH$

7.59 4.26 7.86 6.39

4.2 Iodochlorination Studies

The reaction of some octadecenols with Wijs reagent was examined. The products were separated on TLC and examined spectroscopically.

(iv) Octadec-cis-6-enol

The alcohol (124 mg) when treated with iodine monochloride gave a product (200 mg) which on TLC gave a less polar band A(11%) and a more polar band B (89%).

The less polar band is probably 6(7)-chloro-7(6)-iodo-octadecyl acetate. The infrared spectrum shows carbonyl absorption at 1740 cm^{-1}. The ECL value on a DEGS column is 19.5. The NMR spectrum showed a singlet at 8.00τ due to $-CH_2OCOCH_3$ protons.

The more polar fraction is the iodo chloro alcohol. The infrared spectrum shows OH group absorption at 3640 cm^{-1}. The iodochlorides (89 mg) were dehydroiodinated, and the product (67 mg)

showed OH group and trisubstituted alkene absorption at 3625 cm^{-1} and 1660 cm^{-1} respectively. On ApL its TMS ether had a major peak at ECL 19.7 and a small peak (16%) at ECL 18.0. On DEGS the TMS ether had a major peak at 17.17 and a minor one at 14.8. The MS are recorded in section 6 (spectra 27 and 33).

NMR spectra

threo-6(7)-chloro-7(6)-iodo-octadecanols

$$-\overset{6.24}{CH_2}\overset{}{CHCl}\overset{5.71}{CHI}\overset{}{CH_2}-$$

ene-chlorides

$$-\overset{4.62}{CH}=CCl-$$

(v) Octadec-cis-5-enol

When treated with ICl the Δ5 alcohol (102 mg) gives a product (160 mg) which separates into 3 bands, A, B and C on TLC.

Band A (16%)

This fraction has an ECL of 16.0 (with decomposition) on DEGS. The NMR spectrum does not show the triplet at 6.4τ associated with $-CH_2OH$ protons and is possibly a 2-tridecyl THP derivative. The MS is given in section 6 (spectra 38).

Band B (6%)

Band B could contain the acetoxy-iodochloride. In the NMR spectrum it had a singlet at 8.00τ.

Band C (78%)

This band contains the iodochloro octadecanol, and

has about the same polarity on TLC as starting material. When reacted (93 mg) with sodium methoxide the product (62 mg) on GLC had ECL 17.6 and 14.7 (15%) as TMS ethers. The MS are recorded in section 6 (spectra 30 and 35).

threo-5,6-iodochloro octadecanol

$$-CH_2\overset{6.22}{C}HCl\overset{5.70}{C}HICH_2-$$

ene-chlorides

$$-CH_2\overset{4.60}{C}H{=}CCl-$$

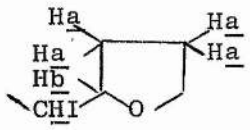
(vi) Octadec-cis-4-enol

The alcohol (100 mg) when treated with iodine monochloride gives a product (166 mg) which separates into three bands on TLC.

Band A (83%)

This least polar compound has an ECL of 16.9 (DEGS decomposition) and is probably a 2-tetradecyl THF derivative. The MS is recorded in section 6 (spectrum 39).

NMR spectra



Ha = 7.8 to 8.4τ

Hb, CHI 5.8 to 6.5τ

After treatment with sodium borohydride this component (51 mg) gave a product (37 mg) of ECL 15.9 (DEGS). Its MS is given in section 6 (spectrum 40).

Band B (6%)

Band B is possibly the acetoxy iodochloride. On GLC it had an ECL of 19.3 (DEGS) and the infrared spectrum showed carbonyl absorption at 1740 cm^{-1}.

Band C (11%)

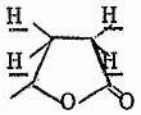
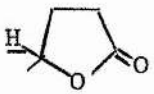
This fraction had the same polarity as starting material and is possibly the iodochloro octadecanol.

5.1 Stearolactone from Oleic Acid

The reaction procedure outlined by Swern[55] was followed. Oleic acid (1.5 g) was treated with 50% perchloric acid (52.1 g) at 100°C for 3 hours under a stream of nitrogen. The product was extracted and passed through a florisil column which retains most of the acidic and oxidised material. It was further purified on TLC using petroleum, ether and acetic acid (36:15:1). In this developing solvent oleic acid is less polar than the γ-lactone.

On GLC (DEGS) γ-stearolactone has an ECL of 26.4 and on ApL an ECL of 19.6. The IR spectrum shows diagnostic absorption at 1780 cm^{-1} due to the lactone carbonyl group. The MS is given in section 6 (spectrum 41).

