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Some reactions
of
Methyl 12-mesyloxyoleate
A thesis
Presented for the degree of
Master of Science
in the Faculty of Science of the
University of St. Andrews
by
Ahmed Ahbeil Said



DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes the results of research carried out in the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. F.D. Gunstone since my admission as a research student.

I hereby certify that Ahmed Ahbeil Said has spent more than seven terms at research work under my supervision, has fulfilled the conditions of ordenance No.51 (St. Andrews), and is qualified to submit this thesis in application for the degree of Master of Science.

Research Supervisor

ACKNOWLEDGEMENTS

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I must express my gratitude to all my colleagues, and especially R.P. Inglis and G.G. Abbot, for their co-operation and help in many things.

Thanks are due to Mr. A. Watson and Mr. C. Millar for running my NMR and Mass Spectra respectively, and to Miss Kirk for typing the thesis.

Finally I must thank the Libyan Government for providing the research grant.

SUMMARY

Methylricinoleate contains a homoallylic hydroxy group and is therefore a potential source of homoallylic carbonium ions which can undergo an interesting rearrangement and furnish cyclopropane compounds. This thesis reports a study of the reaction of methyl 12-mesyloxyoleate, the mesyloxy group being a better leaving than a hydroxy group.

Reactions carried out in methanol, acetic acid, and aqueous acetonitrile, in the presence of a suitable buffer to control the pH, gave interesting methoxy, acetoxy, and hydroxy cyclopropane esters. In the absence of buffer the solution becomes acidic and the major product is the trans isomer of methyl 12-methoxy (acetoxy, hydroxy) octadecenoates. The substituted cyclopropane esters are very reactive and undergo rearrangement reactions.

In other solvents (dimethylsulphoxide, acetonitrile, triglyme) sodium methoxide promotes an elimination reaction giving mixtures of conjugated and non-conjugated methyl octadecadienoates.

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Discussion of results

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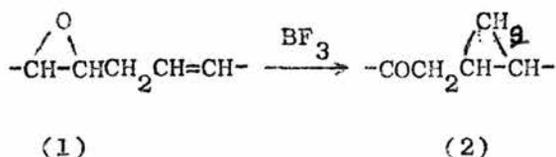
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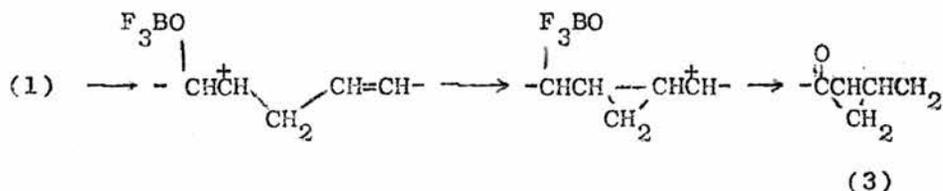
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INTRODUCTION

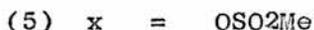
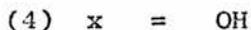
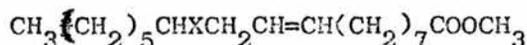
Conacher and Gunstone¹ recently showed that methyl vernolate (12,13-epoxyoleate, (1)) was convertedⁱⁿ to an oxo cyclopropane ester (2) by reaction with boron trifluoride:



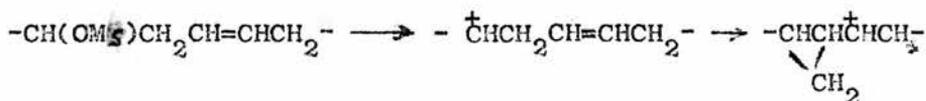
At one stage they wrongly considered that their oxo-cyclopropane had structure (3)^{and} that this was formed by a homo-allylic rearrangement:



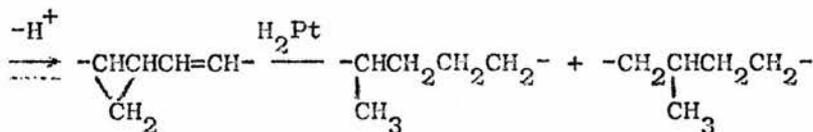
On this basis it was considered that methyl ricinoleate (4), after modification of the hydroxyl group to a better leaving group, might show similar reactivity. Preliminary experiments showed promising results with the mesyloxy ester (5).



This suggested a number of interesting new reactions of methylricinoleate and it was hoped, for example, that it might be possible to convert this common unsaturated hydroxy ester to a saturated branched-chain ester (6) which would be expected to have interesting properties.



methyl 12-mesyloxyoleate (5)

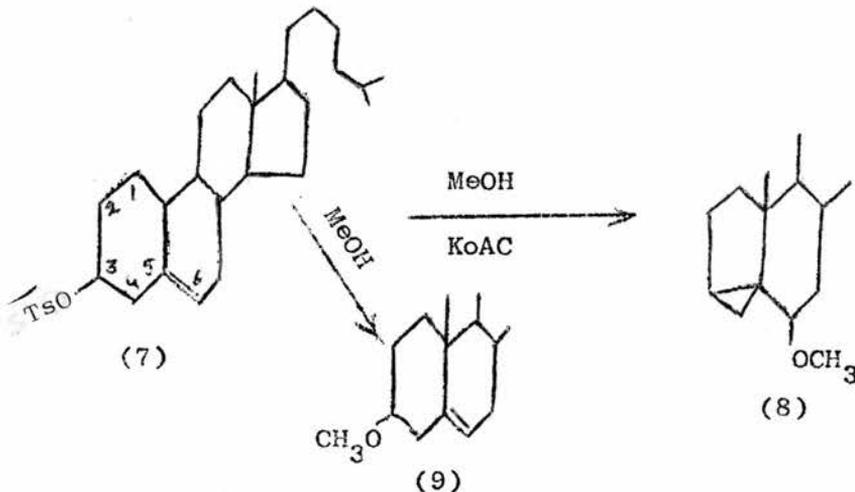


(methyl 10- and 11-methylheptadecanoates)

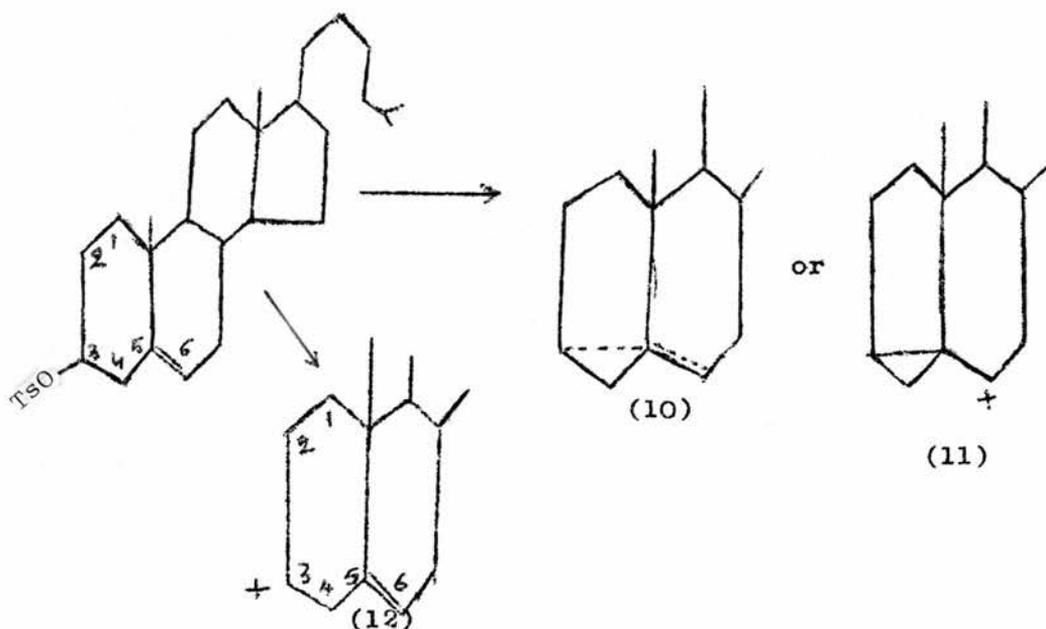
(6)

The unusual properties of homo-allylic compounds have been known for some time, though most studies have been concerned with cyclic rather than acyclic compounds. Some of these are briefly reviewed along with related work by a French group² which appeared whilst our study was in progress,

Winstein and Adams^{3,4} showed, in 1948, that the reaction of cholesteryl p-toluenesulphonate (7) with potassium acetate in methanol gave rise to the i-ether (8), though the normal ether (9) is obtained in the absence of potassium acetate.



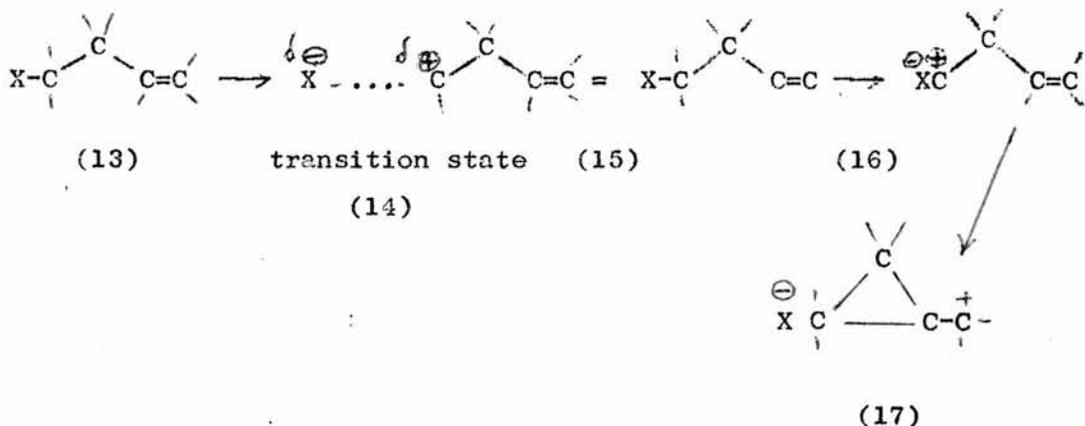
They considered that the i-sterol rearrangement ($7 \rightarrow 8$) represented an example of participation in a nucleophilic displacement reaction by an appropriately situated ethylenic linkage. The most likely general mechanism for this rearrangement would seem to involve the non-classical carbonium ion (10) or the rearranged carbonium ion (11).



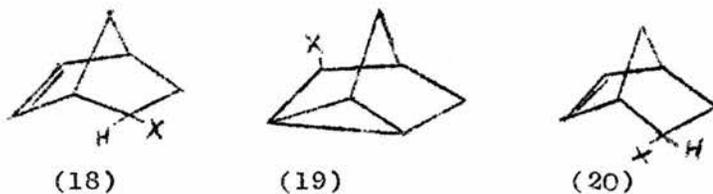
The intermediate (10 or 11) then reacts with nucleophilic reagents more rapidly at C_6 than C_3 .

Irrespective of the actual product of the rate determining step in solvolysis reactions of homoallylic compounds of the type $X-\overset{O}{\underset{|}{C}}-\overset{|}{C}-\overset{|}{C}=\overset{|}{C}$, Roberts, Bennett and Armstrong⁵ considered the transition state for the ionization of the C-X bond to be stabilized to some extent by the contribution of resonance forms such as (17) involving the neighboring

double bond.

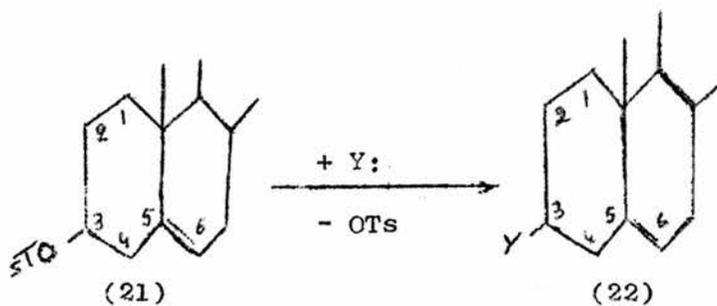


Winstein, Walborsky and Schreiber⁶ found that the solvolysis of (18) and (20) gave mainly the homo-allylic rearrangement product (19).

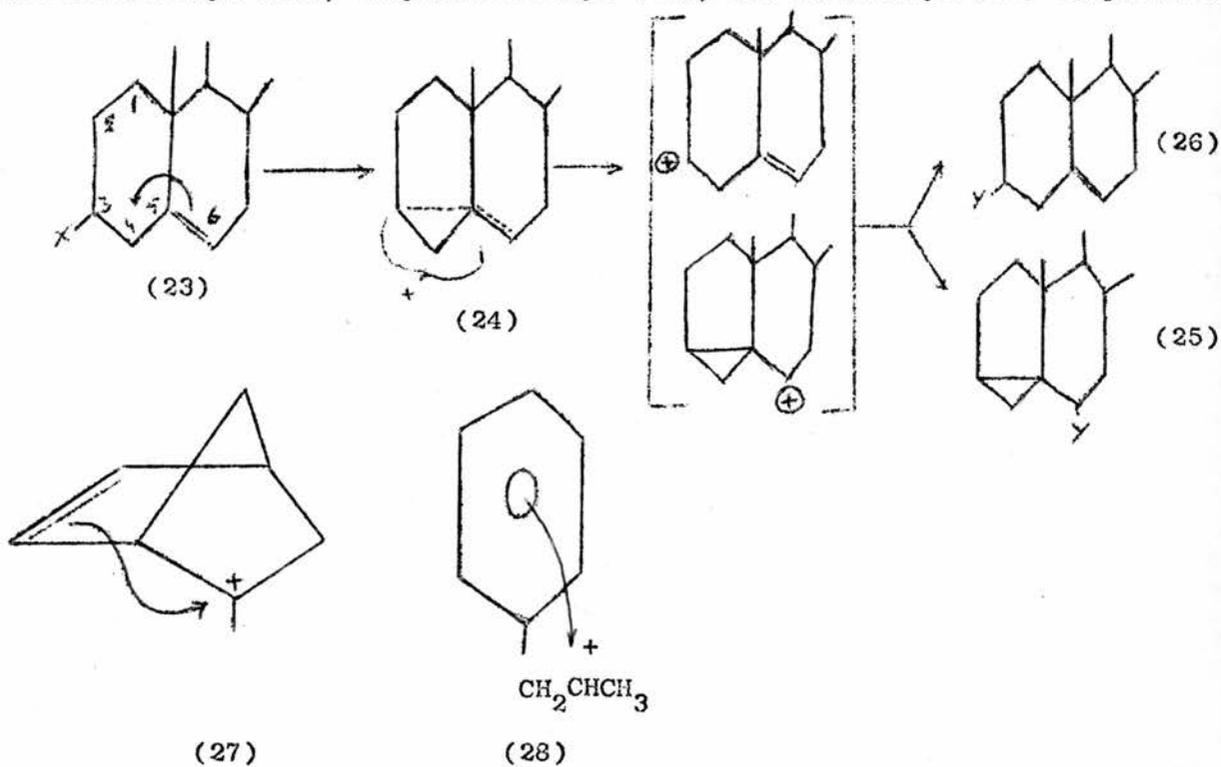


These workers concluded that the double bonds in (18) and (20) exert no very substantial driving force of the type postulated for cholesteryl compounds, presumably, because the geometry is less favourable for participation of the olefinic linkage in the conjugation process.

Winstein, Brown, Scheeber, and Schlesinger⁷ further showed that in homo-allylic rearrangement, nucleophilic substitution at C₃ of a substance such as cholesteryl p-toluene sulphonate (21) proceeds with over all retention of conjugation due to participation of the electron cloud of the neighboring olefinic system in the replacement process.

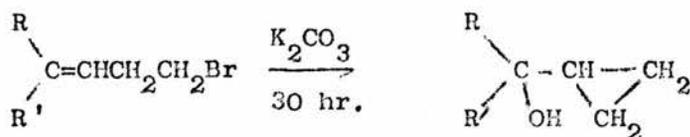


The same group^{8,9} later demonstrated on evidence from stereochemistry and reaction kinetics the existence of an important interaction between the carbonium ion centre and a π -electron containing β substituent such as a vinyl or phenyl group, as for example in the ions derived from the cholesteryl (23), dehydronorbornyl (27), and homobenzyl (28) compounds.

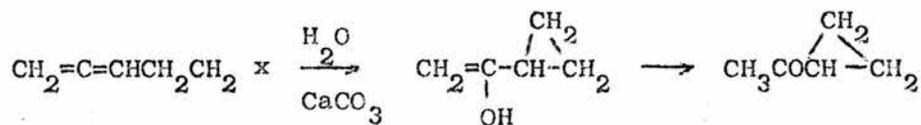


These examples of homo-allylic interaction are typical and illustrate their importance in homocyclic compounds. Examples among less rigid acyclic compounds are much less extensive.

Julia et al¹⁰ obtained cyclopropane compounds during the solvolysis of some short-chain 3-enylbromides:



Hannack and Haffner¹¹ have examined some allenic compounds (3,4-pentadienyl derivatives) and obtained cyclopropane compounds from their reactions with water and calcium carbonate, with acetic acid and sodium acetate, and with formic acid and sodium formate.

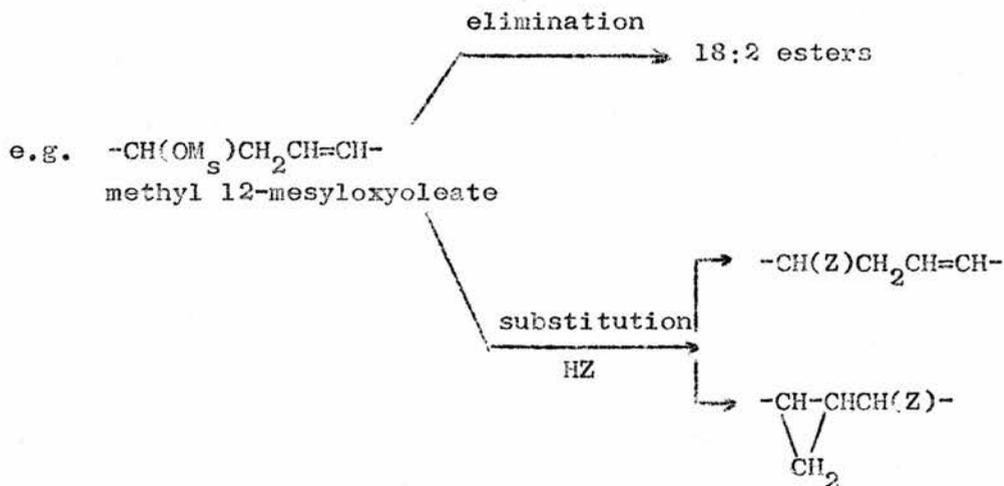


Ucciani, Vantilland, and Naudet¹² have recently described their experiments with methyl 12-tosyloxyelaidate. This homo-allylic compound is converted to a hydroxy cyclopropane by reaction with water and calcium carbonate in acetone and in several other polar solvents.

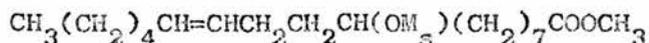
DISCUSSION

The reactions which have been carried out on various methyl mesyloxy (and tosyloxy) octadecenoates will first be described mainly in terms of the qualitative and quantitative identification of the products. This will be followed by a discussion of the overall reactions and the mechanisms which are considered to operate.

We have been mainly concerned with reactions of methyl 12-mesyloxy (tosyloxy) oleate which can undergo elimination or substitution and which sometimes forming cyclopropane compounds thus:



We have also compared these results with the products of similar reactions with methyl 9-mesyloxyoctadec-12-enoate. This isomer differs in having two methylene groups between the two reactive centres.



In addition we have examined some of the properties of the cyclopropane compounds, in particular, their interconversion and their hydrogenolysis.

1. The conversion of mesyloxy compounds to methoxyderivatives:
- 1.1 Reaction of methyl 12-mesyloxyoleate with methanol and sodium methoxide.

Preliminary reactions showed that methyl 12-mesyloxyoleate reacts with boiling methanol and that whilst the reaction is not changed by addition of sulphuric acid, it gives different products in a buffered solution (as in the presence of sodium methoxide). The reaction is complete after four hours, and in general the product is separated by TLC into three fractions of differing polarity. The least polar products (fraction A) are usually elimination products, substitution products (fraction B) are of intermediate polarity. The most polar fraction (C) is usually small and is a mixture of ricinoleate and unchanged mesyloxy ester.

After boiling methyl 12-mesyloxyoleate with methanol and sodium methoxide for four hours the product gave four peaks on GLC indicating two elimination products (15%), and two substitution products (85%). Preparative TLC gave fractions A (14%), B (80%) and C (6%). The infra-red spectrum suggested that fraction C was a mixture of methyl ricinoleate and unchanged mesyloxy ester and this was born out by GLC examination which showed a peak with the retention behaviour of methyl ricinoleate (26.0, 60%)* and a characteristic series of peaks at 19.4, 20.4, 20.6 and 21.0 which are associated with the mesylates. These are thought to be non-conjugated and stereoisomeric conjugated

* ECL's refer to a DEGS column unless indicated otherwise, in this discussion.

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methyl octadecadienoates resulting from on-column decomposition
of the mesylate

Fraction A The ECL's of fraction A (14%) on DEGS and ApL, before and after hydrogenation indicate that this is mainly a mixture of conjugated (probably 9,11) and non-conjugated (probably 9,12) dienoates.

	before hydrogenation	after hydrogenation
DEGS	19.4(15%), 20.4(67%), 20.6(11%), 20.9(7%)	18.0
ApL.	17.0(2%), 17.6(13%), 18.9(65%), 18.4(16%) 18.6(4%)	17.3(3%) and 18.0(97%)

The small peak at 17.3 (ApL) after hydrogenation is unexpected and we were unable to identify it.

This fraction was capable of further division by silver ion chromatography into three sub-fractions. The material with highest R_f value (A₁, 11%) was a mixture of methyl octadeca-9,11-dienoates containing mainly a cis, trans isomer. This conclusion is derived from the infra-red spectrum (960 and 990 cm⁻¹), the ultra-violet spectrum (λ max at 233 nm) and from GLC data (20.4, 70%; 20.6, 20%; and 20.96, 10%). These probably refer to conjugated cis, trans; cis, cis; and trans, trans isomers respectively. Since von-Rudloff

14-17
24-26

oxidation gives nonanedioic acid as the only dibasic acid, these must be 9,11-dienoates. The smaller sub-fractions A2,(2%) and A3,(1%) are probably 9,12t and 9,12c dienoates. Both have ECL's about 19.4 and both give nonanedioic acid when oxidised. Only A2 shows trans unsaturation in its infra-red spectrum (975 cm^{-1}).

Fraction B: Substitution products are the major product (~80%) of this reaction. GLC showed the presence of two components on a packed column (21.2, 70% and 21.4, 30%) but when this was examined later on a capillary column a third component was apparent (20.95, 21%; 21.15, 43%; 21.35, 35%)

The infra-red spectrum and the NMR spectrum indicated the presence of ether groups (1100 cm^{-1} and 6.75τ) and of a cyclopropane system (1020 and 3070 cm^{-1} and 9.55 , 9.65 and 9.75τ).¹⁸⁻²³

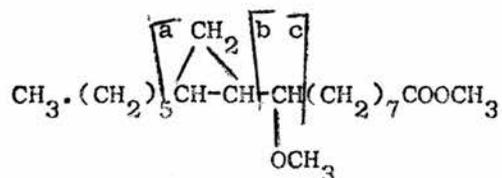
This fraction was separated into two components (B1, 56% and B2, 24%) by two procedures. It became apparent that one component was saturated and the other unsaturated, so that the former remained as unchanged (neutral) ester after von-Rudloff oxidation whilst the latter gave acidic degradation products (see below). The saturated and unsaturated components were also separated after reaction with mercuric acetate in methanol.²⁷ The unsaturated ester could then be regenerated by reaction with methanolic hydrochloric acid (see general methods). The saturated component was further separated by silver

ion TLC into an upper and lower band (BlU 33.6% and BlL 22.4%).

The two saturated components had the same ECL on a packed column (DEGS, 21.2 ApL 18.4) though the evidence cited above suggests that they differ on a capillary DEGS column. Their infra-red spectra are also similar and show the presence of ether (1100 cm^{-1}) and cyclopropane (1020 and 3070 cm^{-1}) groups. The NMR spectra of these two components showed the presence of an OCH_3 group and the absence of olefinic protons. The signals arising from cyclopropane protons differ slightly.

BlU 9.78 and 9.88 \uparrow BlL 9.55 and 9.65 \uparrow .

The mass spectrum is consistent with the following structure:



The cleavage patterns shown in the above structure are particularly significant and give rise to peaks of m/e values 241 (25%, a), 201 (1.3%, b), 169 (100%, c and/or b-32) 137 (9%, 169-32). There is

a small molecular ion peak at 326 (4%).

The unsaturated component is shown to be methyl 12-methoxyoleate on the basis of the evidence set out below. To confirm this an authentic sample was made by methylation of methylricinoleate with methyl iodide and silver oxide²⁸ and its properties were compared with that of fraction B2.

(i) Fraction B2 had ECL's of 21.4 on DEGS (21.2 after hydrogenation) and 18.6 on ApL and was not separated from the authentic ester on either column.

(ii) The two samples had similar infra-red spectra^{14, 29, 30} and showed absence of trans unsaturation.

(iii) The two samples had similar NMR spectra and showed, in particular, the presence of OCH_3 protons (6.75 τ) and olefinic protons (4.65 τ).

(iv) When oxidised, both gave nonanedioic acid and a second product which after methylation had an ECL of 12.0. This is presumably methyl 3-methoxy~~nonanoate~~.

(v) The hydrogenated samples had ~~the~~ similar mass spectra which indicated a structure of methyl 12-methoxystearate. In addition to a small molecular ion peak (328, 0.6%) there were significant peaks at 243 (25%), 211 (5%), 129 (100%) and 97 (74%) arising from cleavage α to the CHOCH_3 group with subsequent loss of 32 mass units. (see page 88)

Conclusion

The products of this reaction are therefore:

elimination	{	18:2 (9cl1t and other conjugated isomers)	11%
		18:2 (9cl2t and 9cl2c)	3%
substitution	{	methyl 9-methoxy-10,11-methyleneheptadecanoate (two isomers)	56%
		methyl 12-methoxy oleate	24%
others	{	methyl 12-hydroxyoleate	6%
		methyl 12-mesyloxyoleate	

The reaction of methyl 12-mesyloxyoleate with methanol and sodium methoxide for different periods of time.

Methyl 12-mesyloxyoleate was refluxed with methanol and sodium methoxide for several periods of time. The products of these reactions were examined by GLC, TLC and by infra-red spectroscopy. The results showed that 4 hours was the optimum time for the reaction.

1.2 Reaction of methyl 12-mesyloxyoleate with methanol

The products of reaction between methyl 12-mesyloxyoleate and boiling methanol (4 hours) was readily separated by TLC into three fractions.

A	(elimination products)	8%
B	(substitution products)	82%
C	(polar material)	10%

Fraction A. This fraction shows the following GLC behaviour. Its infra-red spectrum indicates the presence of trans unsaturation (980 cm^{-1}).

	before hydrogenation	after hydrogenation
DEGS	19.4(62.), 20.4(24%), 20.6(2%), 20.9(5%) 21.4(3%), 23.0(2%), 23.3(2%)	17.3(13%), 18.0(87%)
ApL	17.3(6%), 17.6(53%), 18.2(1%), 18.4(2%) 18.6(14%), 19.7(6%)	17.3(13%), 18.0(87%)

On this basis alone we consider these elimination products to be qualitatively similar to those obtained with methanol and sodium methoxide, viz stereoisomers of methyl octadeca-9,11 and 9,12-dienoates. The quantitative differences are discussed later.

24-26

Fraction B: von-Rudloff oxidation of this fraction gave only a minor amount of unoxidised ester (8%, ECL 21.2) and a considerable quantity (74%) of oxidised fragments. After methylation the latter have the same GLC behaviour as the oxidation products derived from 12-methoxyoleic acid-viz nonanedioic acid and 3-methoxynonanoic acid.

The presence of methyl 12-methoxyoctadecenoate in fraction B is also indicated by the following experiments.

(i) The NMR spectrum shows the presence of a CHOCH_3 group (6.7τ) and of olefinic protons (4.65τ)

(ii) After hydrogenation the sample had a mass spectrum comparable with that of methyl 12-methoxystearate with significant peaks at m/e 243 (98%) and 129 (100%) resulting from cleavage α to the methoxy group (see page 98). Also present were some additional peaks, particularly those of m/e 201 (23%) and 169 (16%), attributable to the small amount of methyl 9-methoxy-10,11-methyleneheptadecanoate which was contained in fraction B.

The infra-red spectrum shows a strong band due to a trans alkene (980 cm^{-1}) and although the fraction appeared homogeneous on GLC with a packed column (DEGS 21.4 (21.2 after hydrogenation) ApL 18.6) a capillary column (DEGS) indicated a more complex mixture with peaks at 21.00, 21.10, and 21.30 (together (10%), 21.35 (57%) and 21.45 (33%).

We consider that fraction B contain some cyclopropane ether (10%) but that it is mainly a mixture of trans (57%) and cis (33%) methyl 12-methoxyoctadecenoates.

Fraction C: This fraction again appears to be a mixture of methyl ricinoleate and its mesylate on the basis of its infra-red spectrum and its behaviour on GLC.

Conclusion

The products of this reaction are therefore:

elimination	{	18:2 conjugated isomers	3%
		18:2 non conjugated isomers	5%
substitution	{	methyl 12-methoxyoleate	24%
		methyl 12-methoxyelaidate	50%
		methyl 9-methoxy-10,11-methylene-heptadecanoate	8%
others	{	methyl 12-hydroxyoleate	10%
		methyl 12-mesyloxyoleate	

Reaction of methyl 12-mesyloxyoleate with methanol for different periods of time

The products of these reactions also show that four hours is the shortest period of time in which methyl 12-mesyloxyoleate reacts completely with methanol.

1.3 Reaction of methyl 12-mesyloxyoleate with methanol and sulphuric acid

The reaction product after four hours reflux was separated by preparative TLC into three fractions:

A	(elimination products)	8%
B	(substitution products)	86%
C	(polar material)	6%

Fraction A: This fraction was again a mixture of conjugated (ECL on DEGS, 20.4 and 20.6, 50%) and non-conjugated [ECL (DEGS) 19.4, 70%] octadecadienoates containing trans unsaturation (infra-red peaks at 960, 980 and 995 cm^{-1}) and giving nonanedioic acid as the only dibasic acid after von-Rudloff oxidation.

Fraction B: was similar to the B fraction obtained by reaction with methanol only. It contains a small amount of unoxidisable product (8%) which is probably cyclopropane ether on the basis of some minor peaks in the mass spectrum of fraction B (see page 103). The major component [DEGS, 21.4 (21.2 after hydrogenation) and ApL. 18.7] contains trans unsaturation (980 cm^{-1}), shows signals for olefinic protons and for CHOCH_2 in its NMR spectrum, and is oxidised to nonanedioic acid and 3-methoxynonanoic acid. The mass spectrum of the hydrogenated product shows it to be methyl 12-methoxystearate (page 103).

Fraction C is a mixture of methyl mesyloxyoleate and methyl ricinoleate.

Conclusion

The products of this reaction are therefore:

elimination	}	18:2 conjugated isomers	2.4%
		18:2 non-conjugated isomers	5.6%
substitution	}	methyl 12-methoxyoleate	
		methyl 12-methoxyelaidate	36%
		methyl 9-methoxy-10,11-methylene-heptadecanoate	
others	}	methyl 12 hydroxyoleate	
		methyl 12 mesyloxyoleate	6%

1.4 Simple modifications of the reaction between methyl 12-mesyloxyoleate and methanol.

1.4a Reaction of methyl 12-tosyloxyoleate with methanol and sodium methoxide:

When refluxed with methanol and sodium methoxide, methyl 12-tosyloxyoleate behaved in the same way as the mesyloxy derivatives. The product was separated and examined by the same procedures with the following results:

elimination	{ 18:2 (9c11t and other conjugated isomers)	24%
	{ 18:2 (9c12t and 9c12c)	
substitution	{ methyl 12-methoxyoleate	20%
	{ methyl 9-methoxy-10,11-heptadecanoate	56%

1.4b Reaction of methyl 12-mesyloxyelaidate with methanol and sodium methoxide.

The trans isomer of methyl 12-mesyloxyoleate reacted in a similar way when heated with methanol and sodium methoxide. The product was separated by TLC and examined by chromatographic, spectroscopic, and oxidative procedures. The results resemble those reported for the cis isomer except that, as expected, the methyl methoxyoctadecenoate has the trans configuration.

elimination	{ 18:2 (9t11t and other conjugated isomers)	13%
	{ 18:2 (9t12t and 9t12c)	6%
substitution	{ methyl 12-methoxyelaidate	24%
	{ methyl 9-methoxy-10,11-heptadecanoate	57%

1.4c Reaction of methyl 12-mesyloxystearolate with methanol and sodium methoxide.

When this acetylenic mesyloxy ester was treated with methanol and sodium methoxide the less polar elimination products (95%) greatly exceeded the substitution products (5%).

The elimination products which behaved as indicated on GLC; were shown to contain olefinic protons (4.6τ) and trans unsaturation.

	before hydrogenation	after hydrogenation (96.5 cm^{-1})
DEGS	21.1 (60%) 23.0 (40%)	18.0
ApL.	17.65 (58%) 18.80 (42%)	18.0

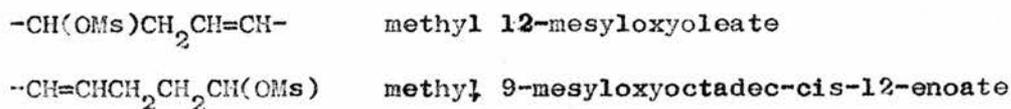
They probably consist mainly of the 9a11t and 9a12t isomers. The substitution products contain one major (90%, 23.0 on DEGS) and one minor component (10%, 24.6 on DEGS).

Conclusion

elimination	{	18:2 conjugated, probably 9a11t	38%
		18:2 non-conjugated, 9a12t	57%
substitution		not identified	5%

1.5 Reaction of methyl 9-mesyloxyoctadec-cis-12-enoate.

The previous reactions have been concerned with derivatives of methyl 12-hydroxyoleate in which a good leaving group is situated on a β -carbon atom to an unsaturation group. We have compared these results with those obtained with derivatives of methyl-9-hydroxyoctadec-12-enoate where the leaving group is on the α -carbon atom with respect to the unsaturated centre -



1.5a Reaction with methanol and sodium methoxide

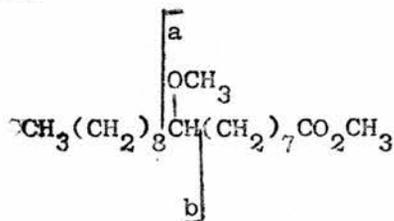
After the normal four hour reflux period the product was separated into three fractions.

The elimination products (fraction A, 25%) were further separated into five fractions by silver ion TLC. Each of these was examined in the usual way with the following results:

	ECL (DEGS)*	infra-red NMR (975 cm^{-1})(7.4 τ)	oxidation dibasic acid	possible structure
A1 1%	16.0, 18.3	weak -	C ₉ only	18:1 (9c)
A2 1%	18.5	weak -	C ₉	18:1 (9c)
A3 10%	19.4	strong large	C ₉ only	18:2 (9t12c)
A4 9%	19.4	strong small	C ₈ + C ₉	18:2 (8t12c and 9t12c)
A5 4%	19.4	weak -	C ₈ + C ₉	18:2 (8cl2c and 9cl2c)

* On a capillary column (DEGS) fraction A showed peaks at 19.0 (32%)
19.1 (30%), 19.2 (10%) and 9.3 (28%).

The substitution product (fraction B, 69%) showed only a single peak on GLC. On silver ion TLC there were some elimination products (3%), an unidentified component (3%), and one major component (63%) which was shown to be methyl 9-methoxyoctadec-12-enoate by comparison with an authentic sample prepared by methylation (Ag_2O , MeI) of the appropriate hydroxy ester. They had the same ECL on DEGS (21.4 before hydrogenation and 21.2 after hydrogenation) and ApL (18.7). In the infra-red both showed the presence of an ether group (1100 cm^{-1}) and absence of trans unsaturation. Their NMR spectra indicated the presence of OCH_3 (6.75τ) and olefinic protons (4.75τ). When oxidised, both gave hexanoic acid and a second product of ECL 23.3 after methylation (presumably methyl 4-methoxydodecanedioate). The two esters had similar mass spectra after hydrogenation, with the fragmentation expected of methyl 9-methoxy stearate.



	(a)	(b)	(201-32)	(171-32)	(169-31)	(169-32)
significant peaks	201	171	169	139	138	137
intensity in reaction product (B)	100	70	18	24	20	39
intensity in authentic sample	100	60	19	7	7	29

Conclusion

The products of this reaction therefore are

elimination	{ 18:2 8,12 and 9,12 isomers)	25%
substitution	{ methyl 9-methoxyoctadec-12-enoate	69%
others	{ methyl 9-hydroxyoctadec-12-enoate methyl 9-mesyloxyoctadec-12-enoate	6%

1.5b Reaction with methanol

When treated with methanol alone, methyl 9-mesyloxyoctadec-12-enoate gave the same products as when the reaction was carried out in the presence of sodium methoxide. These were examined as already described.

Conclusion

elimination	18:2 8,12 and 9,12)	30%
substitution	methyl 9-methoxyoctadec-12-enoate	64%
others	{ probably methyl 9-hydroxyoctadec-12-enoate and methyl 9-mesyloxyoctadec-12-enoate	6%

1.5c Reaction with methanol and sulphuric acid.