NMR spectrum[56]

τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.74	singlet	-$(\underline{CH}_2)_n$-
7.66	multiplet	
5.64	multiplet	

Attempted synthesis of a δ-lactone from methyl octadec-cis-4-enoate

Methyl octadec-cis-4-enoate (113 mg) was stirred with mercuric acetate (135 mg) in glacial acetic acid (10 ml) for two days. The product was demercurated and recovered (118 mg). After purification on TLC the acetoxy ester (60 mg, ECL 19.8 on ApL) had signals at 8.0τ (-CHOCOC$\underline{H}_3$) and 5.20τ (-C$\underline{H}$OCOCH$_3$) in its NMR spectrum.

The acetoxy ester (57 mg) was hydrolysed and the product (46 mg) with IR absorption at 1710 cm^{-1}, 1740 cm^{-1} and 1780 cm^{-1} could be a mixture of acid and γ - and δ-lactones. After heating at 200°C for an hour the product gave ECL 26.4 and 27.1 on GLC, possibly due to γ - and δ-lactones. No attempt was made to separate these two lactones.

5.2 Iodochlorination of Octadec-cis-4-enoic Acid

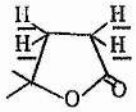
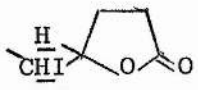
Wijs reagent was added to octadec-cis-4-enoic acid (116 mg) and the recovered product separated into two main bands (A and B) when chromatographed (TLC) with petroleum, ether and acetic acid

(45:5:5) as developing solvent.

Band B (61%)

This more polar band showed absorption at 1770 cm^{-1} in the IR spectrum.

NMR spectrum (This compound was not very soluble in carbon tetrachloride)

τ value and no. of protons	Appearance	Assignment
9.11	triplet(poorly resolved)	$\underline{CH}_3(CH_2)_n$-
8.74	singlet	-$(\underline{CH}_2)_n$-
8.22	multiplet	
7.5(3H)	multiplet	
5.8(2H)	multiplet	

We could not make an assignment to the signal at 8.22τ and the integration of the signal at 7.5τ amounted to only 3 protons. The MS is recorded in section 6 (spectrum 42).

Sodium Borohydride Reductions

A mixture of methyl oleate and γ -stearolactone was treated with sodium borohydride and the product examined on GLC. The trace obtained was similar to that obtained prior to the borohydride treatment showing that the lactones was not affected by sodium borohydride.

The iodolactone (7 mg) was heated with sodium borohydride in DMF (2 ml). The product (4 mg) showed absorption at 1785 cm^{-1}

in its infrared spectrum and gave two peaks on GLC [ApL 19.0 (20%), 19.6 (80%), DEGS 24.6 and 26.4 (major component)].

Band A (31%)

Band A is possibly the chloro-iodo acid. Its infrared spectrum showed absorption at 1710 cm^{-1}. An NMR spectrum could not be obtained due to its insolubility in the usual organic solvents.

Band A (42 mg) was heated with DBU and the product (30 mg), after esterification (CH_2SO_4, MeOH), was separated into four components on TLC (PE10): A (23%), B (15%), C (34%) and D (26%). The amount of material in each fraction was too small for identification purposes.

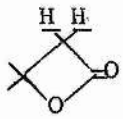
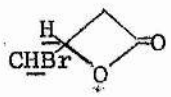
5.3 Bromination of Octadec-cis-3-enoic Acid

The acid (172 mg), dissolved in aqueous sodium bicarbonate, ether (a few ml) and bromine were shaken together for 15 min on a mechanical shaker. The product (205 mg) after washing with sodium thiosulphate and water were separated into two fractions A (36%) and B (64)% by elution from a column of florisil, firstly with benzene and then with a mixture of benzene and methanol.

Fraction A

This fraction is less polar than δ-stearolactone, but more polar than oleic acid, on the TLC system used, (petroleum, ether and acetic acid, 35:95:1). The IR spectrum had an absorption band at 1840 cm^{-1}.

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.12	triplet(poorly resolved)	$\underline{CH}_3(CH_2)_n$-
8.7	singlet	-$(\underline{CH}_2)_n$-
8.18	broad	
6.64	triplet	
5.94 to 5.86	multiplet	
5.48	quartet	impurity?

The fact that the signal at 6.64τ is a triplet is somewhat surprising.

Fraction B

The IR spectrum showed absorption at 1785 cm^{-1} and perhaps slight absorption at 1710 cm^{-1}, suggesting it could contain a δ -lactone ring. The substance was not soluble in carbon tetrachloride or chloroform and so an NMR spectrum could not be obtained.

6. Mass spectra

In the following data major peaks (m/e) are reported along with peak-intensity relative to the base peak (100) and, where possible, a tentative explanation of the origin of the peak.

Spectra were recorded at 16 and/or 70 ev.

There was some difficulty in counting the higher m/e values and this may account for some of the apparent discrepancies between similar spectra.