The same products were also obtained in the presence of sulphuric acid.

elimination	{ 18:2 8,12 and 9,12	28%
substitution	{ methyl 9-methoxyoctadec-12-enoate	66%
others	{ probably methyl 9-hydroxyoctadec-12-enoate methyl 9-mesyloxyoctadec-12-enoate	6%

SUMMARY

ester	reagent	elimination products		substitution		other
		conjugated	non-conjugated	alkene	cyclo-propene	
§ 12M\$09c	MeOH, NaOMe	11	3	24 ^a	56	6
"	MeOH	3	5	74 ^b	8	10
"	MeOH, H ₂ SO ₄	2	6	78 ^b	8	6
§ 12T\$09c	MeOH, NaOMe			20 ^a	56	-
§ 12M\$09t	MeOH, NaOMe	13	6	24 ^c	57	-
§ 12M\$09a	MeOH, NaOMe	38	57	-	5 -	-
§ 9M\$012c	MeOH, NaOMe	-	25	69 ^a	-	6
"	MeOH	-	30	64 ^a	-	6
"	MeOH, H ₂ SO ₄	-	28	66 ^a	-	6

a cis alkenoate

b cis and trans alkenoates

c trans alkenoate

2 The conversion of mesyloxy compounds to acetoxy derivatives

2.1a Reaction of methyl 12-mesyloxyoleate with acetic acid and sodium acetate

Methyl 12-mesyloxyoleate was heated at 100° for four hours with a mixture of acetic acid and sodium acetate. The product was isolated and separated into three fractions (A-C) of increasing polarity by preparative TLC.

Fraction A. This fraction (9%) was found to be a mixture of conjugated and non-conjugated dienoates on the basis of the following information.

1. GLC (DEGS) showed a major peak at 19.4 which is the ECL of methyl linoleate and its geometrical isomers, and a series of smaller peaks of higher ECL (20.4, 20.8, 21.1) usually associated with conjugated 18:2 esters.

2. By Ag⁺ TLC, fraction A was separated into three sub fractions. The GLC behaviour of these suggests that they are mainly:

- A1. conjugated 18:2 esters.
- A2. non-conjugated 18:2 esters, probably a cis-trans isomer.
- A3. non-conjugated 18:2 ester, probably methyl linoleate.

3. The NMR spectrum confirms the presence of conjugated dienes (small signal at 7.2 τ) and of non-conjugated olefinic protons (signals around 4.65 τ).

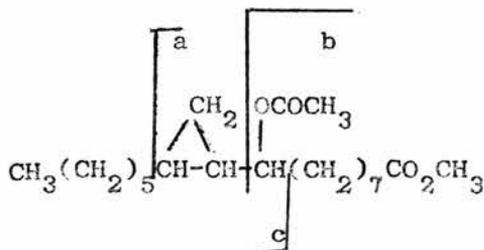
4. Nonanedioic acid is the only dibasic acid obtained by von-Rudloff oxidation of fraction A.

This evidence suggests that fraction A contains several methyl octadecadienoates including probably the 9c12c, 9c12t, 9c11c, 9c11t and 9t11t isomers.

Fraction B. The GLC of this fraction (34%) shows it to contain two major components. The infra-red spectrum shows the presence of a trans double bond and a cyclopropane group. The latter is also apparent from the NMR spectrum. The fraction was further divided by TLC separation after reaction with mercuric acetate into one component (B1) which did not react with this reagent and a second (B2) which did.

Fraction B1 (30%). showed no change in its GLC behaviour (DEGS, 24.1) after treatment with hydrogen and palladium charcoal. Its infra-red spectrum showed the presence of an acetoxy group (1250 and 1370 cm^{-1}), a cyclopropane group (1030 cm^{-1}) and complete absence of any trans alkene. The NMR spectrum contained signals at $8.04\text{ } \tau$ (3H) due to acetate and at $9.4\text{ } \tau$ and $10.3\text{ } \tau$ (cyclopropane) but no signals for olefinic protons. 1,2-Di-¹⁸substituted cyclopropanes are reported to give a single signal ($9.3\text{ } \tau$, 4H) for the trans isomer and two signals ($9.4\text{ } \tau$, 3H and $10.3\text{ } \tau$, 1H) for the cis isomer.

The mass spectrum is consistent with the structure shown below:



Fragments associated with cleavage (a), (b) and (c) are particularly significant (see page 117).

This fraction (B1) was further separated by TLC into an upper (20%) and lower (10%) band, but these showed no other significant chromatographic or spectroscopic differences. We consider these to be diastereoisomeric forms of the acetoxy cyclopropanes.

Fraction B2: This fraction (54%) proved to be methyl 12-acetoxy elaidate³¹ though it may also contain some of the cis isomer. This conclusion is based on the following evidence which included a comparative study of an authentic sample of methyl 12-acetoxyelaidate.

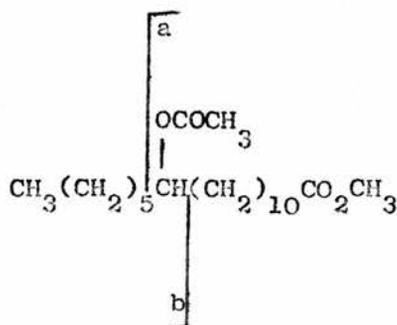
(1) This fraction had an ECL of 24.6 on DEGS (24.3 after hydrogenation) and 18.6 on ApL, as did the authentic sample.

(2) The two samples had similar NMR spectra with characteristic signals for olefinic protons (4.65 \uparrow) and for acetate (8.05 \uparrow).

(3) The infra-red spectrum confirmed the presence of trans unsaturation (980 cm^{-1}) and of acetate (1250 and 1370 cm^{-1}).

(4) When oxidised by von-Rudloff oxidation, both esters gave nonanedioic acid and a second product (ECL on DEGS 15.2 after methylation) which was presumably, methyl 3-acetoxynonanoate.

(5) The mass spectra of both hydrogenated esters were consistent with the structure of methyl 12-acetoxystearate. The more significant peaks are tabulated. (See page 118).



peaks	313 (M-43),	281 (313-32),	271 (a),	229 (a-43+1),	157 (b)
B2	28*	44	24	100	28
authentic samples	36*	46	50	100	11

* These figures indicate intensity with respect to the base peaks (-100).

Fraction C: This is the most polar fraction (7%). It had ECL's (DEGS) of 19.4, 20.8, 21.1 and 23.3 (total 30%) [probably due to the decomposition of the mesyloxy ester] and 25.7 and 26.0¹³ (total 70%). Its infra-red spectrum showed the presence of a trans alkene (980 cm^{-1}) and a hydroxyl group (3500 cm^{-1}) in addition to mesyloxy ester absorption bands (920 and 1180 cm^{-1}).

The NMR spectrum also contained signals for mesyloxy protons (7.14τ) and for olefinic protons (4.65τ). When oxidised by von-Rudloff oxidation fraction C gave mainly nonanedioic acid and (presumably) 3-hydroxynonanoic acid (DEGS, 16.0), along with some other products possibly from the mesyloxy ester.

We conclude that this fraction probably contains methyl 12-mesyloxyoleate, methylricinelaidate, and methylricinoleate.

Conclusion:

The products of this reaction are therefore:

elimination	{	18:2 (9cl1t and other conjugated isomers)	4.5%
		18:2 (9cl2t and 9cl2c)	4.5%
substitution	{	methyl 9-acetoxy-10,11-methyleneheptadecanoate (2 isomers)	30%
		methyl 12-acetoxyoleate	54%
others	{	methyl 12-mesyloxyoleate	2%
		methyl ricinelaidate	
		methyl ricinoleate	5%

Reaction of methyl 12-mesyloxyoleate with acetic acid and sodium acetate for different periods of time

Methyl 12-mesyloxyoleate was heated with acetic acid and sodium acetate for different periods of time at 100°. The products were examined on GLC and the table below shows the changes in the relative amounts of the three major peaks.

time (mins)	Area % under major peaks (DEGS)			time (hrs)	Area % under major peaks (DEGS)		
	23.3	24.1	24.6		23.3	24.1	24.6
5	33	30	36	2	15	31	54
10	17	43	40	4	4	29	67
15	10	52	38	6	10	13	77
30	0	52	48	8	6	9	85

These three peaks represent an unidentified compound (23.2), the cyclopropane ester (24.1) and methyl acetoxyoctadecenoate (24.6).

The results suggest that some unknown compound is formed

initially but subsequently reacts further. Of the two acetoxy esters, the cyclopropane is formed more quickly in the early stages of the reaction, but gradually gives place to the

unsaturated acetoxy ester which is largely trans. The optimum yield (52%) of the cyclopropane ester occurs after about half an hour.

2.1b Reaction of methyl 12-mesyloxyoleate with formic acid and sodium formate.

The mesyloxy ester was heated (100°) with formic acid (98%) and sodium formate for four hours. The product which had one major peak on GLC, was separated by preparative TLC into a minor fraction (A, 5%) and a major fraction (B, 95%).

The minor fraction (A) was considered, on the basis of its behaviour on GLC, to be a mixture of non-conjugated (70%, DEGS, 19.4) and conjugated (30%, DEGS, 20.4 and 21.1) octadecadienoates.

The major fraction (B, 95%) was considered to be methyl formoxyelaidate on the basis of the following evidence. Some formoxyoleate may also be present. There was no evidence of any saturated cyclic formate.

(i) GLC behaviour ECL's of 25.3 (DEGS) and 19.4 (Apl) became 24.8 and 19.7 respectively after hydrogenation and the TMS ether has E.C.L.'s of 19.7 after de-formylation with sodium methoxide and methanol.

(ii) The NMR spectrum contained signals due to olefinic protons (4.65 τ) and formate protons (2.05 τ).

Reaction of methyl 12-mesyloxyoctadec-9-ynoate with acetic acid and sodium acetate.

The mesyloxy ester was heated at 100° with acetic acid and sodium acetate for four hours. The product was separated by preparative TLC into three fractions: A, B and C.

Fraction A (22%) has ECL's of 21.1 (36%), 21.7 (57%, which agree with values for authentic 9a12c and 9c12a), and 22.9 (7%) (agrees with 9a11t)

on a DEGS column. These probably represent conjugated (9a11c and/or 9a11t) and non-conjugated (9a12a and/or 9a12t) isomers. The infra-red spectrum confirmed the presence of a trans unsaturated alkene (980 cm^{-1}).

Fraction B: This fraction (28%) was considered to be methyl 12-acetoxyoctadec-9-ynoate, on the basis of its behaviour on GLC (a single peak at 26.0 on DEGS) and its infra-red spectrum which showed the presence of the acetate group ($1035, 1250$ and 1370 cm^{-1}).

Fraction C: This polar fraction (50%) is probably unreacted mesyloxy ester. It gave a series of wide overlapping peaks of ECL's (DEGS) around 21.3, 21.9, 23.0 and 24.4 probably due to decomposition of the mesyloxy ester. The infra-red spectrum confirmed the presence

of the mesyloxy ester with absorption bands at 920, 1180 and 1360 cm^{-1} .

Conclusion:

The products of this reaction are therefore:

elimination	{ 9a11t/c and 9a12c/t	22%
substitution	{ methyl 12-acetoxyoctadec-9-ynoate	28%
others	{ methyl 12-mesyloxyoctadec-9-ynoate	50%

Reaction of methyl-9-mesyloxyoctadec-cis-12-enoate with acetic acid and sodium acetate:

The methyl 9-mesyloxy ester was heated at 100° for four hours with acetic acid and sodium acetate. The products after isolation gave two peaks on GLC corresponding probably to the elimination and the substitution products. It was then separated by preparative TLC into three fractions (A, B and C).

Fraction A: This fraction (44%) had an ECL of 19.4 (DEGS) and showed trans unsaturation on its infra-red spectrum (980 cm^{-1}). It was considered to be a mixture of non-conjugated octadecadienoates (probably 8c12c, 8t12c, 9c12c and 9t12c) which are the expected elimination products from methyl 9-mesyloxyoctadec-cis-12-enoate. These were examined more fully in the reaction with methanol and sodium methoxide.

Fraction B: This fraction (41%) was expected to be methyl 9-acetoxyoctadec-cis-12-enoate. Its GLC showed one major peak at 24.6 (DEGS) or 19.6 (ApL).

The infra-red spectrum showed the presence of an acetate group ($1030, 1250$ and 1380 cm^{-1}) and of alkene unsaturation (3020 cm^{-1}). Similar properties were displayed by an authentic sample of methyl 9-acetoxyoctadec-cis-12-enoate prepared by acetylation of methyl 9-hydroxyoctadec-cis-12-enoate.

Fraction C (15%) was the most polar fraction with an ECL of 26.0 (DEGS). This high value suggests the presence of a hydroxyl group which was confirmed by an absorption band at 3500 cm^{-1} in the infra-red spectrum. It is probably methyl 9-hydroxyoctadec-12-enoate.

Conclusion

The products of this reaction are therefore:

elimination	{ 18:2 (8c12c, 8t12c and 9t12c)	44%
substitution	{ methyl 9-acetoxyoctadec-cis-12-enoate	41%
polar product	{ methyl 9-hydroxyoctadec-cis-12-enoate	15%

3.1 Reaction of methyl 12-mesyloxyoleate with metal hydrides.

3.1a Reaction of methyl 12-mesyloxyoleate with lithium aluminium hydride in tetrahydrofuran.

When the mesyloxy ester was refluxed with lithium aluminium hydride in tetrahydrofuran the products were alcohols (rather than esters) which were separated by preparative TLC into three fractions (A, 4%; B, 87%; and C 9%). The major component was shown to be oleyl alcohol on the basis of the evidence set out below.

Fraction A of ECL 19.3 was not further investigated.

Fraction B. This fraction was shown to be mainly oleyl alcohol by comparison with an authentic sample of this compound.

(i) Both showed ECL's of 20.6, 14.1 (as TMSI derivatives), and 15.1 (as methyl ether) on a DEGS column.

(ii) The two compounds showed absorption bands at 1060 cm^{-1} (alcohol), 3350 cm^{-1} (hydroxyl group) and 3010 cm^{-1} (alkenes) in their infra-red spectra.

(iii) Olefinic protons (4.7τ) and CHOH protons ($6.4 - 6.7\tau$) apparent in the NMR spectra.

(iv) Von-Rudloff oxidation of both compounds gave a fragment having ECL (after methylation) of 19.4 (24,25 13.0 as TMSI derivatives and 13.9 as methyl ether).

Fraction C of ECL 27.7 was not identified.

3.1b Reaction of methyl 12-mesyloxy oleate with methanol and sodium borohydride.

When methyl 12-mesyloxy oleate was refluxed with methanolic sodium borohydride the product contained several components which were tentatively identified on the basis of GLC behaviour only. The infra-red spectrum confirmed the presence of OCH_3 and cyclopropane groups (1100 cm^{-1} and 3070 cm^{-1} respectively).

19.4 (7%)	18:2 (9,12 isomers)
20.4 and 20.9 (4%)	18:2 (9,11 isomers)
21.2 (60%)	methyl 9-methoxy-10,11-methyleneheptadecanoate.
21.4 (29%)	methyl 12-methoxy oleate

3.2 Reactions of methyl 12-mesyloxy oleate in acetonitrile as solvent.

3.2a Reaction of methyl 12-mesyloxy oleate with water and calcium carbonate in acetonitrile.

The mesyloxy ester was refluxed for four hours with water and calcium carbonate in acetonitrile. The product was shown to contain cyclopropane and hydroxyl groups on the basis of its infra-red spectrum. It was separated by preparative TLC into three fractions: A (16%), B (54%) and C (30%).

Fraction A: This fraction showed ECL's of 19.3 (68%, probably 18:2 (9,12) ester) and 20.4, 20.8 and 21.1 (32%, probably 18:2 (9,11) ester). The infra-red spectrum of this fraction confirmed the presence of isolated and conjugated ^{14,15} trans alkenes.

Fraction B: This major fraction (54%) was subdivided into three components by silver ion TLC: B1 (33%), B2 (5%) and B3 (16%).

Fraction B1 is considered to be methyl 9-hydroxy-10,11-methylene heptadecanoate on the basis of the following evidence.

(1) On a DEGS column it gave virtually a single peak of ECL 25.75 but on an ApL column at least five peaks of much lower carbon number were observed (ECL's 17.5, 17.85, 18.25, 19.70 and 19.40). These are probably indicative of Qn-column decomposition.

(11) The infra-red spectrum revealed the presence of a cyclo^{18, 19}propane system (1030 and 3070 cm^{-1}), an ester group (1740 cm^{-1}) and hydroxyl group (3500 cm^{-1}). The NMR spectrum confirmed the presence of the cyclopropane group (signal at 9.6 τ) and the absence of any olefinic protons.

Fraction B2 is a small component which was not completely identified. On the basis of its GLC behaviour it probably contains appreciably amount of B3 with some B1.

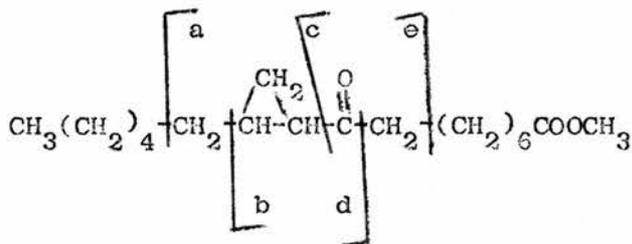
Fraction B3 with ECL's of 26.0 (DEGS) and 19.4 (ApL) is probably a mixture of methyl ricinoleate and ricinelaideate. The NMR spectrum indicates the presence of olefinic protons (4.6 τ) and its infra-red spectrum contains diagnostic bands at 980 cm^{-1} (trans unsaturation) and 3500 cm^{-1} (hydroxyl group).

Fraction C: The evidence presented below suggests that this fraction, like B1, is methyl 9-hydroxy-10,11-methylene heptadecanoate. The two fractions probably represent diastereoisomers which have been separated by TLC.

(1) On a DEGS column one major peak was observed (25.6) but on ApL there were several peaks (17.5, 17.75, 18.15, 18.75 and 19.45) probably as a result of decomposition.

(11) The infra-red and the NMR spectra confirmed the presence of a cyclopropane system (1030 and 3070 cm^{-1} , and 9.55 and 9.75 τ), the presence of a hydroxyl group (3500 cm^{-1}), and the absence of olefinic unsaturation.

(iii) After oxidation of the hydroxy ester to an oxo ester its mass spectrum was examined and shown to be consistent with the structure of methyl 9-oxo-10,11-methylene heptadecanoate ^{24,30,33,34.}



Cleavage as shown above is particularly significant and gives rise to peaks of m/e values 239 (7%, a), 225 (9%, b), 185 (19%, c), 153 (100%, d), 168 (29%, e) in addition to the molecular ion peak 310 (10%). (See page 132).