The following are fragments more commonly eliminated and those which occur in several spectra:

-18 loss of H_2O

-32 loss of CH_3OH

-50 loss of H_2O and CH_3OH

-57 loss of $CH_3(CH_2)_3$ from derivatives of methyl 9-hydroxyoctadec-12-enoate

-59 loss of CH_3COO from acetates

-60 loss of CH_3COOH from acetates

-85 loss of $CH_3(CH_2)_5$ from derivatives of methyl ricinoleate

-86 loss of $CH_3(CH_2)_5$ and H from derivatives of methyl ricinoleate

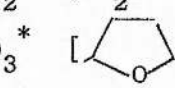
-117 loss of 85 and 32 mass units

-157 loss of $(CH_2)_7CO_2Me$

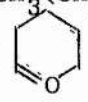
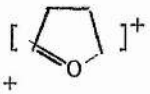
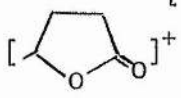
-X, -XH, $-X_2$, $-X_2H$, $-X_2H_2$ loss of one or two halogen atoms (or OAc and Br) with two or less hydrogen atoms

P(225) $C_{13}H_{21}O_3^*$ $[O{\equiv}CCH_2CH{=}CH(CH_2)_7CO_2Me]^+$

Q(197) $C_{12}H_{21}O_2^*$ $[CH_2CH{=}CH(CH_2)_7CO_2Me]^+$

R(227) $C_{13}H_{23}O_3^*$  or $[C_3H_4CH(OH)(CH_2)_7CO_2Me]^+$

S(187) $C_{10}H_{19}O_3^*$ $[CH(OH)(CH_2)_7CO_2Me]^+$

T(155)	$C_{10}H_{19}O^*$	$[CH_3(CH_2)_4CH{=}CHCH_2CH_2CH(OH)]^+$
U(85)	$C_5H_9O^*$	
V(71)	$C_4H_7O^*$	
W 85	$C_4H_5O_2$	

* These charged fragments probably have the structure shown or that of a closely related isomer.

1. Methyl threo-9,10-dibromostearate (70 ev)

Peaks at: 377 (M-X, 3), 375 (M-X, 3), 295 ($M-X_2H$, 11), 263 (295-32, 14), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(2), 115(2), 129(3), 143(3), 157(1), 171(2), 185(1), and 199 (2),

also at: 117(67), 119(100), and 121(67).

2. Methyl threo-9,10-dichlorostearate (16 ev)

Peaks at: 295 ($M-X_2H$ · 1), 294 ($M-X_2H_2$, 7), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(26), 115(15), 129(36), 143(76), 157(16), 171(27), 185(20), 199(28), 213(10), 227(16), 241(5)

also at: 110(36), 117(100), 119(96), 121(34), and 270(25).

3. Methyl threo-9(10)-chloro-10(9)-iodostearate (70 ev)

Peaks at: 333 (M-X, 8), 331 (M-X, 20), 296 ($M-X_2$, 34), 295 ($M-X_2H$, 68), 264 (296-32, 62), 263 (295-32, 100), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(30), 115(30), 129(32), 143(52), 157(18), 171(12), 185(16), 199(26), 213(10), 241(20)

also at: 109(88), 110(40), 111(84), 115(30), 123(64), 125(50), 127(32), 128(66), 137(50), 151(40), 165(40), 179(34), and 245(50).

4. Methyl 9(10)-bromo-octadec-(Z)-9-enoate (16 ev)

Peaks at: 344 (M-32, 5), 342 (M-32, 5), 295 (M-X, 100), 294 (M-XH, 77), 263 (295-32, 100), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(20), 115(20), 129(40), 143(73), 157(14), 171(18), 185(19), 199(20), 213(15), 227(36)

also at: 109(47), 110(52), 111(67), 123(43), 124(40), 125(38), 137(31), 151(34), 152(41), 164(37), 165(36), 179(33), 245(39), and 269(82).

5. Methyl 9(10)-chloro-octadec-(Z)-9-enoate (70 ev)

Peaks at: 332 (M, 1), 330 (M, 4), 299 (M-31, 10), 294 (M-XH, 100), 263 (294-31, 34), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(18), 115(20), 129(20), 143(10)

also at: 109(70), 110(70), 111(40), 121(32), 123(40), 124(44), 245(50), and 253(34).

6. Methyl threo-9,10-dibromo-12-hydroxystearate (16 ev)

Peaks at: 388 (M-86, 24), 386 (M-86, 41), 384 (M-86, 23), 356 (388-32, 25), 354 (386-32, 44), 352 (384-32, 27),

311 ($M-X_2H$, 44), 310 ($M-X_2H_2$, 21), 293 (311-18, 58), 279 (311-32, 77), 225 (P, 64), 198 (Q+1, 53), 197 (Q, 100), 193 (225-32, 29), 166 (198-32, 88), 165 (197-32, 97), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(15), 115(24), 129(25), 143(15), 157(11), 171(5), 185(13), 199(24), 213(12), 227(6) also at: 109(32), 110(38), 111(41), 123(65), 124(59), 125(32), 147(32), 149(32), 155(38), 181(65), 277(39), and 329(29).

7. Methyl erythro-9,10-dibromo-12-hydroxystearate (70 ev)

Peaks at: 389 (M-85, 13), 387 (M-85, 27), 385 (M-85, 13), 357 (389-32, 13), 355 (387-32, 27), 353 (385-32, 13), 311 ($M-X_2H$, 7), 293 (311-18, 33), 279 (311-32, 50), 225 (P, 30), 198 (Q+1, 20), 197 (Q, 15), 166 (198-32, 27), 165 (197-32, 100), members of the series $[(CH_2)_nCO_2Me]^+$ at 101(9), 115(13), 129 (10), 143(4), 157(12), 171(5), 185(4), 199(4), 213(1), 227(1) also at: 107(33), 109(47), 111(30), 123(67), 147(40), 149(50), 193(30).

8. Methyl threo-9(10)-acetoxy-10(9)-bromo-12-hydroxystearate (16 ev)

Peaks at: 393 (M-59, 1), 391 (M-59, 1), 361 (393-32, 1), 359 (391-32, 1), 311 ($M-X_2H$, 18), 307 (393-86, 7), 305 (391-86, 7), 293 (311-18, 14), 279 (311-32, 32), 226 (P+1, 34), 225 (P, 100), 198 (Q+1, 9), 197 (Q, 35), 166 (198-32, 9), 165 (197-32, 32), members of the series $[(CH_2)_nCO_2Me]^+$ as minor peaks from 101-227

also at: 123(34), 155(35), 187(35), and 201(34).

9. Methyl threo-9,10-dichloro-12-hydroxystearate (70 ev)

Peaks at: 311 ($M-X_2H$, 13), 310 ($M-X_2H_2$, 17), 279 (311-32, 13), 225 (P, 100), 193 (225-32, 47), 166 (Q+1-32, 33), 165 (Q-32, 37)

also at: 105(100), 109(43), 111(40), 117(75), 119(73), 135(45), 149(40), 155(93), 183(93), and 201(50).

10. Methyl threo-9(10)-chloro-12-hydroxy-10(9)-iodostearate (70 ev)

Peaks at: 346 (M-XH, 9), 315 (346-31, 8), 312 ($M-X_2$, 20), 293 (311-18, 70), 279 (311-32, 73), 225 (P, 73), 198 (Q+1, 47), 197 (Q, 94), 193 (225-32, 19), 166 (198-32, 97), 165 (197-32, 97), members of the series $[(CH_2)_nCO_2Me]^+$ as minor peaks from 101-129

also at: 107(53), 109(64), 110(47), 111(48), 113(67), 115(51), 121(59), 123(87), 124(100), 125(40), 127(54), 128(48), 135(46), 137(65), 147(56), 155(59), and 253(93).

11. Methyl 10-bromo-12-hydroxyoctadec-(E)-9-enoate (70 ev)

Peaks at: 310 (M-XH, 2), 293 (311-18, 8), 279 (311-32, 13), 275 (M-117, 2), 273 (M-117, 2), 261 (311-50, 3), 225 (P, 6), 197 (Q, 70), 196 (Q-1, 57), 165 (197-32, 100), 164 (196-32, 47)

also at: 107(27), 109(30), 111(30), 121(27), 123(63), and 147(50).

12. Methyl 10-bromo-12-hydroxyoctadec-(Z)-9-enoate (70 ev)

Peaks at: 392 (M, 11), 390 (M, 11), 293 (311-18, 63), 279 (311-32, 15), 197 (Q, 96), 196 (Q-1, 100), 165 (197-32, 81), 164 (196-32, 44)

also at: 109(25), 121(30), 123(68), 138(20), 147(50), and 198(26).

13. Methyl 9-bromo-12-hydroxyoctadec-(E)-9-enoate (70 ev)

Peaks at: 311 (M-X, 2), 310 (M-XH, 5), 293 (311-18, 3), 279 (311-32, 17), 197 (Q, 61), 196 (Q-1, 70), 165 (Q-32, 100), 164 (196-32, 46)

also at: 110(46), 111(39), 122(36), 123(64), 129(33), 149(30), and 181(39).

14. Methyl 9(10)-chloro-12-hydroxyoctadec-(Z)-9-enoate (70 ev)

Peaks at: 279 (311-32, 8), 225 (P, 18), 197 (Q, 7), 196 (Q-1, 36), 165 (197-32, 56), 164 (196-32, 100)

also at: 105(28), 109(24), 110(29), 111(24), 122(44), 123(22), 135(20), 155(35), and 225(18).