Conclusion: The products of this reaction are therefore:

A (elimination)	$\left\{ \begin{array}{l} 18:2 \text{ (non-conjugated dienates, probably 9,12 isomers)} \\ 18:2 \text{ (conjugated dienates, probably 9,11 isomers)} \end{array} \right.$	11%
		5%
(substitution)	$\left. \begin{array}{l} \text{methyl 9-hydroxy-10,11-methylene} \\ \text{heptadecanoate} \\ \text{methyl 9-hydroxy-10,11-methylene-} \\ \text{heptadecanoate} \\ \text{methyl ricinoleate and methyl ricinolaidate} \end{array} \right\}$	probably
		isomers
		33%
		30%
		21%

3.2b Reaction of methyl 12-mesyloxy oleate with sodium methoxide and calcium carbonate in acetonitrile.

Refluxing the mesyloxy ester for 12 hours with sodium methoxide and calcium carbonate in acetonitrile gave a product containing several compounds (GLC). The infra-red spectrum showed it to contain conjugated cis-trans dienes system (960 and 995 cm^{-1}). The product was separated by preparative TLC into four fractions: A (9%), B (70%), C (8%) and D (14%). Fraction A was considered from its GLC behaviour (DEGS, 19.6) to be non-conjugated dienoate isomers.

The major fraction (B) was mainly a mixture of conjugated dienoate (96%) with a little (4%) of the non-conjugated isomers. This mixture was examined before and after reaction with iodine³⁵ in carbon disulphide. This reagent effects stereomutation of the double bonds producing mainly trans trans dienoates and some cis trans/trans cis isomers and the results are interpreted in the following way.

	D E G S			A P L		
	9c11t	9c11c	9t11t	9c11t	9c11c	9t11t
Before reaction	20.4 (56%)	20.8 (26%)	21.0 (14%)	18.15	18.4	18.65
after reaction						18.65*

* = major peak

In the infra-red spectrum there were two strong absorption bands before reaction with iodine ($960 + 995 \text{ cm}^{-1}$) due to the predominant *cis* isomers, and a single band after reaction with iodine (995 cm^{-1}) due to the predominant *trans* isomer.

Fraction C (DEGS, 21.4) with infra-red bands at 980 cm^{-1} (trans alkene) and 1100 cm^{-1} (ether) is methyl 12-methoxy octadec-9-enoate. The trans isomer predominates but some cis isomer may also be present.

Fraction D (DEGS, 25.8) is probably methyl ricinoleate with a small amount of methyl ricinelaidate (with absorption at 980 cm^{-1}).

Conclusion: It appears from the information listed above that the products of this reaction are:

elimination (A and B)	18:2 non conjugated dienoates (probably 9,12 isomers)	12%
	18:2 conjugated dienoates	
	9c11t (39%)	
	9c11c (17%)	66%
	9t11t (10%)	
substitution (c)	methyl 12-methoxyoctadec-9-enoate	8%
(D)	methyl 12-hydroxy octadec-9-enoate	14%

3.2c Reaction of methyl 12-mesyloxyoleate with lithium chloride and calcium carbonate in acetonitrile

The mesyloxy ester was refluxed with lithium chloride (hydrated) and calcium carbonate in acetonitrile, for 12 hours. The product was separated by preparative TLC into three fractions: (A, 79%); B, 14% and C, 7%).

In this experiment fraction A (79%) was the major component, probably because the expected substitution product has similar polarity to the elimination products.

In addition to peaks normally associated with the elimination products (DEGS: 19.2, 19.4, 20.4, 20.6 and 21.0, 25%) an additional peak (23.3, 75%) may be due to methyl 12-chlorooctadec-9-enoate. This compound could not be separated from the elimination products.

Von-Rudloff oxidation gave nonanedioic acid and a new product (ECL of methyl ester 13.8 on DEGS) which might be 3-chlorononanoic acid.

Fraction B gave two major peaks on a DEGS column (25.6, 30% and 25.9, 70%) which may correspond with methyl 9-hydroxy-10,11-methylene heptadecanoate and methyl 12-hydroxy octadec-9-enoate. The infra-red spectrum confirmed the presence of trans unsaturation (980 cm^{-1}), of a cyclopropane group (3070 cm^{-1}) and of a hydroxyl group (3500 cm^{-1}).

Fraction C contains more of the hydroxy cyclopropane ester and also some free acid(s).

(The unexpected hydroxy compounds formed in this reaction probably arise from water present in hydrated lithium chloride).

Conclusion: The products of this reaction are therefore:

elimination	{	18:2 (conjugated dienoates, probably 9,11 isomers)	19%
		18:2 (non-conjugated dienoates, probably 9,12 isomers)	
substitution	{	methyl 12-chloro-octadec-9-enoate	60%
		methyl 9-hydroxy-10,11-methylene heptadecanoate and	21%
		methyl 12-hydroxy octadec-9-enoate	

3.3 Reaction of methyl 12-mesyloxyoleate in dimethyl sulphoxide as solvent

3.3a Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide.

The mesyloxy ester was heated (at 100°C) for four hours ~~was in~~ in dimethyl sulphoxide solution. The product was separated by preparative TLC into two fractions: A (74%) and B (26%).

Fraction A: This fraction (74%) was shown to be a mixture of conjugated and non-conjugated dienoates on the basis of the evidence obtained from GLC and infra-red spectrum. GLC (DEGS) of this fraction gave ECL's of 19.4 (31%), 20.4 (38%), and 21.0 (31%) which correspond to the 9,12, 9c11t; and 9t11t octadecadienoates respectively. The infra-red spectrum (960 cm^{-1} and 995 cm^{-1} , large) confirmed the presence of conjugated cis-trans and trans-trans dienoates.

Fraction B: This fraction was shown to be methyl ricinoleate containing some methyl ricinoleaidate and about 5% unreacted mesyloxy ester.

The GLC showed ECL's of 19.4, 20.4, 20.8 and 21.0 (5%, due to the mesyloxy ester decomposition), 25.8, and 26.0 (major) (which are probably methyl ricinoleaidate and methyl ricinoleate). The infra-red spectrum confirmed the presence of a little trans alkene (980 cm^{-1}), of mesyloxy ester (920 and 1180 cm^{-1}) and of a hydroxyl group (3500 cm^{-1}).

Conclusion: The products of this reaction are therefore:

elimination	{	18:2 (conjugated dienoates isomers 9,11)	51%
		18:2 (non-conjugated dienoates 9,12 isomers)	23%
substitution	{	methyl 12-hydroxyoctadec-9-enoate and	26%
		methyl 12-mesyloxy oleate	

3.3b Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide and calcium carbonate.

The mesyloxy ester was heated (100°) for four hours with dimethyl sulphoxide and calcium carbonate. The product (which showed two series of peaks on GLC) was separated by preparative TLC into three fractions (A, B and C).

Fraction A: The GLC (DEGS) behaviour of this fraction (50%) indicated it to be mainly a mixture of conjugated (70%, probably 9,11) and non-conjugated (30% probably 9,12) octadecadienoates. The presence of the conjugated system was confirmed by the infra-red spectrum which showed absorption bands at 960 and 995 cm^{-1} . There was also a band at 980 cm^{-1} due to the presence of the non-conjugated trans alkene.

Fraction B (26%): This fraction was shown to be mainly methyl 12-oxo-oleate which ^{was} possibly accompanied by some 12 oxo-elaidate on the basis of the evidence set out below. It was compared with an authentic sample of methyl 12-oxo oleate prepared by oxidation³² of methyl ricinoleate.

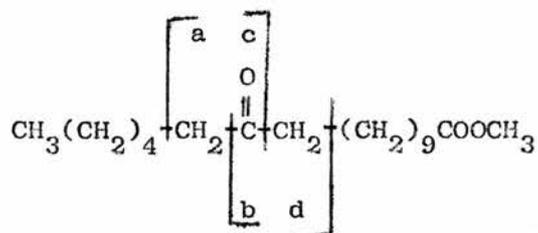
(1) The product (ECL [DEGS] 25.0 before hydrogenation, 24.9 after hydrogenation) was not separated on GLC from the authentic sample of 12-oxo-oleate.

(2) The two samples had similar infra-red spectra apart from evidence of a little trans unsaturation in B.

(3) When oxidised, both gave nonanedioic acid as the only dibasic acid.

(4) The two hydrogenated samples had similar mass spectra which corresponded to methyl 12-oxo-stearate. ^{30,33,34}

In addition to the molecular ion peak there were significant peaks arising from cleavage expected in an oxo ester (page 139) thus:



	(M)	(M-31)	(M-32)	(a)	(b)	(a-31)	(b-32)	(c)	(d)
peak	312	281	280	242	227	211	195	113	128
B(%)	7	65	7	80	100	20	25	95	95
authentic sample (%)	9	51	13	84	100	35	33	100	100

Fraction C: This fraction (24%) was shown to be a mixture of unreacted mesyloxy ester (5%) and methyl ricinelaideate (95%) on the basis of the following evidence.

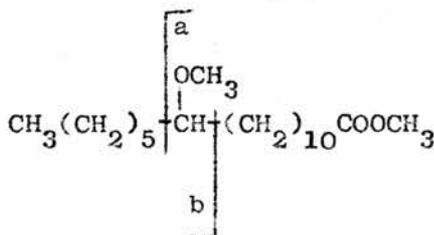
(1) This fraction showed the chromatographic behaviour (DEGS) expected of methyl 12-mesyloxyoleate (5%, decomposition¹³ peaks at 19.4, 20.4, 20.6 and 23.3) and methyl ricinelaideate (95%, 25.5; 21.4 after methylation).

(2) The infra-red spectrum showed the presence of trans unsaturation (980 cm^{-1}), of the unreacted mesyloxy ester (920 and 1180 cm^{-1}) and of the hydroxyl group (3500 cm^{-1}). After methylation the hydroxyl band was replaced by an ether band (1100 cm^{-1}).

(3) Nonanedioic acid and (presumably) 3-hydroxynonanoic acid (the ester of which had an ECL of 16.0 on DEGS) were obtained by von-Rudloff oxidation.

(4) The methylated²⁸ product after hydrogenation had a similar mass spectrum to that of an authentic sample of methyl 12-methoxystearate.

The significant peaks arising from cleavage α to the methoxy group with subsequent loss of 32 mass units in both samples are shown in the table. (see also page 89)



	(M-31)	(M-32)	(297-32)	(296-32)	(a)	(a-32)	(b)	(b-32)
peak	297	296	265	264	243	211	129	97
C(%)	11	3	15	20	90	18	100	77
authentic sample (%)	4	2	15	3	92	9	100	34

Conclusion: From the evidence above it appears that the products of this reaction are:

elimination	{	18:2 (9cl1t and other isomers)	35%
		18:2 (9cl2t and 9cl2c)	15%
substitution		methyl 12-oxo-oleate and some 12-oxo-elaidate	26%
other	{	methyl 12 hydroxyoctadec 9-enoate	24%
		methyl 12-mesyloxyoctadec 9-enoate	

3.3c Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide and sodium methoxide

The mesyloxy ester was heated (at 100°C) for four hours with dimethyl sulphoxide and sodium methoxide. The product was shown to be a mixture of methyl octadecadienoates (9c11t, 28% and 9t11t, 72%).

GLC gave ECL's of 20.4 (28%, conjugated cis-trans dienoates) and 21.0 (72%, trans-trans conjugated dienoates) on a DEGS column. These appeared at 18.15 (35%) and 18.6 (65%) on an ApL column.

The infra-red spectrum of this product showed absorption bands at 960 and 995 cm^{-1} (the second band is much bigger than the first because alone it represents the trans-trans conjugated system and with the first represent the cis-trans conjugated system).

When this product was treated with iodine³⁵ and carbon disulphide solution it showed only one band on the infra-red spectrum at 995 cm^{-1} (trans-trans conjugated system).

Conclusion: The products of this reaction are therefore:

elimination	18:2 (9c11t)	28%
	18:2 (9t11t)	72%

3.3d Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide and lithium chloride

When heated with lithium chloride (hydrated) and dimethyl sulphoxide at 100° for four hours, the methyl 12-mesyloxyoleate gave a product which was separated by preparative TLC into two fractions: A (90%) and B (10%).

On the basis of GLC and infra-red evidence, the major fraction (A) was shown to be a mixture of elimination products (22%, probably conjugated and non-conjugated dienoates) and substitution product (68%, probably methyl 12-chloro-oleate).

The GLC (DEGS) showed ECL's (19.3, 20.4, 20.8 and 21.0 total of 25%) associated with the usual elimination products. The major peak (23.3, 75%) is probably due to methyl 12-chloro-oleate. The infra-red spectrum showed only small absorption bands at 960 and 995 cm^{-1} due to the conjugated cis-trans system present in the elimination products.

The small fraction B (DEGS 25.9) contained an alkene group (3020 cm^{-1}) and a hydroxyl group (3500 cm^{-1}). It is probably methylricinoleate.

Conclusion: The products of this reaction are therefore:

elimination	{ 18:2 (conjugated and non-conjugated dienoates isomers)	22%
substitution	{ methyl 12-chlorooleate	68%
	{ methyl ricinoleate	10%

3.3E Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide, lithium chloride and calcium carbonate.

Heating the methyl 12-mesyloxy ester 100° for four hours with dimethyl sulphoxide solution, lithium chloride (hydrated) and calcium carbonate gave a product which was separated by preparative TLC into two fractions: A (87%) and B (13%).

The major fraction again appears to be a mixture of elimination products (15%, DEGS 19.4, 20.4, 20.8 and 21.1) and of a second product (85%, DEGS 23.3) which is probably methyl 12-chloro-oleate. The infra-red spectrum contained significant peaks at 800 cm^{-1} (small, probably chloro group) and 3020 cm^{-1} (alkene) and the NMR spectrum confirmed the presence of olefinic protons (4.6τ). When oxidised, by Von-Rudloff oxidation, this fraction gave nonanedioic acid and a second compound possibly 3-chloronanoic acid whose methyl ester had an ECL (DEGS) of 13.8.

Fraction B is probably methyl ricinoleate on the basis of its behaviour on GLC (DEGS, 25.9) and its infra-red spectrum (3500 cm^{-1} , hydroxyl).

Conclusion: The products of this reaction are therefore:

elimination	{ 18:2 (conjugated and non-conjugated dienoates)	12%
substitution	{ methyl 12-chloro-oleate	75%
	{ methyl ricinoleate	13%

3.3F Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide, magnesium bromide and calcium carbonate:

The mesyloxy ester was heated with dimethyl sulphoxide solution, magnesium bromide (hydrated $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$) and calcium carbonate at 100°C for four hours. The product was separated by preparative TLC into two fractions: A (75%) and B (25%).

Fraction A: The behaviour of this fraction (75%) on GLC and infra-red spectrum suggests it to be mainly a mixture of unsaturated dienoates.

The DEGS column showed peaks of ECL 19.3 (22% probably non-conjugated dienoates), 20.4 (49%, probably conjugated cis-trans), 20.8 (12%, probably conjugated cis-cis) and 21.1 (9%, conjugated trans-trans) dienoates and 24.5 (8%, perhaps methyl 12-bromo-oleate).

The infra-red spectrum confirmed the presence of the conjugated systems (960 cm^{-1} and 995 cm^{-1}).

Fraction B: This fraction is probably methyl ricinoleate since it has an ECL of 25.9 (DEGS) and its infra-red spectrum shows it to contain a hydroxyl group (3500 cm^{-1}).

Conclusion: The products of this reaction are therefore:

elimination	{	18:2 (conjugated dienoates, probably 9,11 isomers)	53%
		18:2 (non-conjugated dienoates, probably 9,12-isomers)	17%
substitution	{	methyl ricinoleate	25%
		unknown (possibly methyl 12-bromo-oleate)	5%

3.3G Reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide, potassium iodide and calcium carbonate:

The product resulted by heating the mesyloxy ester (100°) with dimethyl sulphoxide solution in the presence of potassium iodide and calcium carbonate for four hours, was separated by preparative TLC into two fractions: A (78%) and B (22%).

Fraction A was shown to be a mixture of the usual elimination products which result from the 12-mesyloxy ester. GLC (DEGS) showed ECL's of 19.4 (28%, methyl linoleate and its isomers), 20.4 (25%, conjugated cis-trans dienoates) and 21.1 (46%, conjugated trans-trans dienoates). The presence of both conjugated systems was confirmed by the infra-red spectrum (weak absorption at 960 cm^{-1} and strong absorption at 995 cm^{-1}). It also showed an absorption band at 980 cm^{-1} due to the presence of an isolated trans alkene.

From this evidence this fraction appears to contain: non-conjugated dienoate isomers (22%), conjugated cis-trans (20%) and conjugated trans-trans (30%) dienoates.

Fraction B was considered to be methyl ricinoleate on the basis of its ECL (DEGS, 26.0) and its infra-red spectrum (hydroxyl group, 3500 cm^{-1}).

Conclusion: The products of this reaction are therefore:

* elimination	{ 18:2 (non-conjugated, probably 9,12 isomers)	22%
	{ 18:2 (conjugated, probably 9,11 isomers)	56%
substitution	<u>methyl ricinoleate</u>	22%

* It is possible that if any methyl 12-iodo-oleate were formed it would decompose on the GLC column to give the observed elimination products.

3.4 Reaction of methyl 12-mesyloxyoleate with different reagents in acetone:

The mesyloxyoleate was refluxed for 12 hours in acetone solution in the presence of several reagents. The product was recovered and examined in the usual way. In several reactions unreacted mesyloxyoleate remained: thus conclusion is based on a combination of the evidence from the infra-red spectrum (distinctive absorption bands at 920, 1180 and 1370 cm^{-1}), the TLC behaviour, and the GLC pattern in which the mesyloxyoleate is decomposed to a characteristic pattern of elimination products.

The results are summarised below and it is concluded that acetone is not a very favourable solvent for these reactions.

	elimination products and/or unchanged mesyloxyoleate	other products
CaCO_3	100% (mainly mesyloxyoleate)	-
$\text{NaOMe}/\text{CaCO}_3$	61% (" ")	methoxy ester (33%) + hydroxy ester (6%)
$\text{NaOAc}/\text{CaCO}_3$	100% (mainly mesyloxyoleate)	-
$\text{H}_2\text{O}/\text{CaCO}_3$	66% (" ")	unsaturated and saturated (cyclopropane) esters (34%)
$\text{LiCl} \cdot \text{H}_2\text{O}/\text{CaCO}_3$	84% (" ")	probably 12-chloro-oleate (16%)

3.5 Reaction of methyl 12-mesyloxyoleate in other solvents.

3.5a The thermal decomposition of methyl 12-mesyloxyoleate in boiling triglyme:

The mesyloxyoleate decomposed when heated to 190°C giving a mixture of conjugated and non-conjugated octadecadienoates. The product was separated by TLC first on silica and then on silica impregnated with AgNO₃ and the recovered material was examined by GLC and by infra-red spectroscopy. There was no evidence of any unchanged mesyloxyoleate.

Conclusion: This reaction gives only elimination products

18:2 non-conjugated isomers [9cl2t (48) 9cl2c (6%)]	54%
18:2 conjugated isomers [9cl1t (16%), 9cl1c (9%), 9t11t (7%)	32%
others (unidentified)	14%

3.5b The reaction of methyl 12-mesyloxyoleate with lithium chloride and calcium carbonate in tetrahydrofuran:

After the usual reaction time of four hours the product still contained some unreacted mesyloxyoleate (920, 1180 and 1370 cm⁻¹). The GLC showed the usual series of peaks correspond^{ing} to elimination products (75%, probably decomposition of the unreacted material) along with some methyl 12-chloro-oleate (18%) and an unidentified product (7%).