15. Methyl threo-12,13-dibromo-9-hydroxystearate (70 ev)

Peaks at: 311 ($M-X_2H$, 2), 279 (311-32, 10), 227 (R, 4), 195 (227-32, 5), 188 (S+1, 5), 187 (S, 44), 156 (188-32, 14), 155 (Tor 187-32, 100)

also at: 109(38), 115(24), 129(53), 149(33), 158(47), and 283(11).

16. Methyl threo-12,13-dichloro-9-hydroxystearate (70 ev)

Peaks at: 311 ($M-X_2H$, 1), 279 (311-32, 1), 227 (R, 12), 195 (227-32, 5), 188 (S+1,23), 187 (S, 197), 156 (188-32, 36), 155 (T or 187-32, 100)

also at: 109(76), 115(62), 129(26), 135(21), 159(30), and 158(91).

17. Methyl threo-12(13)-chloro-9-hydroxy-13(12)-iodostearate (70 ev)

Peaks at: 311 ($M-X_2H$, 2), 310 ($M-X_2H_2$, 9), 294 (293+1, 10), 293 (311-18, 31), 279 (311-32, 33), 227 (R, 22), 209 (227-18, 10), 195 (227-32, 30), 187 (S, 19), 177 (227-50, 16), 155 (T or 187-32, 73)

also at: 107(22), 110(28), 111(32), 113(27), 115(20), 123(30), 127(22), 128(37), 129(22), 135(27), 137(23), and 149(100).

18. Methyl 12-bromo-9-hydroxyoctadec-(E)-12-enoate (70 ev)

Peaks at: 312 (311+1, 3), 311 (M-X, 8), 310 (311-1, 2), 294 (312-18, 4), 293 (311-18, 18), 279 (311-32, 15), 227 (R, 23), 209 (227-18, 7), 195 (227-32, 24), 188 (S+1,20), 187 (S, 35), 185 (S-2, 38), 177 (227-50, 100), 156 (188-32, 6), 155 (T or 187-32, 55)

also at: 109(30), 137(23), 149(78), 178(20), 179(20), 181(55), 182(20), and 190(23).

19. Methyl 13-bromo-9-hydroxyoctadec-(E)-12-enoate (70 ev)

Peaks at: 312 (311+1, 5), 311 (M-X, 26), 310 (311-1, 21), 294 (312-18, 4), 293 (311-18, 19), 280 (311-32, 8), 279 (311-32, 32), 254 (311-57, 31), 209 (227-18, 3), 195 (227-32, 11), 188 (S+1,13), 187 (S, 6), 185 (S-2, 5), 177 (227-50, 6), 156 (188-32, 6), 155 (T or 187-32, 45)

also at: 109(100), 113(71), 123(30), 149(94), 163(61), and 201(30).

20. Methyl 12(13)-bromo-9-hydroxyoctadec-(Z)-~~9~~ 12-enoate (70 ev)

Peaks at: 312 (311+1, 11), 311 (M-X, 57), 310 (311-1, 35), 294 (312-18, 24), 293 (311-18, 92), 280 (312-32, 22), 279 (311-32, 91), 254 (311-57), 253 (310-57, 49), 227 (R, 27), 209 (227-18, 10), 195 (227-32, 19), 188 (S+1,8), 187 (S, 24), 185 (S-2, 18), 177 (227-50, 14), 156 (188-32, 8), 155 (T or 187-32, 71)

also at: 109(100), 111(87), 113(95), 121(30), 123(64), 125(48), 127(32), 135(40), 137(35), 143(51), 149(32), 151(33), and 153(32).

21. Methyl 12(13)-chloro-9-hydroxyoctadec-(Z)-~~9~~ 12-enoate (70 ev)

Peaks at: 312 (311+1, 9), 311 (M-X, 43), 310 (311-1, 34), 294 (312-18, 16), 293 (311-18, 68), 280 (312-32, 19), 279 (311-32, 79), 254 (311-57, 7), 253 (310-57, 33), 227 (R, 39), 209 (227-18, 11), 195 (227-32, 36), 188 (S+1, 21), 187 (S, 16), 185 (S-2, 10), 177 (227-50, 16), 156 (188-32, 8), 155 (187 or T-32, 71)

also at: 107(39), 109(100), 110(39), 111(75), 123(61), 125(39), 135(46), 137(32), 151(33), 153(32), and 163(32).

22. Methyl 13-bromo-9,12-epoxystearate (70 ev)

Peaks at: 393 (M+1, 2), 392 (M, 1), 391 (M±1, 4), 390 (M, 3), 389 (M-1, 3), 388 (M-2, 3), 362 (393-31, 1), 361 (393-32, 5), 360 (392-32, 2), 359 (391-32, 7), 357 (389-32, 2), 311 (M-X, 6), 310 (M-XH, 2), 293 (311-18, 3), 279 (311-32, 8), 228 (227+1, 17), 227 (R, 92), 209 (227-18, 23), 196 (228-32, 100), 195 (227-32, 75), 177 (227-50, 17)

also at: 109(30), 111(18), 113(15), 135(17), and 149(13).

23. Methyl 13-iodo-9,12-epoxystearate (70 ev)

Peaks at: 312 (311+1, 5), 311 (M-X, 24), 310 (M-XH, 5), 294 (312-18, 4), 293 (311-18, 10), 280 (312-32, 6), 279 (311-32, 31), 228 (227+1, 6), 227 (R, 43), 209 (227-18, 10), 196 (228-32, 5), 195 (227-32, 34), 177 (227-50, 13)

also at: 109(15), 113(23), 128(17), 129(100), 135(12), 144(11), and 149(48).

24. Methyl 13-chloro-9,12-epoxystearate (70 ev)

Peaks at: 311 (M-X, 3), 310 (M-XH, 6), 293 (311-18, 6), 292 (310-18, 11), 279 (311-32, 7), 228 (227+1, 17), 227 (R, 100), 209 (227-18, 25), 196 (228-32, 17), 195 (227-32, 97), 177 (227-50, 31)

also at: 101(41), 105(30), 107(38), 109(86), 110(31), 111(52), 115(35), 121(31), 123(38), 125(34), 133(31), 135(55), 143(45), 149(52), 155(45), 185(26), 187(48), 189(26), and 201(35).

25. Methyl 9,12-epoxystearate (70 ev)[53]

Peaks at: 313 (M+1, 4), 312 (M, 9), 311 (M-1, 2), 295 (313-18, 3), 294 (312-18, 2), 279 (311-32, 7), 228 (227+1, 17), 227 (R, 89), 209 (R-18, 19), 196 (228-32, 11), 195 (227-32, 67), 177 (227-50, 17), 156 (155+1, 19), 155 (M-157, 100), 137 (155-18, 47)

also at: 109(19), 111(15), 113(17), 135(16), 149(58), 159(16), and 200(21).

26. threo-6,7-Dibromo-octadecanol (70 ev)

Peaks at: 268 ($M-X_2$, 11), 267 ($M-X_2H$, 53), 250 (268-18, 9), 249 (267-18, 32), members of the series C_nH_{2n-1} (55-167) and C_nH_{2n-3} (67-221), base peaks at 55, 67, 69, 81, 83, and 95

also at: 54(41), 68(44), 82(51), 85(30), and 96(36)

27. threo-6(7)-Chloro-7(6)-iodo-octadecanol (16 ev)

Peaks at: 305 (M-I, 2), 303 (M-I, 7), 268 ($M-X_2$, 19), 267 ($M-X_2H$, 88), 250 (268-18, 11), 249 (267-18, 29), and members of the series C_nH_{2n+X} where x = +1 (57-183), -1 (55-181), -3 (67-221), base peaks at 83 and 95

also at: 68(23), 82(51), 96(41), and 110(21).

28. threo-6(7)-Chloro-7(6)-iodo-octadecyl acetate (70 ev)

Peaks at: 267 ($M-X_2H$, 43), 266 (267-1, 8), 250 ($M-X_2H$-60, 23), 249 (250-1, 14), and members of the series C_nH_{2n+X} where x = +1 (57-127), 0 (56-168), -1 (55-181), -2 (68-222), -3 (67-207), base peak at 82.

29. threo-5,6-Dibromo-octadecanol (16 ev)

Peaks at: 349 (M-X, 11), 347 (M-X, 12), 331 (349-18, 1), 329 (347-18, 1), 268 ($M-X_2$, 25), 267 ($M-X_2H$, 100), 250 (268-18, 11), 249 (267-18, 40), and members of the series C_nH_{2n+X} where x = +1 (57-141), -1 (55-167), and -3 (67-221)

also at: 82(26), and 96 (23).

[a spectrum run at higher sensitivitiy shows a series of peaks at 408-412 (M-18)]

30. threo-5(6)-Chloro-6(5)-iodo-octadecanol (70 ev)

Peaks at: 268 ($M-X_2$, 11), 267 ($M-X_2H$, 59), 250 (268-18, 6), 249 (267-18, 14), and members of the series C_nH_{2n+X} where x = +1 (57-99), -1 (55-125), and -3 (67-151), base peak at 95

also at: 68(24), 82(40), 96(32), 98(26), 117(69), 119(67), and 121(22).