4 Some reaction of the cyclopropane esters.

4.1 Reaction of methyl 9-methoxy-10,11-methyleneheptadecanoate under acidic conditions.

When the methoxy cyclopropane ester is refluxed with methanolic sulphuric acid for two hours the ester is isomerised to a product believed to be methyl 12-methoxy elaidate (possibly with some of the cis isomer) on the basis of the following evidence.

(I) The ECL (DEGS) of the ester changes from 21.2 before reaction to 21.4 after reaction.

(II) The infra-red spectrum shows strong absorption bands at 980 cm^{-1} (trans alkene) and 1100 cm^{-1} (ether) and none of the characteristic absorption associated with the cyclopropane compound.

(III) The NMR spectrum confirms the appearance of olefinic protons (4.65τ) and the disappearance of cyclopropane protons ($9.4-10.3\tau$). Both compounds are shown to contain the $-\text{CHOCH}_3$ group (6.78τ).

(IV) Oxidation (V.R.) gives two products which, after methylation, have ECL's of (DEGS) 17.6 (nonanedioic ester) and 12.0 presumed to be 3-methoxynonanoic ester).

Refluxing with methanol without added sulphuric acid produces no change in the methoxy cyclopropane ester on the basis of an unchanged ECL and I.R. spectrum.

Methyl 12-methoxyoleate was also unchanged after refluxing with methanolic sulphuric acid. In particular there was no evidence of trans unsaturation.

The methoxy cyclopropane ester was submitted to Von-Rudloff oxidation, treated with methanolic boron trifluoride (to methylate any acidic degraded products), and examined by GLC and IR spectroscopy. There was no evidence of any short chain compounds but the cyclopropane ester had been converted into the methoxy octadecenoate which was wholly or mainly the trans isomer. This change is probably caused by the methanolic boron trifluoride.

4.2 Reaction of methyl 9-acetoxy-10,11-methyleneheptadecanoate.

When refluxed with methanolic boron trifluoride the acetoxy cyclopropane ester is converted into methyl 12-methoxy octadec-9-enoate. This is evident from the change in ECL. The infra-red spectrum confirms the disappearance of the cyclopropane and acetyl groups and indicates that the unsaturation is largely, if not entirely, trans.

Heated with acetic acid and sodium acetate the acetoxy cyclopropane ester gave a mixture of products which on the basis of their GLC behaviour are:

methyl octadecadienoates	5%
unidentified component	25%
methyl 9-acetoxy-10,11-methyleneheptadecanoate	35%
methyl 12-acetoxyoctadec-9-enoate	35%

It was possible to convert the acetoxy cyclopropane ester to the methoxy cyclopropane by stirring with methanolic hydrochloric acid at room temperature.

The reaction was rapid in its early stages and then slower.

time minutes	5	10	20	40	90	150
acetoxy ester	35	44	46	55	70	86
methoxy ester	65	56	54	45	30	14

4.3 Interconversion of the various cyclopropane esters.

As a further check on the structure of the various cyclopropane esters we studied their interconversion and oxidation to an oxo cyclopropane ester. These changes were followed by GLC (DEGS). The presence of the cyclopropane group in each product was confirmed by infra-red and NMR spectroscopy where required.

The acetoxy ester (ECL 24.1) gave the hydroxy ester (ECL 25.7) on deacetylation with sodium methoxide and methanol and this furnished the methoxy ester (ECL 21.2) when methylated with methyl iodide and silver oxide.

Acetylation of the hydroxy ester proved more difficult. Reaction with boiling acetyl chloride (15 min) gave some acetoxy cyclopropane ester (ECL 24.1, 17%) along with some acetoxy octadecenoates (ECL 24.6, 12%) and unidentified products of ECL 22.8 (5%) and 23.3 (66%). With boiling acetic anhydride (8 hr.) the products include acetoxy cyclopropane ester (ECL 24.1, 18%), acetoxyoctadecenoate (ECL 24.6, 62%) and (presumably) methyl octadecadienoates (ECL 19.3 and 19.6, 20%)

The hydroxy cyclopropane was oxidised by chromic acid to the corresponding oxo cyclopropane ester (ECL 25.0 on DEGS and 19.1 on APL). This structure was confirmed by infra-red, NMR, and mass spectrometry (p49).

5 Hydrogenolysis of some cyclopropane esters ^{36.37}

The hydrogenolysis of the esters listed below has been examined. These were available from the reactions of mesyloxy esters (see section 1,2,3), or were prepared from the corresponding olefinic esters by the Simmons-Smith reaction. The compounds prepared by this latter method had infra-red spectra and NMR spectra which confirmed the presence of the cyclopropane group.

methyl cis-9,10-methyleneoctadecanoate

methyl trans-9,10-methyleneoctadecanoate

methyl 9-methoxy-10,11-methyleneheptadecanoate

methyl 9-acetoxy-10,11-methyleneheptadecanoate

methyl 9-hydroxy-10,11-methyleneheptadecanoate

Hydrogenolysis was effected in acetic acid solutions with Adams catalyst at 40°C for one hour.

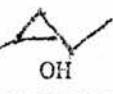
a Methyl 9,10-methylene octadecanoates

The cis isomer reacted completely and after one hour the product gave only a single peak on GLC (DEGS 18.35). This suggests that hydrogenolysis has occurred with formation of methyl 9 and/or 10-methyloctadecanoate and without production of any methyl nonanedecanoate.

This was in marked contrast to the trans isomer which even after 6 hours reaction still contained some cyclopropane compound on the basis of its infra-red spectrum. The product shows two peaks on GLC (DEGS) at 18.35 (methyl 9- and/or 10-methyloctadecanoate) and 19.0 (methyl nonanedecanoate and/or methyl trans-9,10-methyleneoctadecanoate).

b Methyl 9-methoxy, 9-acetoxy and 9-hydroxy-10,11-methyleneheptadecanoates.

The information obtained from GLC and infra-red spectra of these three compounds (listed in the table), after hydrogenolysis, suggest that the cyclopropane ring has been opened and gave mainly straight chain rather than the branched chain as in (a), (which is probably due to the effect of the functional group on the ring opening). The functional groups also have been partly eliminated and partly changed from one to another.

ester	GLC (DEGS) after hydrogenolysis	functional groups shown by IR spectrum
	17.3 (trace), 18.0 (20%), 21.2 (14%), 24.2 (31%) and 25.6 (33%)	OMe, OAc, OH with the complete disappearance of the cyclopropane ring
	17.3 (8%), 18.0 (26%) - , 24.2 (31%) and 25.6 (34%)	- OAc, OH
	17.3 (4%), 18.0 (27%), 22.3 + 23.2 (5%) 24.2 (30%), 25.5 (36%)	OAc, OH

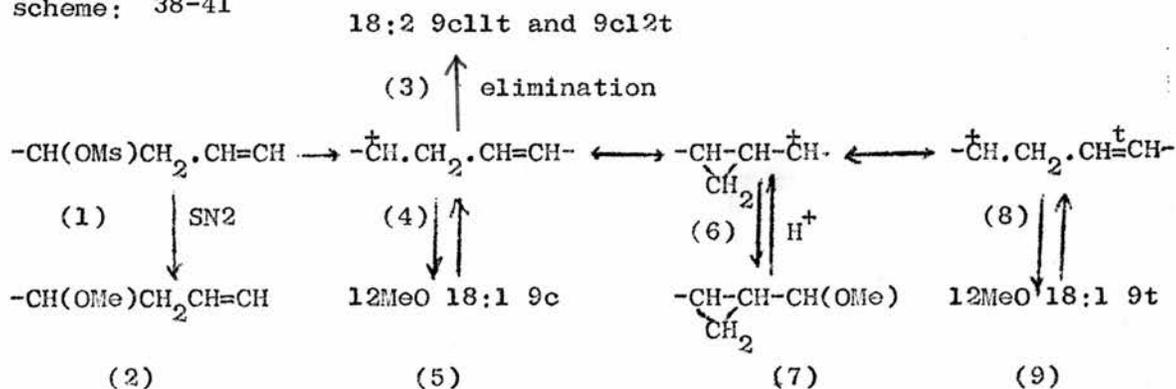
The small component showed by GLC at 17.3 is probably (branched chain ester), methyl 10 and/or 11-methyl heptadecanoates.

Methyl 12-acetoxyoleate and methyl 12-hydroxyoleate were treated similarly with Adams catalyst in acetic acid and the products examined on GLC. The first gave ECL's of (DEGS) 18.0 6% (24.2 (92%), and 24.9 (2%). The second gave ECL's of (DEGS) 18.0 (24%), 24.2 (4%, acetoxy stearate), and 25.5 (72%, hydroxy stearate).

Discussion of results.

1. When methyl 12-mesyloxyoleate is heated in methanol solution it decomposes to give mainly elimination (8-14%) and substitution (80-86%) products. The former is a mixture of conjugated (mainly 18:2 9c11t) and non-conjugated (mainly 18:2 9c12t) octadecadienoates. The substitution products are more complex and depend on the reaction conditions. In methanol alone or in methanol containing sulphuric acid cyclopropane compounds are present in very small amounts ($\sim 8\%$) and the major substitution product is methyl 12-methoxyoctadecenoate predominantly, if not entirely, in the trans form. When the reaction mixture is kept from becoming acidic by addition of sodium methoxide the substitution products are methyl 9-methoxy-10,11-methylene heptadecanoate (56%) along with methyl 12-methoxyoleate (24%). Under these conditions therefore the substitution product is mainly a cyclopropane compound and the unsaturated methoxy ester also formed is wholly cis.

These products are considered to result from the following reaction scheme: 38-41



In the absence of acid the reaction is under kinetic control and the major product is the cyclopropane ester (7) formed from the most stable of the possible carbonium ions (6). Since the methoxyoctadecenoate also formed is entirely cis this probably results from bimolecular substitution of the original mesyloxy oleate. In the presence of acid the reaction is reversible and comes under thermodynamic control. Under these conditions very little cyclopropane ester remains and the methoxyoctadecenoate is predominantly the trans isomer.

2. These effects are not apparent in similar reactions carried out on methyl 9-mesyloxyoctadec-12-enoate. This system is not homoallylic and therefore the ion arising from unimolecular decomposition cannot show the resonance possibilities discussed above. There is little difference in the products formed when the reaction is carried out in methanol or methanol and sulphuric acid or methanol and sodium methoxide.

Elimination products (18:2 9,12 and 8,12) are formed in slightly larger amount (25-30%) and the substitution product (64-69%) is wholly methyl 9-methoxyoctadec-cis-12-enoate.

3. Some other esters related to methyl 12-mesyloxyoleate were treated with methanol containing sodium methoxide. The 12-tosyloxyoleate behaved in a similar way to the mesyloxy ester and gave the cyclopropane ester (7) in good yield (56%). Mesyloxyelaidate also gave a similar mixture of ~~elimination~~ (19%) and substitution (81%) products. The expected cyclopropane ester was accompanied by the acyclic methoxy ester which was, of course, the trans isomer.

The reaction of methyl 12-mesyloxystearolate followed a different course and gave almost entirely elimination products (95%).

4. Attempts were made to find other reaction conditions which would lead to high yield of cyclopropane esters, and procedures yielding acetoxo and hydroxy cyclopropanes were successful.

Reaction with sodium acetate and acetic acid gave methyl 9-acetoxo-10,11-methylene heptadecanoate (30%) and methyl 12-acetoxyoctadecenoate (54%). The yield of cyclopropane ester was lower than in the corresponding methylation reactions.

A similar mixture of sodium formate and formic acid gave no cyclopropane ester, but instead a high yield of methyl 12-formoxyoctadecenoate (95%) which was mainly the trans isomer. This suggests that the cyclopropane compound is not stable under the reaction conditions.

5. The hydroxy cyclopropane ester was obtained in good yield (63%) when methyl 12-mesyloxyoleate was heated with water in acetonitrile solution in the presence of calcium carbonate. Methyl 12-mesyloxyoleate (21%) and elimination products (16%) were also formed. The reaction probably follows a mechanism similar to that described for the methylation process.

6. The methoxy, acetoxo, and hydroxy cyclopropane esters are unstable under acidic conditions. It was shown that methyl 9-methoxy-10,11-methyleneheptadecanoate gives methyl 12-methoxyoctadecenoate (mainly trans) when heated with methanolic sulphuric acid. This cyclopropane

withstands Von-Rudloff oxidation, but is again isomerised to substituted alkenoic ester when heated with methanol and boron trifluoride.

With methanolic boron trifluoride the acetoxy cyclopropane ester gives methoxyoctadecenoates and by further heating with sodium acetate and acetic acid (the condition under which it is produced) it is partially decomposed to acetoxyoctadecenoates and to an unidentified component. When stirred with cold methanolic hydrochloric acid, the acetoxy group was slowly replaced by methoxy, the cyclopropane group remaining intact.

It was possible to convert the acetoxy cyclopropane ester to the hydroxy cyclopropane ester by deacetylation with sodium methoxide and to methylate the hydroxy cyclopropane ester to give the methoxy cyclopropane compound. Attempts to acetylate the hydroxy cyclopropane ester, however, were unsuccessful. The hydroxy ester was readily oxidised to an oxo-cyclopropane ester.

7. When subjected to hydrogenolysis, (platinum dioxide, acetic acid, 40°) the cis isomer of methyl-9,10-methyleneoctadecanoate gave a mixture of methyl 9- and 10-methyloctadecanoates with little or no evidence of any methyl nonadecanoate. The trans isomer was much less reactive and was incompletely reduced even after 6 hours.

When the methoxy, acetoxy, and hydroxy cyclopropane esters were submitted to similar hydrogenolysis reactions, the results were rather complex. Loss of the functional group occurred (20-30%) and in addition hydroxy and acetoxy esters for the methoxy cyclopropane compound). These changes were much less in the hydrogenolysis of methyl 12-acetoxy (and hydroxy) oleate.

8. Attempts to effect a similar cyclisation reaction using hydride ion (from metal hydrides) as the nucleophile were unsuccessful. Lithium aluminium hydride (in tetrahydrofuran) gave oleyl alcohol (87%) as the only identified product whereas sodium borohydride (in methanol) gave elimination and substitution products similar to those obtained with methanol and sodium methoxide. This suggests that the sodium borohydride serves only to keep the solution from becoming acidic.
9. Reference has already been made (5) to the reaction of methyl 12-mesyloxyoleate with water in acetonitrile solution. Two other reactions were conducted in this solvent: reaction with sodium methoxide and with lithium chloride. With lithium chloride substitution predominated and the major product was methyl 12-chloro-oleate. Since it was completely oxidised under Von-Rudloff oxidation there was no evidence of any cyclopropane compounds. Some hydroxy esters were also formed (possibly resulting from the water present in hydrated lithium chloride) and these

appeared to be a mixture of olefinic and cyclopropane hydroxy ester. Elimination products were also present.

With sodium methoxide the elimination products were dominant (78%) and were mainly conjugated dienoates (66%). Since these are readily separated from the minor amounts of methoxy and hydroxy esters also formed this is a convenient way of preparing methyl octadecadienoate from methyl ricinoleate.

10. The reaction of methyl 12-mesyloxyoleate in dimethylsulphoxide solution with several reagents has been examined. When heated alone in this solvent or along with calcium carbonate or sodium methoxide elimination products are dominant. These probably have the following structures:

	9c12t	9c11t	9t11t	other products
DMSO	23%	21%	30%	12-hydroxy and 12-mesyloxyoleate (26%)
DMSO, CaCO ₃	15	35		12 oxo 18:1 (26%), 12OH and 12 OMs 18:1 (24%)
DMSO, NaOMe	-	28,	72	

It is clear that reaction with sodium methoxide and dimethyl sulphoxide provides a very efficient way of making the conjugated dienoate. We are not able to explain the formation of the oxo-oleate in the reaction with calcium carbonate.

With lithium chloride the major product ($\sim 70\%$) is probably methyl 12-chloro-oleate. Similar reactions with magnesium bromide and with potassium iodide seemed to give mainly elimination products (70-78%) but since the expected bromo and iodo-oleates are not easily separated from the elimination products and might undergo an elimination decomposition on the GLC column it is uncertain at what stage the elimination products were formed.

11. Less satisfactory results were obtained using acetone as solvent. In many cases a considerable proportion of the mesyloxyoleate remained unchanged after 12 hours boiling. Insofar as reaction occurred, elimination and substitution products resulted but none of them merited extensive examination.
12. In a single experiment in tetrahydrofuran solution methyl 12-mesyloxyoleate and lithium chloride did not undergo extensive reaction.
13. When heated in boiling triglyme methyl 12-mesyloxyoleate decomposed to give methyl octadecadienoates (non-conjugated isomers 54% and conjugated isomers 32%) as the only identified products.

Conclusion

When methylricinoleate is converted into its mesyloxy ester to furnish a better leaving group it undergoes a number of interesting reactions

In solvents of moderate polarity (dimethyl sulphoxide, acetonitrile, triglyme) and in the presence of base (sodium methoxide) the major reaction is elimination leading to mixtures of conjugated and non-conjugated methyl¹octadecadienoates.

Under other conditions substitution reactions become more significant and in buffered solutions it is possible to isolate cyclopropane compounds in good yield (~30-63%). If the solution is acidic the cyclic compounds are unstable and the final product is mainly the trans isomer of a 12-substituted octadecenoate. The substituted cyclopropane esters are very reactive and readily undergo rearrangement reactions.

EXPERIMENTAL

Purification of Solvents

All solvents used in the reactions and for extraction were distilled before use. Dry methanol was prepared by Vogel's procedure. Pyridine was dried over potassium hydroxide, distilled, and kept over potassium hydroxide. Carbon disulphide was distilled and stored over calcium chloride. 46

42-45

Thin layer chromatography (TLC)

Two types of TLC plates were used, silica gel and silica gel impregnated with silver nitrate (10%). The analytical plate layers were 0.25 mm thick when wet and the preparative layers 1 mm thick when wet.

The glass plates (20 x 20 cm) were first cleaned and dried. Silica gel G (100 g for 1 mm layer and 30 g for 0.25 mm layer) was added to distilled water (190 ml, for 1 mm and 60 ml for 0.25 mm layer) in a 1 litre flask. Five plates are placed together on the template. The spreader is adjusted to give the correct thickness. The silica is shaken with the water for 2-3 minutes, and poured quickly into the spreader which is then pulled across the plates at an even rate. The spreader is removed, and the template agitated slightly to allow the layer to settle evenly. After standing for a few minutes, the plates are placed in a rack and activated in an oven at 105°C for 2-3 hours. The plates are stored in a storage cabinet and should be

completely cooled before use. Preparation of the silver nitrate plates is carried out by the same technique, but silver nitrate (10% of the weight of silica) is first dissolved in the water before silica is added.