[a spectrum run at higher sensitivity show a series of peaks at 408-412 (M-18), 344-350 (M-X and M-XH), and 326-332 (further loss of water)]

31. threo-5(6)-Chloro-6(5)-iodo-octadecyl acetate (16 ev)

Peaks at: 268 ($M-X_2$, 20), 267 ($M-X_2H$, 92), 266 (267-1, 13), 250 ($M-X_2H-60$, 31), 249 (250-1, 41), and members of the series C_nH_{2n+X} where x = +1 (57-225), 0 (56-224), -1 (55-237), -2 (54-222), -3 (67-207), base peak at 98

32. 6(7)-Bromo-octadec-(Z)-6-enol (70 ev)

Peaks at: 330 (M-18, 2), 328 (M-18, 2), 268 (267+1, 7), 267 (M-X, 32), 250 (268-18, 5), 249 (267-18, 16), and members of the series C_nH_{2n+X} where x = +1 (57-155), -1 (55-223), and -3 (53-221), base peak at 95

also at: 54(31), 56(28), 65(21), 66(22), 68(34), 70(21), 80(20), 82(34), 96(33), and 149(29).

33. 6(7)-Chloro-octadec-(Z)-6-enol (16 ev)

Peaks at: 286 (M-18, 4), 284 (M-18, 11), 267 (M-X, 8), 266 (M-XH, 14), 250 (268-18, 19), 249 (267-18, 33), 248 (266-18, 15), and members of the series C_nH_{2n+X} wher x = +1 (57-141), -1 (55-181), -3 (67-221)

also at: 68(86), 70(28), 82(100), 96(76), 98(29), 110(28), and 149(47).

34. 5(6)-Bromo-octadec-(Z)-5-enol (16 ev)

Peaks at: 367 (M-X, 21), 266 (M-XH, 95), 249 (267-18, 12), 248 (266-18, 17), and members of the series C_nH_{2n+X} where x = +1 (57-141), 0 (56-140), -1 (55-153), -2 (54-166), -3 (53-221), -4 (66-220), base peaks at 82, 94, 96.

35. 5(6)-Chloro-octadec-(Z)-5-enol (16 ev)

Peaks at: 304 (M, 26), 302 (m, 27), 286 (M-18, 5), 284 (M-18, 12), 268 (M-XH, 17), 267 (M-X, 72), 266 (M-XH, 27), 250 (268-18, 52), 249 (267-18, 41), 248 (266-18, 17)

also at: 180(27), 194(48), 201(27), 205(22), 222(40), 223(29), 287(99), 289(100), and 291(33).

[Peaks below 170 not recorded]

36. 3(4)-Bromo-octadec-(Z)-3-enol (70 ev)

Peaks at: 267 (M-X, 1), 266 (M-XH), 249 (267-18, 6), and members of the series C_nH_{2n+X} where x = +1 (57-99), -1 (55-139), -3 (53-137), base peak at 55

also at: 54(20), 56(45), 68(30), 70(37), 82(33), 84(29), 96(20), and 149(73).

37. 2-(1'-Bromotridecyl)-tetrahydropyran (70 ev)

Peaks at: 267 (M-X, 3), 266 (M-XH, 3), 111 (98+13, 11), 98 (85+13, 28), 85 (U, 100).

38. 2-(1'-Iodotridecyl)-tetrahydropyran (16 ev)

Peaks at: 268 (267+1, 20), 267 (M-X, 94), 266 (M-XH, 12), 111 (98+13, 44), 98 (85+13, 100), 85 (U, 76).

39. 2-(1'-Iodotetradecyl)-tetrahydrofuran (70 ev)

Peaks at: 268 (267+1, 9), 267 (M-X, 44), 97 (84+13, 53), 84 (71+13, 28), 71 (V, 100).

40. 2-(Tetradecyl)-tetrahydrofuran (70 ev)[53]

Peaks at: 267 (M-1, 1), 250 (M-18, 2), 71 (V, 100)

also at: 95(39), 96(22), and 97(59).

41. δ-Stearolactone (70 ev)

Peaks at: 283 (M+1, 5), 282 (M, 6), 265 (283-18, 7), 264 (282-18, 31), 85 (W, 100), and members of the series C_nH_{2n+x} where x = +1 (57-253), 0 (56-224), -1 (55-237), -2 (54-250), -3 (53-249).

42. 5-Iodo-δ-stearolactone (70 ev)

Peaks at: 282 (281+1, 6), 281 (M-X, 30), 264 (282-18, 4), 263 (281-18, 16), 85 (W, 74), and members of the series C_nH_{2n+x} where x = +1 (57-141), -1 (55-181) and -3 (53-193), base peak at 55

also at: 101(56).

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APPENDIX

Preparation of methyl-12-amino-oleate

Several methods are available for making aliphatic amines, most of them proceeding from the corresponding alkyl halide[1]. Methyl ricinoleate also contains a double bond and an ester function which must remain unchanged during the preparative sequence.

Methyl ricinoleate is readily converted to methyl 12-bromo-oleate by adaptation of the procedure described in reference 4, but we have found methyl 12-mesyloxyoleate to be a more useful intermediate.