The methyl esters were applied to the plates and eluted with a suitable solvent such as 25% ether in petroleum ether (abbreviated as PE25). The plates are visualised by iodine vapour, by spraying with an ethanolic solution (0.2%) of 2,7-dichlorofluorescein^{cein} and viewing under ultra violet light, or by heating the oven for a few minutes after spraying with 10% phosphomolybdic acid in ethanol. (Only dichlorofluorescein was suitable for preparative plates).

47-53

Gas liquid chromatography (GLC)

For normal information about the type of acids present, the methyl esters were normally run on a polar column [columns were of stainless steel or glass (5 feet x 1/4 of an inch), packed with Gaschrom Z coated with 20% diethylene glycol succinate polyester (DEGS)], and a non-polar column [columns were packed with Gaschrom Z coated with 5% Apeizon L grease (ApL)]. The columns were fitted in to a Pye 104 machine operated at 190° and 210° respectively for these two columns. In some cases and for better separation of the methyl esters, capillary columns (DEGS and ApL) were used. These were operated on the same machine at 175°C. The methyl esters were injected in ether

solutions (20 mg/ml). Retention times are reported as equivalent chain lengths (ECL) (carbon numbers) and the areas of the peaks were calculated by multiplying the peak height by peak width at half height or by using a peak analyser machine (Du Pont 310 Curve Resolver).

Spectroscopic analysis

14-20

Infra-red spectrum IR.

The infra-red spectrum gives information about the configuration of the double bond as it shows absorption bands between 960 and 995 cm^{-1} for the trans monoene and for the conjugated dienes (cis-trans and trans-trans). Methoxy (1100 cm^{-1}), acetoxy (1250 and 1370 cm^{-1}), oxo (1710 cm^{-1}) and hydroxy (3500 cm^{-1}) groups also give diagnostic absorption bands on the infra-red spectrum. Samples were usually run as thin films in sodium chloride discs or as carbon disulphide solutions (1%), using 1 mm pathlength liquid cells with sodium chloride windows. The machines used were Perkin Elmer 237 and 257 grating infra-red spectrophotometers. More accurate spectra were recorded on a Perkin Elmer 621 grating spectrophotometer.

14-20

Nuclear magnetic resonance spectra (NMR)

Spectra were recorded on a Perkin Elmer R10 spectrometer operating at 60 Mc/sec using 15-20% solutions in carbon tetrachloride with tetramethylsilane as internal standard. This gives useful information

about the presence of unsaturation (4.65 τ) and of some functional groups, like formate (2.05 τ), acetate (8.05 τ), methoxy (6.75), cyclopropane ring (9.4-10.3 τ) etc.

Mass spectra (MS). ^{29,15}

MS were measured using an AEI MS902 machine.

General chemical methods:

Hydrogenation

Hydrogenation was carried out in a hydrogen atmosphere for 15 minutes at room temperature in dry methanol using 10% palladium charcoal as catalyst. The catalyst was removed by filtration and destroyed before it dries. The solvent was evaporated under reduced pressure and the material recovered. Many hydrogenations were effected on 20 mg of sample dissolved in 5 ml of methanol in the presence of 10-15 mg of catalyst.

Esterification ^{54,14}

Esterification was carried out by refluxing (10-20 minutes) the acid (100 mg) with methanolic boron trifluoride solution [14% solution (2 ml) diluted with methanol (10 ml)]. The reaction mixture poured into water, extracted with ether, and washed with 5% sodium bicarbonate solution.

24-26

Von-Rudloff oxidation (V.R.)

The position of unsaturated centre was determined by oxidation with V.R. reagent prepared by dissolving potassium permanganate (0.2 g) and sodium metaperiodate (10.4 g) in water (500 ml).

The sample (20 mg) was shaken overnight with potassium carbonate solution (0.5%, 3 ml), water (3 ml), tertiary butanol (distilled, 10 ml), and V.R. reagent (6 ml). Thereafter sulphur dioxide was passed through to destroy excess oxidising agent. The solution was basified with potassium pellets, the solvents removed under reduced pressure, and the residue acidified with dilute hydrochloric acid, saturated with sodium chloride, and extracted with ether. The product was removed from the solvent and methylated (by methanolic boron trifluoride) to be examined by GLC.

55

Hydrazine reduction

Hydrazine reduction was carried out by adding hydrazine hydrate (3 ml, 4%) and glacial acetic acid (0.1 ml) to the diunsaturated methyl ester (50 mg), dissolved in methanol (5 ml) and the solution heated at 50° for three hours. Air was bubbled through the solution continuously. The solution then acidified and extracted with ether. The product separated on silver ion TLC and examined on GLC and I.R. spectrum.

The separation and isolation methods.

The principal separation procedures used were:

(I) Separation of oxygenated esters from one another and from non-oxygenated esters, usually carried out by silica column chromatography⁴⁵ and/or thin layer chromatography (1 mm thick layer of silica using PE25 as developing solvent).

(II) Thin layers of silica impregnated with silver nitrate (10%) were used for separation of unsaturated esters from one another and from saturated esters.

(III) Separation of unsaturated esters from saturated esters was also carried out by thin layer chromatography after reaction with mercuric acetate.²⁷ This reacts with unsaturated esters, increases their polarity and so renders them separable from saturated esters. After extraction from the silica, the unsaturated esters are regenerated by stirring with 5% solution of methanolic hydrochloric acid. The mercuric acetate reagent was prepared by dissolving mercuric acetate (14 g) in methanol (250 ml), glacial acetic acid (2.5 ml) and water (1 ml). This solution (3 ml) was kept in the dark for 24 hr. with the mixture of saturated and unsaturated esters (100 mg). The product was extracted as usual and separated by preparative TLC (PE 25).

(IV) Separation of saturated and unsaturated esters was also carried out in some cases, by V.R. oxidation. The reagent oxidises the unsaturated component in the mixture to free acids which dissolve in the alkaline solutions, whilst the (neutral) saturated component remains unchanged. When extracted with latter goes in the ether layer. The acidic degradative products can be recovered from the alkaline extract by acidification and re-extraction.

Preparation of methylricinoleate.

Neutral castor oil (10 g) was refluxed with methanol (120 ml) containing (0.5 g) of sodium, for one hour. After dilution with water the mixed methyl esters (8.5 g) were extracted with ether and recovered in the usual way.

Methyl ricinoleate was isolated from the esters (2 g) by chromatography using a silica column (50 x 2½ cm) and eluting with petroleum ether containing increasing proportions of ether (10%, 20%, 30%, 40%) collecting 200 ml from each elute. These elutions were examined on TLC and the fractions rich in methylricinoleate were combined (1.7 g). These were finally purified by preparative TLC using PE25 as developing solvent. Methylricinoleate was extracted from the plates with ether and shown to be pure by GLC.

ECL: 25.8 (DEGS) and 19.7 (ApL).

Preparation of methyl 9-hydroxyoctadic-cis-12-enoate:

This hydroxy acid was available as concentrates (30-60%) prepared from various *Strophanthus* oils by partition of the mixed acids between petroleum and aqueous methanol (80%). The concentrates were methylated by refluxing with methanolic solution of boron trifluoride and the hydroxy ester was isolated by column chromatography (silica Gel, 50 x 2½ cm) by elution with petroleum containing increasing proportions of ether (10%, 20%, 30% ... etc.) Eleven fractions (200 ml each) were collected and examined by TLC. Fractions rich in hydroxy ester were combined and further purified by TLC (PE25). In a typical experiment 1.8 g of ester (37% pure), gave 600 ng of pure product.

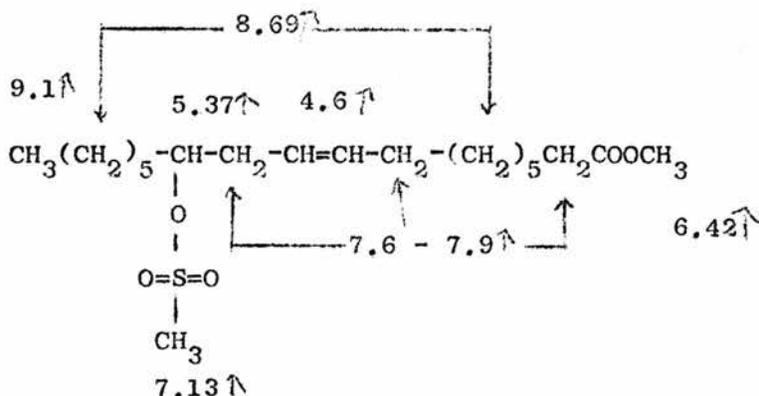
ECL: 25.9 (DEGS) and 19.7 (ApL); TMSI ether 19.7 (DEGS).

57

Conversion of hydroxyester to mesyloxy ester.

Methyl 12-mesyloxyoleate

Methylricinoleate (1.5 g) was stirred with methyl sulphonyl chloride (1 ml) and pyridine (10 ml) for four hours at 10°C and then poured into hydrochloric acid (2M, 20 ml). The product (1.6 g) was extracted with ether and purified by preparative TLC (PE25). The NMR spectrum showed the following signals.



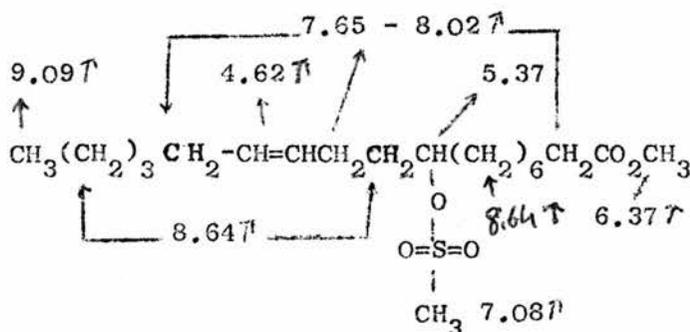
The infra-red spectrum showed absorption bands at 920, 1180 and 1370 cm^{-1} (very strong), and complete absence of the hydroxyl absorption band (3500 cm^{-1}).

On GLC (DEGS) the mesyloxyoleate gave a reproducible series of peaks at 19.4 (50%), 20.4 (21%), 20.8 (14%), 21.1 (10%) and 23.3 (5%) which are thought to arise from on-column decomposition of the ester.

57

Methyl 9-mesyloxyoctadec-cis-12-enoate:

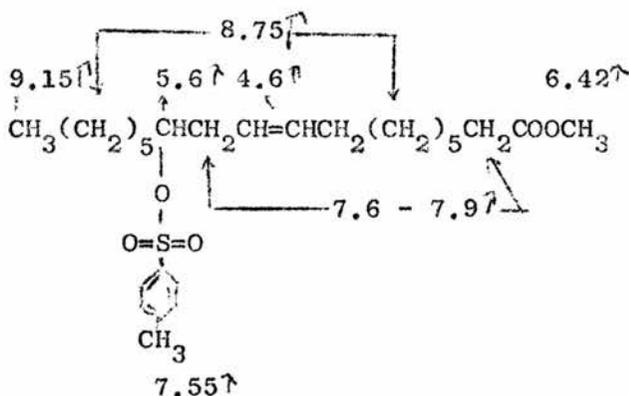
Methyl 9-hydroxy ester (2.7 g), treated similarly with mesyl chloride (1 ml) and pyridine (10 ml), gave methyl 9-mesyloxyoctadec-cis-12-enoate (2.20 g) which was purified by TLC in the same way as above. The NMR showed the following signals.



57b

Conversion of hydroxy ester to tosyloxy ester:

Methylricinoleate (200 mg) was stirred with toluene-p-sulphonyl chloride (100 mg) and pyridine (~3 ml) for four hours at room temperature (~10°C). Poured into dilute hydrochloric acid (2M, 20 ml) and extracted as usual with ether to give the tosyloxy ester (180 mg). Its NMR spectrum showed the following signals.



Preparation of trans hydroxyoctadecenoates⁵⁸⁻⁵⁹

The trans-ester was prepared by isomerization of the cis-ester with nitric acid and sodium nitrite

Methyl ricinelaideate:⁵⁸⁻⁵⁹

Ricinoleic acid (4 g) was shaken vigorously with nitric acid (6M, 30 ml) and freshly prepared sodium nitrite (2M, 50 ml) for half an hour. The recovered acid was esterified by methanolic boron trifluoride (14% solution) and a portion of the product (1.0 g) was purified on preparative TLC impregnated with silver nitrate using PE25 as developing solvent. The trans ester (520 mg) was recovered from the appropriate band. It had an ECL of 25.6 (DEGS) and strong absorption at 978 cm^{-1} in its infra-red spectrum due to the trans double bond.

Methyl 9-hydroxyoctadec-trans-12-enoate:

The cis hydroxy ester (1 g) was hydrolysed by boiling with sodium hydroxide (10%, 5 ml) and methanol (10 ml) for one hour. After the acidification, the acid (900 mg) was recovered. This acid (500 mg) was isomerized by shaking vigorously with nitric acid (6M, 4 ml) and sodium nitrite (2M, 6 ml) for 20 minutes. The recovered acid was methylated (by methanolic boron trifluoride) and the ester purified by preparative silver ion TLC (PE25). Extraction of the appropriate band with ether gave the trans ester (220 mg) which had an ECL of 25.6 (DEGS), and showed the trans absorption band in its infra-red spectrum (970 cm^{-1}).

Conversion of the hydroxy ester to methoxy ester:²⁸

Hydroxy esters were converted to methoxy esters by reaction with silver oxide and methyl iodide.

The silver oxide was freshly prepared by mixing aqueous solutions of silver nitrate (10%) and sodium hydroxide (10%, 10 ml). The liquid was decanted from the precipitated oxide which was thoroughly washed with water (12 x 10 ml) and with ether (6 x 10 ml).

Methyl 12-methoxyoleate:²⁸

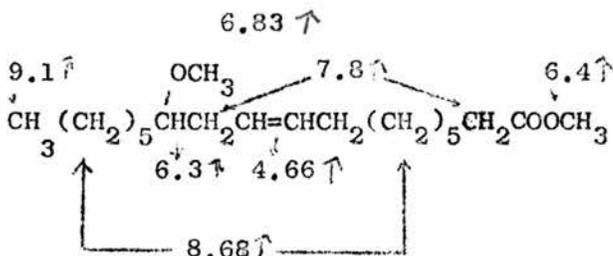
Methyl 12-hydroxyoleate (300 mg) was refluxed with silver oxide (120 mg) and methyl iodide (2 ml) for four hours. After addition of ether (10 ml) the reaction mixture was filtered and the product was purified by preparative TLC (PE25). The methoxy ester (210 mg) was 99% pure by GLC, and showed the following properties:

GLC_ (DEGS) 21.4, (ApL) 18.7

IR spectrum: showed an ether peak (1100 cm^{-1}), ester peak (1740 cm^{-1}) and the complete absence of a hydroxyl peak (3500 cm^{-1}).

The NMR spectrum showed signals for the methyl ether (6.83') and for olefinic protons (4.66').

The structure is:



Von-Rudloff oxidation gave nonanedioic acid and (presumably) 3-methoxy nonanoic acid (ECL after methylation, DEGS, 12.0).

Hydrogenation gave methyl 12-methoxy stearate (DEGS) 21.2, (ApL) 18.6.

Mass spectrum (after hydrogenation) see page 89.

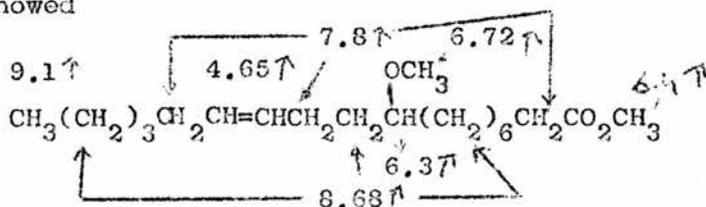
Methyl 9-methoxyoctadec-cis-12-enoate:

Methyl 9-hydroxyoctadec-cis-12-enoate (175 mg) was refluxed with silver oxide (60 mg) and methyl iodide (1 ml) for four hours. After addition of ether (5 ml), the reaction mixture was filtered and the product was purified by preparative TLC using (PE25) as developing solvent. The ester (120 mg) was about 98% pure by GLC and showed the following properties:

GLC: (ECL (DEGS) 21.4, (ApL) 18.7

IR spectrum: absorption bands at 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester) with the complete absence of the hydroxyl group.

NMR spectrum: showed



V.R. oxidation: gave hexanoic acid and (presumably) 4-methoxydodecanedioic acid (ECL of methyl ester 23.3 on DEGS).

Hydrogenation: gave methyl 9-methoxystearate (DEGS) 21.2; (ApL) 18.7

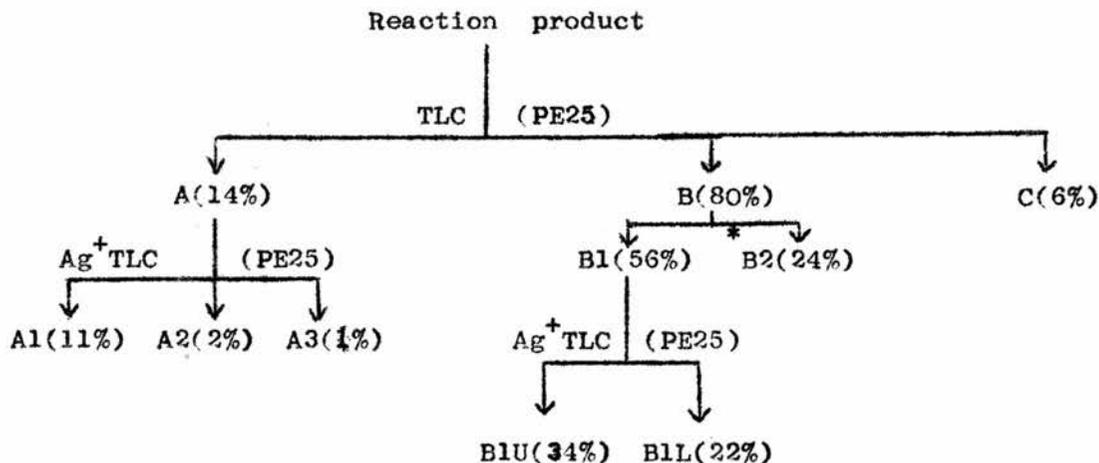
Mass spectrum: (after hydrogenation) see page

The reaction of methyl-12-mesyloxyoleate with methanol and sodium methoxide:

The mesyloxy ester (200 mg) was refluxed for four hours with methanol (30 ml), and sodium methoxide (30 mg). The product (180 mg), recovered by neutralization with acetic acid, addition of water and extraction with ether, was separated as shown in scheme (1).

Chromatographic and spectroscopic information about each fraction is presented.

Scheme (1)



* Fraction B was divided into (B1) and (B2) in two ways:-

1. V. Rudloff oxidation:²³⁻²⁶ oxidises the unsaturated component (B2) to free acids which can be separated from the neutral unoxidised ester (B1) (see general methods). This procedure is recommended for getting the saturated component.
2. By TLC after reaction with mercuric acetate.²⁷ This reacts with the unsaturated component only and increases its polarity making it separable from the saturated component. The unsaturated component was regenerated by stirring with methanolic hydrochloric acid. (See general methods).

Reaction product:

GLC (DEGS) 19.4 (4%), 20.4 (11%), 21.2 (60) and 21.4 (25%)

IR spectrum:

960 and 995 cm^{-1} (conjugated cis-trans dienes), 1020 and 3070 cm^{-1} (cyclopropane), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3500 cm^{-1} (small, hydroxyl).

Fraction A and subfractions A1, A2, and A3:GLC: Before hydrogenation:

(DEGS) 19.4 (15%), 20.4 (67%), 20.6 (11%) and 20.9 (7%)

(ApL) 17.0 (2%), 17.6 (13%), 18.2 (65%), 18.4 (16%)

and 18.6 (4%).

After hydrogenation:

(DEGS) 18.0

(ApL) 17.3 (3%) and 18.0 (97%).

Subfraction A1:GLC (DEGS) 20.4 (70%), 20.6 (20%) and 20.95 (10%).IR spectrum: 960 cm^{-1} and 990 cm^{-1} (conjugated cis-transdienes), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes).UV spectrum: 233 nm (conjugated dienes).Von Rudloff oxidation: nonanedioic acid.Subfraction A2:GLC (DEGS) 19.4IR spectrum: 975 cm^{-1} (trans alkenes), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkenes).Von Rudloff oxidation: nonanedioic acid

Subfraction A3:

GLC (DEGS) 16.0 (3%), 19.6 (86%), 20.55 (5%) and 21.65 (6%)

IR spectrum: 1740 cm^{-1} (ester), and 3010 cm^{-1} (alkenes).

Von Rudloff oxidation: nonanedioic acid.

Fraction B:

GLC (DEGS) 21.2 (70%) and 21.4 (30%).

Capillary column (DEGS) 20.2 (1%), 20.95 (21%), 21.15 (43%) and 21.35 (35%).

IR spectrum: 1620 cm^{-1} and 3010 cm^{-1} (alkenes), 1100 cm^{-1} (ether) 1740 cm^{-1} (ester) and 3070 cm^{-1} (cyclopropane).

NMR spectrum: 4.65 τ , (aliphatic protons), 6.75 τ (OCH_3), and 9.55 τ , 9.65 and 9.75 τ (cyclopropane protons).

Fraction E1:

This fraction contains two components (as shown in scheme 1, BIU and BIL). These two components had the same ECL, the same infra-red absorption spectrum, and the same mass spectrum but they differed in their NMR spectra in one respect. The ester in the upper band (BIU) had signals at 9.78 τ and 9.88 τ whilst in the lower band (BIL) these appeared at 9.55 τ and 9.65 τ .

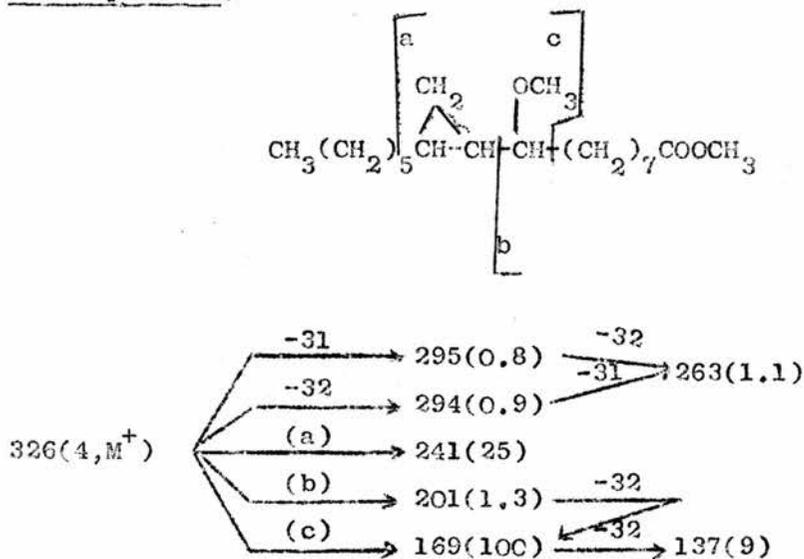
GLC (DEGS) 19.1, 19.4, 22.1 (8%) and 21.2 (92%)

(ApL) 17.3, 17.7 and 18.4 (major)

IR spectrum: 1020 cm^{-1} and 3070 cm^{-1} (cyclopropane),
 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

NMR spectrum: 6.75τ (ether $\text{O}-\text{CH}_3$); 9.55τ and 9.65τ
 (BIL); 9.78τ and 9.88τ (BIU) (cyclopropane protons).

Mass Spectrum:



Fragment (a) results from cleavage α to the cyclopropane ring, fragment (c) results from cleavage α to the methoxy group and fragment (b) from cleavage α to both these groups. These fragments and the molecular ion peak readily lose one or more small fragments of (-31 , CH_3O and -32 , CH_3OH).

Fraction B2:

GLC (DEGS) 21.4 (of 21.2 after hydrogenation)

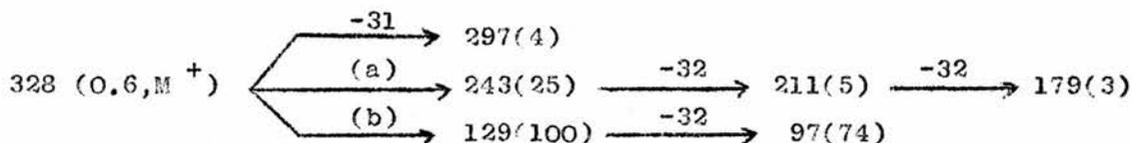
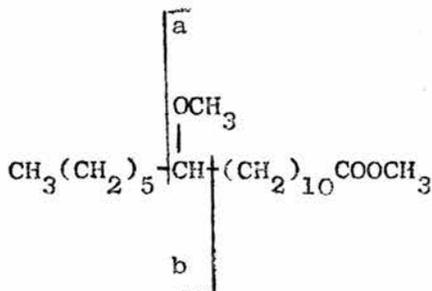
(ApL) 19.6.

IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

NMR spectrum: 4.65 \uparrow (olefinic protons), and 6.75 \uparrow (O-CH₃).

Von-Rudloff oxidation: nonanedioic acid and (presumably 3-methoxy nonanoic acid (DEGS, 12.0).

Mass spectrum: (after hydrogenation).



Fragments (a) and (b) result from cleavage α to the methoxy group.

These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31, CH_3O , and 132, CH_3OH).

Methyl-12-methoxyoleate: An authentic sample of methyl-12-methoxyoleate was prepared from methylricinoleate by reaction with methyl iodide and silver oxide (see general methods). It had the following chromatographic and spectroscopic characteristics

GLC: (DEGS) 21.4 (21.2 after hydrogenation).

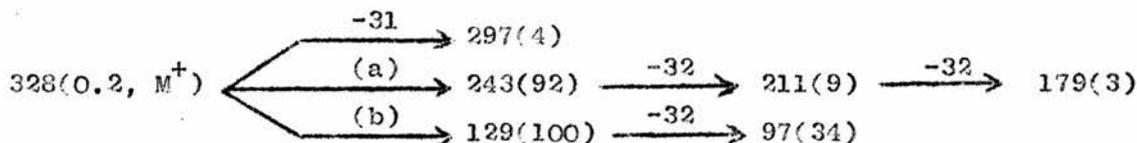
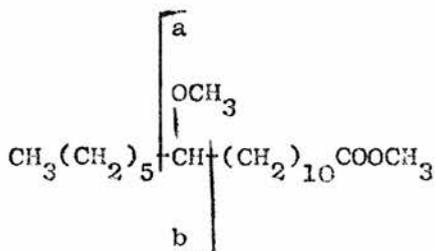
(ApL) 18.6

IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

NMR spectrum: 4.65τ (olefinic protons) and 6.75τ (OCH_3).

Von-Rudloff oxidation: nonanedioic acid and (presumably) 3-methoxynonanoic acid (DEGS 12.0).

Mass spectrum: (after hydrogenation).



Fragments (a) and (b) result from cleavage α to the methoxy group. These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31 and -32).

Fraction C:

GLC: (DEGS) 19.4, 20.4, 20.6 and 21.0 (peaks from unreacted mesyloxy ester, about 40%) and 26.0 (60%).

IR spectrum: 920 cm^{-1} , 1020 cm^{-1} and 1180 cm^{-1} (mesyloxy ester), 1740 cm^{-1} (ester), 3010 cm^{-1} (alkene) and 3500 cm^{-1} (hydroxyl).

The reaction of methyl-12-mesyloxyoleate with methanol in the presence of sodium methoxide for different periods of time:

This reaction has been carried under the same conditions as in (4) but for different periods of time, and the table below shows the changes in the relative amounts of the four major peaks.

Time hr.	Area (%) under major peaks (DEGS)			
	19.4	20.4	21.2	21.4
2	10	12	53	24
4	4	11	59	26
6	4	10	59	27
8	4	11	59	26

The reaction of methyl-12-tosyloxyoleate with methanol and sodium methoxide.

The tosyloxy ester (100 mg) was refluxed with methanol (20 ml) and sodium methoxide (15 mg) for four hours. The product recovered by neutralization with acetic acid, addition of water and extraction with ether was separated by preparative TLC (PE25) into two fractions: A (20%) and B (80%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.4 and 20.4 (20%), 21.2 and 21.4 (80%)

IR spectrum: 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1100 cm^{-1} (ether), and 1740 cm^{-1} (ester).

NMR spectrum: 4.65 \uparrow (olefinic protons), 6.75 \uparrow ($\text{O}-\underline{\text{CH}}_3$), and 9.55 \uparrow and 9.75 \uparrow (cyclopropane protons).

Fraction A:

GLC: (DEGS) 18.5, 19.4, 20.4, 20.8 and 21.0

IR spectrum: 960 cm^{-1} and 990 cm^{-1} (conjugated cis-trans dienes), 1740 cm^{-1} (ester), and 3020 cm^{-1} (alkene).

Fraction B:

GLC (DEGS) 19.3, 21.2 (70%) and 21.4 (25%)

IR spectrum: 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1100 cm^{-1} (ether), and 1740 cm^{-1} (ester).

NMR spectrum: 4.65 τ (olefinic protons), 6.75 τ (OCH_3),
and 9.55 τ (cyclopropane protons).

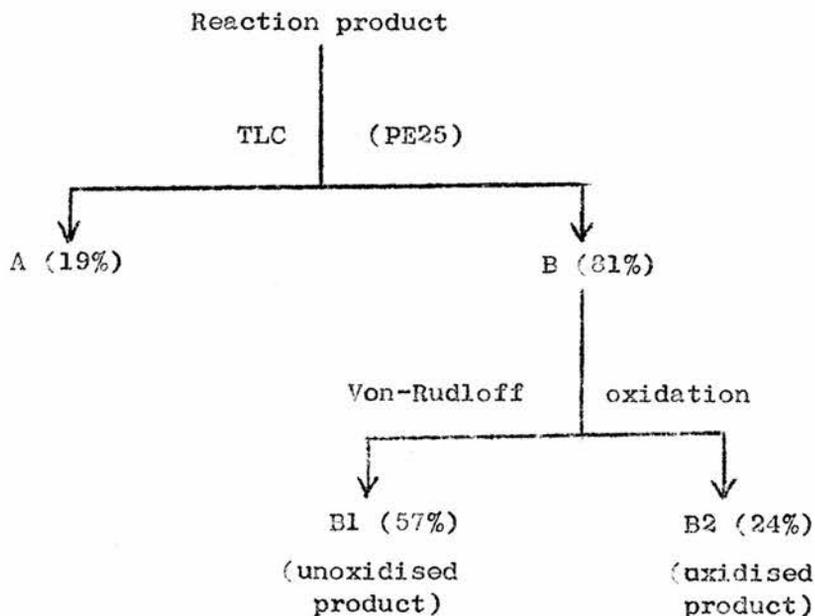
Von-Rudloff oxidation: nonanedioic acid and (presumably)
3-methoxynonanoic acid (DEGS 12.0) 30%) along with unoxidised
ester (cyclopropane ether) (DEGS, 21.2) 70%).

The reaction of methyl-12-mesyloxyelaidate with methanol and sodium methoxide:

The mesyloxy ester (90 mg) was refluxed for four hours with methanol (20 ml) and sodium methoxide (10 mg). The product recovered by neutralization with acetic acid, addition of water and extraction with ether was readily separated as shown in Scheme (2).

Chromatographic and spectroscopic information about each fraction is presented.

Scheme (2).



Reaction product:

GLC: (DEGS) 19.2 and 20.2 (15%) and 21.2 (85%)

(ApL) 17.6, 19.1, 18.4 and 18.6

IR spectrum: 975 cm^{-1} (transalkene), 995 cm^{-1} (conjugated trans-trans diene), 1100 cm^{-1} (ester), 1730 cm^{-1} (ester) and 1030 cm^{-1} and 3065 cm^{-1} (cyclopropane)

NMR spectrum: 4.65 τ (olefinic protons), 6.74 τ (O.CH₃) and 9.55-9.65 τ (cyclopropane protons).

Fraction A:

GLC: (DEGS) 18.5 (13%), 19.2 (30%), 20.3 (25%) and 21.0 (32%)

IR spectrum: 975 cm^{-1} (transalkene), 995 cm^{-1} (conjugated trans-trans diene) and 1740 cm^{-1} (ester).

Fraction B (B1 and B2)

GLC: (DEGS) 19.0 and 19.3 (3%) and 21.2 (97%)

IR spectrum: 975 cm^{-1} (trans alkene), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 1030 cm^{-1} and 3065 cm^{-1} (cyclopropane).

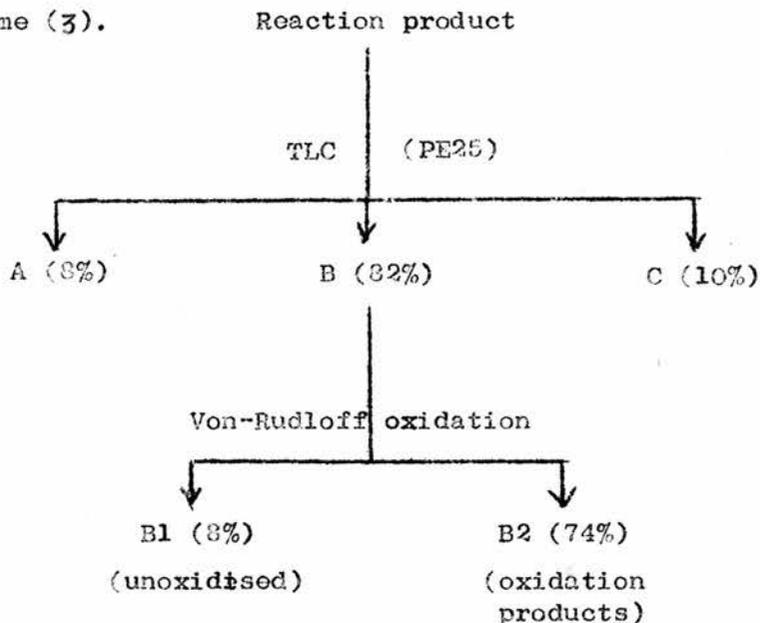
NMR spectrum: 4.65 τ (olefinic protons), 6.75 τ (O.CH₃) and 9.5 τ and 9.65 τ (cyclopropane protons).

Von-Rudloff oxidation: B1 (71%): methoxy cyclopropane (DEGS, 21.2) B2 (29%): nonanedioic acid and presumably 3-methoxy nonanoic acid (DEGS, 12).

The reaction of methyl-12-mesyloxyoleate with methanol:

The mesyloxy ester (150 mg) was refluxed for four hours with methanol. The product (135 mg) recovered by neutralization with sodium bicarbonate (5% solution), addition of water and extraction with ether was separated as shown in scheme (3). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (3).



Reaction product:

GLC: (DEGS) 19.4 (4%), 20.4 and 20.6 (2%), 21.4 (90%) and 23.3 (4%)

(ApL) 17.6 (9%), 18.1 (3%), 18.6 (86%), and 19.5 (2%)

Fraction A:

GLC: Before hydrogenation (DEGS) 19.4 (62%), 20.4 (62%), 20.4 (24%), 20.6 (2%), 20.9 (5%)m 21.4 (3%) and 23.0 (2%), (ApL) 17.3 (6%), 17.6 (53%), 18.2 (19%), 18.4 (2%), 18.6 (14%) and 19.7 (6%).

After hydrogenation (DEGS) 17.3 (13%) and 18.0 (87%)

ApL) 17.3 (13%) and 18.0 (87%).

IR spectrum: 970 cm^{-1} (trans ethane) and 1740 cm^{-1} (ester).

Fraction B:

GLC: (DEGS) 21.4 (21.2 after hydrogenation)

(ApL) 18.7

(DEGS) capillary column 21.00, 21.10 and 21.30 (10%), 21.35 (57%) and 21.45 (33%).

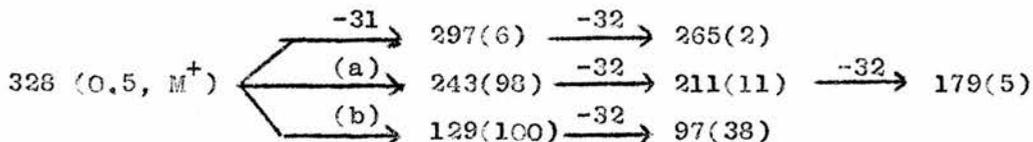
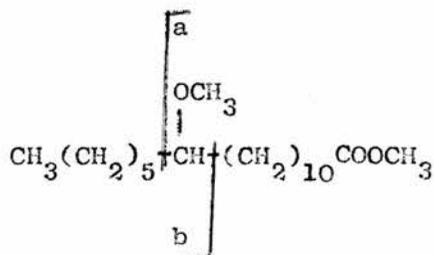
IR spectrum: 980 cm^{-1} (trans alkene), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

NMR spectrum: 4.65 \uparrow (olefinic protons), and 6.75 \uparrow (O.CH₃).

Von-Rudloff oxidation: nonanedioic acid and (presumably 3-methoxy nonanoic acid (DEGS 12.0), along with the unchanged compound of ECL (DEGS 21.2).

* Fraction B was oxidized by Von-Rudloff oxidation to show the relative amounts of the saturated and unsaturated components it contains (see general methods), but not for separation. The saturated component is a minor component in this fraction.

Mass spectrum: (after hydrogenation).

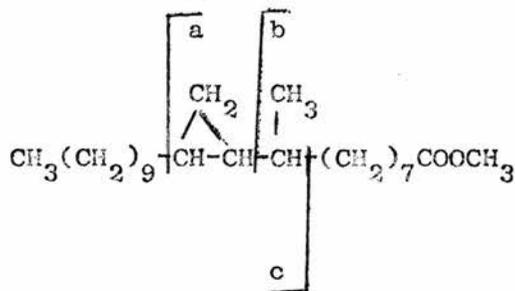


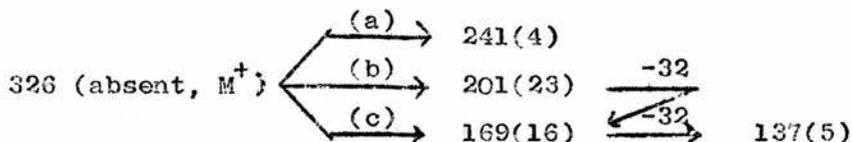
Fragments (a) and (b) result from cleavage α to the methoxy group.