Preparation of methyl 12-bromo-oleate[1]

Phosphorus tribromide (1.5 g) containing a trace of hydrobromic acid (48%, 1 drop per 50 g of phosphorus tribromide) was added dropwise to methyl ricinoleate (3.6 g) contained in a three necked flask. This occurred during 90-105 min and the mixture was stirred throughout and kept at 10-13^{o}C. After stirring for a further 40 min at this temperature the mixture stood overnight. The product (3.54 g) was extracted and purified by column chromatography. The purified product (2.59, ECL 24.5) showed the absence of -OH group absorption in the IR spectrum.

NMR spectrum (60 MHz)

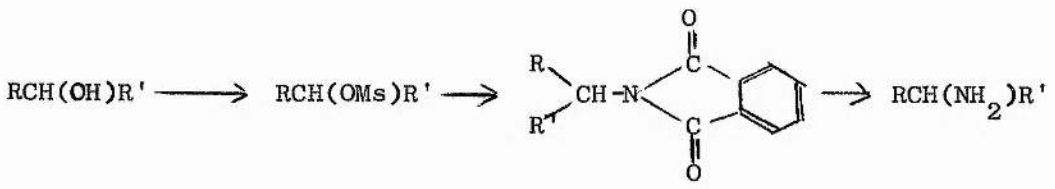
τ value and no. of protons	Appearance	Assignment
9.11	triplet (unresolved)	$\underline{CH}_3(CH_2)_n$-
8.70	singlet	-$(\underline{CH}_2)_n$-
7.8	triplet	-$\underline{CH}_2COOCH_3$ and $\underline{CH}_2CH{=}CHCH_2CHBr$-
7.40	doublet	-CH=CHC$\underline{H}_2$CH(Br)-
6.41	singlet	-COOC$\underline{H}_3$
6.22	broad	-C$\underline{H}$Br-
4.60	multiplet	-C$\underline{H}$=C$\underline{H}$-

Preparation of methyl 12-amino-oleate

Mixed castor esters (5 g) were treated with methanesulphonyl chloride[2] (1 ml in 10 ml pyridine) and the product (4.5 g) was allowed to react with potassium phthalimide (4.6 g)[3,4] in dry DMF (20 ml) at 100°C for 5 hr. The product (4.9 g) separated into four components on TLC. The least polar (22%) was possibly a mixture of non-hydroxy esters from castor oil along with methyl octadecadienoates resulting from an elimination reaction. The more polar component (52%) is though to be the phthalimido derivative mainly because of its NMR spectrum.

NMR spectrum

τ value and no. of protons	Appearance	Assignment
9.15	triplet(unresolved)	$CH_3(CH_2)_n$-
8.68	singlet	-$(CH_2)_n$-
8.05	doublet	-CH=CHCH_2(CH)<
7.80	triplet	-CH_2COOCH_3
5.85	multiplet	-CHN <
4.80	multiplet	-CH=CH-
2.30	singlet	-$CHN(CO)_2C_6H_4$-



The final stage in the reaction sequence was effected by hydrazine. It has been shown that under controlled conditions hydrazinolysis[5] can be effected without reaction at either double bond or ester function. The phthalimido derivative (386 mg) was refluxed under nitrogen for one hour with hydrazine (33%, 0.1 ml) and the product (253 mg) was extracted. After separation by TLC, amino ester (55%) was isolated from the base line of chromatogram.

The IR spectrum showed absorption at 3350 cm^{-1} [6] (N-H stretching). On GLC the trifluoroacetyl derivative, prepared by refluxing the ester (10 mg) with trifluoroacetic anhydride (0.5 ml) for 30 min, has an ECL 27.0[7,8].

NMR spectrum (methyl 12-amino-oleate)

τ value and no. of protons	Appearance	Assignment
9.10	triplet(unresolved)	$\underline{CH}_3(CH_2)_n$-
8.89	singlet	-$(\underline{CH}_2)_n$-
7.80	multiplet	-$\underline{CH}_2COOCH_3$ and -$\underline{CH}\underline{NH}_2$-
6.40	singlet	-$COO\underline{CH}_3$
4.60	multiplet	-$\underline{CH}$=$\underline{CH}$-

Preparation of methyl 12-aminostearate from methyl 12-ketostearate

The preparation was carried out as suggested by J. Cologne and P. Guyol[9]. The ketostearate (1.15 g, ECL 24.9) was refluxed in ethanol containing potassium hydroxide (1.3 g) for 2 hours, after which was added hydroxylamine hydrochloride (800 mg) in water (2 ml). The solution was refluxed for three hr. n-Butanol (5 ml) was cooled and the solution was evaporated to dryness twice. n-Butanol (5 ml) and sodium (600 mg) were added and refluxed for 20 min. The aminostearic acid (508 mg) was esterified and extracted. The trifluoroacetyl derivative had an ECL 26.8 on GLC.

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