These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31, CH_3O and -32, CH_3OH).

The mass spectrum showed some other peaks which probably result from the fragmentation of the methoxy cyclopropane (10%) present in this fraction.

These peaks are as follows





Fragments (a) results from cleavage α to the cyclopropane ring, fragment (c) results from cleavage α to the methoxy group, and fragment (b) results from cleavage α to both these groups. These fragments readily lose one or more smaller fragments of (-31 and -32).

Fraction C:

GLC: (DEGS) 19.4, 20.4, 20.6 and 21.0 (peaks from unreacted mesyloxy ester) and 26.0

IR spectrum: 920 cm⁻¹, 1020 cm⁻¹ and 1180 cm⁻¹ (mesyloxyester), 1740 cm⁻¹ (ester), 3010 cm⁻¹ (alkene) and 3500 cm⁻¹ (hydroxyl).

The reaction of methyl-12-mesyloxyoleate with methanol for different periods of time:

This reaction has been carried under the same conditions as in (19), but for different periods of time and the changes in the relative amounts of the four major peaks (on GLC) are shown in the table below.

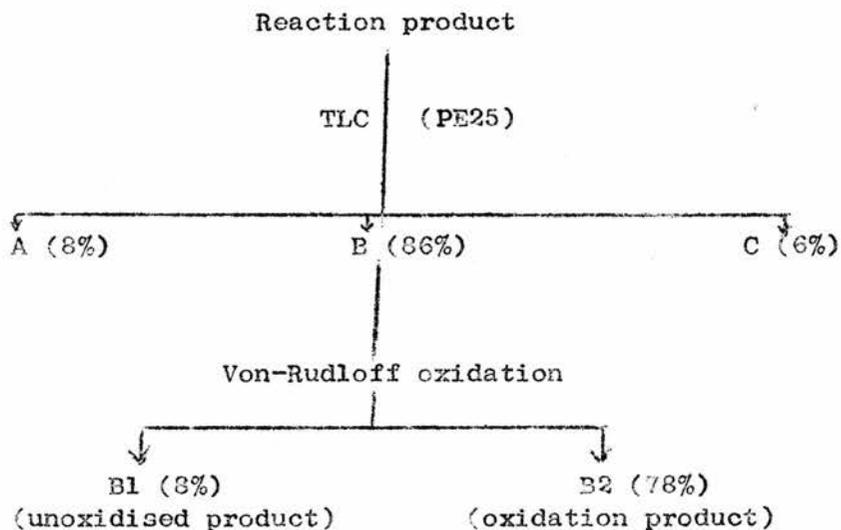
Time hr.	area (%) under major peaks (DEGS)			
	19.4	20.4	21.3	23.1
2	4	9	67	19
4	4	2	90	4
6	4	-	90	6
8	4	-	90	6

The reaction of methyl-1,2-mesyloxyoleate with methanol in the presence of sulphuric acid:

The mesyloxy ester (200 mg) was refluxed for four hours with methanol (20 ml) and sulphuric acid (conc. 0.1 ml). The product (190 mg) recovered by neutralization with sodium bicarbonate (0.5% solution), addition of water and extraction with ether, was separated as shown in scheme (4).

Chromatographic and spectroscopic informations about each fraction is presented.

Scheme (4).



Reaction product:

GLC: (DEGS) 19.4 (5%), 20.4 (2%) and 21.4 (92%)

IR spectrum: 930 cm^{-1} (trans alkene), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

Fraction A:

GLC: (DEGS) 19.4 (70%), 20.4 and 20.6 (30%) before hydrogenation and 18.0 after hydrogenation.

IR spectrum: 980 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 960 cm^{-1} and 995 cm^{-1} (very small, cis-trans conjugated diene).

Von-Rudloff oxidation: nonanedioic acid.

Fraction B:

GLC: (DEGS) 21.4 (21.2 after hydrogenation)

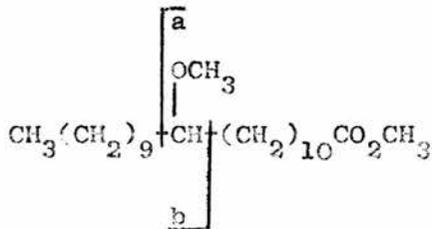
(ApL) 18.7

IR spectrum: 980 cm^{-1} (trans alkene), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

NMR spectrum: 4.65τ (olefinic protons) and 6.75τ (O.CH₃).

Von-Rudloff oxidation: nonanedioic acid and (presumably) 3-methoxynonanoic acid (DEGS, 12.0) along with some unoxidizable product (probably cyclopropane ether) (DEGS, 21.2)

Mass spectrum: (after hydrogenation).



The reaction of methyl 12-mesyloxyoctadec-9-ynoate with methanol and sodium methoxide:

The mesyloxy ester (100 mg) was refluxed for four hours with methanol (15 ml) and sodium methoxide (20 mg). The product (90 mg) recovered by neutralization with acetic acid, addition of water and extraction with ether, was separated by preparative TLC (PE25) into two fractions A (95%) and B (5%).

Chromatographic and spectroscopic information about each fraction is presented.

Reaction Product:

GLC: (DEGS) 21.1 (55%) and 23.0 (45%)

IR spectrum: 965 cm^{-1} (trans alkene), 1100 cm^{-1} (small, ether), 1740 cm^{-1} (ester), and 3030 cm^{-1} (alkene).

Fraction A:

GLC: Before hydrogenation (DEGS) 21.1 (60%) and 23.0 (40%); (ApL) 17.65 (58%) and 19.8 (42%), after hydrogenation DEGS 18.0.

IR spectrum: 965 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 3030 cm^{-1} (alkene).

NMR spectrum: 4.6 \uparrow (olefinic protons).

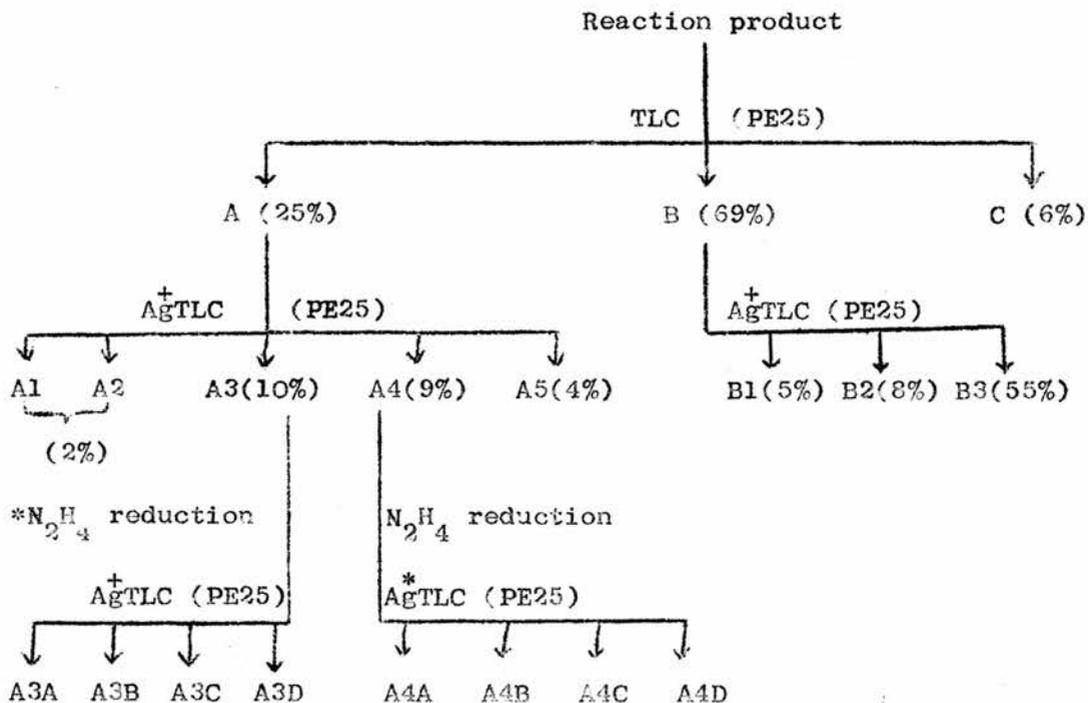
Fraction B:

GLC: (DEGS) 23.0 (90%) and 24.6 (10%)

The reaction of methyl 9-mesyloxyoctadec-cis-12-enoate with methanol and sodium methoxide:

The mesyloxy ester (100 mg) was refluxed for four hours with methanol (20 ml) and sodium methoxide (20 mg). The product recovered by neutralization with acetic acid, addition of water and extraction with ether, was separated as shown in Scheme (5). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (5).



* (general methods)

Reaction product:

GLC: (DEGS) 19.4 (25%) and 21.4 (75%), (ApL) 17.6 and 18.7

IR spectrum: 975 cm^{-1} (trans alkenes), 1100 cm^{-1} (ether)
and 1740 cm^{-1} (ester).

Fraction A and its subfractions:

The following results apply to fraction A except where otherwise stated.

GLC: (DEGS) 16.0 and 18.5 (2%) and 19.4 (98%) (ApL) 17.6 before hydrogenation and 18.0 on both columns after hydrogenation.

On (DEGS) Capillary column 19.0 (32%), 19.2 (10%) and 19.3 (28%).

A1 (DEGS) and 16.0 and 18.5

A2 (DEGS) 18.5

A3 - A5 19.4

IR spectrum: 975 cm^{-1} (trans alkenes) 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes)

A1 and A2 975 cm^{-1} (very small, trans alkenes), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes)

A3 and A4 975 cm^{-1} (very strong, trans alkenes), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes)

A5: 975 cm^{-1} (very small, trans alkene) 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

A3B: 975 cm^{-1} (trans alkenes), 1740 cm^{-1} (ester)

A3A, A3C and A3D 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes C and D only)

A4B: 975 cm^{-1} (trans alkenes) 1740 cm^{-1} (ester)

A4D: 975 cm^{-1} (small trans alkenes) 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes).

NMR spectrum: A3: 7.4 τ (large) and 7.9 τ (small)

A4: 7.4 τ (small) and 7.9 τ (large)

Von-Rudloff-oxidation: A1-A3 gave nonanedioic acid only.

A4 and A5 gave octanedioic acid and nonanedioic acid.

Fraction B (and B1, B2 and B3)

The following results apply to fraction B except where otherwise stated.

GLC: before hydrogenation (DEGS) 21.4 (ApL) 18.7

after hydrogenation (DEGS) 21.2 (ApL) 18.7

B1 (DEGS) 16.0, 18.5 and 19.3 major

B2 (DEGS) 21.4

B3 (DEGS) 21.4, (ApL) 18.7

IR spectrum: 1100 cm^{-1} (ether) 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene)

B1 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene)

B2 and B3 1100 cm^{-1} (ether) 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene)

NMR spectrum: 4.7 τ (olefinic protons) 6.78 τ (O.CH₃)

B1: 4.7 τ (olefinic protons)

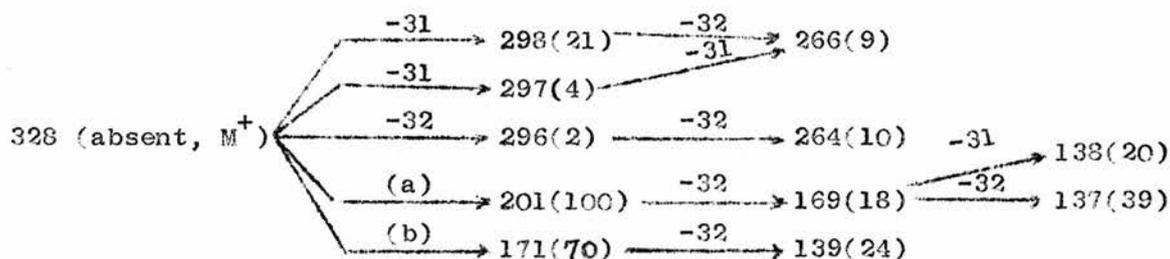
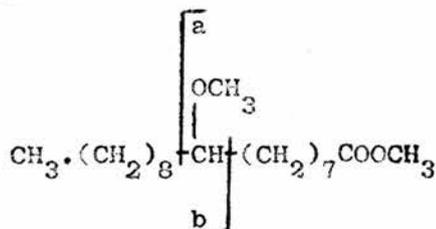
B2: 4.7 τ (olefinic protons) and 6.76 τ (O.CH₃)

B3: 4.7 τ (olefinic protons) and 6.78 τ (O.CH₃)

Von-Rudloff oxidation: hexanoic acid and (presumably)

4-methoxydodicanedioic acid (methylester ECL 23.3, DEGS).

Mass spectrum: (after hydrogenation).



Fragments (a) and (b) result from cleavage α to the methoxy group.

These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31, CH₃O, and -32, CH₃OH).

Methyl 9-methoxyoctadec-cis-12-enoate: An authentic sample of methyl 9-methoxyoctadec-cis-12-enoate was prepared from methyl 9-hydroxyoctadec-cis-12-enoate by refluxing with methyl iodide and silver oxide (see general). This sample gave the following chromatographic and spectroscopic information.

GLC: (DEGS) 21.4 (21.2 after hydrogenation)

(ApL) 18.7 (18.6 after hydrogenation)

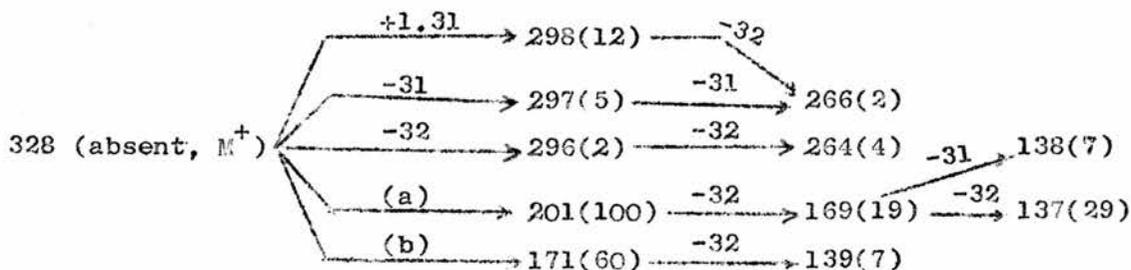
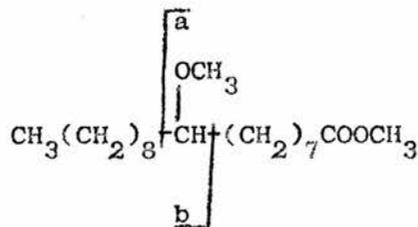
IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene)

NMR spectrum: 4.75 τ (olefinic protons) and 6.75 τ (O-CH₃).

Von-Rudloff oxidation: hexanoic acid and (presumably)

4-methoxydodecanedioic acid (DEGS, 23.3).

Mass spectrum: (after hydrogenation)



Fragments (a) and (b) result from cleavage α to the methoxy group. These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31, CH₃O, and -32, CH₃OH).

The reaction of methyl 9-mesyloxyoctadec-cis-12-enoate with methanol

The mesyloxy ester (100 mg) was refluxed with methanol (20 ml) for four hours. The product (90 mg) recovered by addition of water and extraction with ether, was separated by preparative TLC (DEGS) into three fractions: Fraction A (30%)

B (64%)

C (6%)

chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 16.0, 18.5, 19.2, 19.3 and 21.4

IR spectrum: 975 cm^{-1} (small, trans alkene), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

Fraction A:

GLC: (DEGS) 16.0, 18.5 (23%) and 19.3 and 19.4 (68%) (before hydrogenation) and 16.0 (10%) and 18.0 (90%) after hydrogenation.

On (DEGS) Capillary column the peaks of ECL 19.3 and 19.4 split into 19.05, 19.1 (36%), 19.25 (31%) and 19.35 (33%).

IR spectrum: 978 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

NMR spectrum: 4.72 τ (olefinic protons)

Von-Rudloff oxidation: hexanoic acid, octanedioic acid and nonanedioic acid.

Fraction B:

GLC: Before hydrogenation (DEGS) 21.4

After hydrogenation (DEGS) 18.0 (5%) and 21.2 (95%)

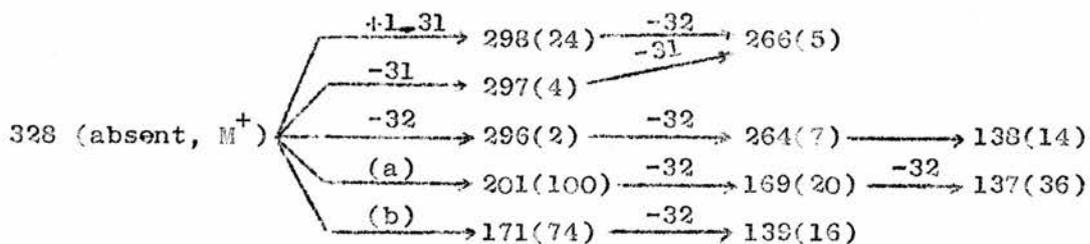
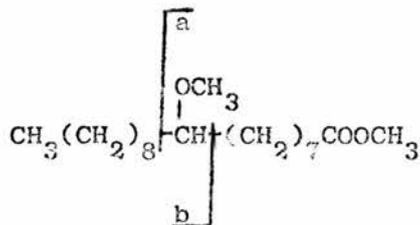
IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene)

NMR spectrum: 4.75 τ (olefinic protons) and 6.77 τ ($\text{O}-\underline{\text{C}}\text{H}_3$)

Von-Rudloff oxidation: hexanoic acid and (presumably)

4-methoxy dodecanedioic acid (DEGS, 23.3).

Mass spectrum: (after hydrogenation)



Fragments (a) and (b) result from cleavage α to the methoxy group.

These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31, CH_3O and -32, CH_3OH).

The reaction of methyl 9-mesyloxyoctadec-cis-12-enoate with methanol and sulphuric acid.

The mesyloxy ester (130 mg) was refluxed for four hours with methanol (20 ml) and sulphuric acid (2 drops). The product (122 mg) recovered by neutralization with acetic acid, addition of water and extraction with ether, was separated by preparative TLC into three fractions: A (28%), B (66%) and C (6%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 16.0, 18.5 and 19.4 (29%) and 21.4 (71%).

IR spectrum: 975 cm^{-1} (trans alkene), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

Fraction A:

GLC: (DEGS) 16.0, 18.5 and 19.4 (major).

IR spectrum: 978 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 3010 (alkene)

Von-Rudloff oxidation: hexanoic acid, octanedioic acid and nonanedioic acid.

Fraction B:

GLC: (DEGS) 21.4 before hydrogenation
21.2 after hydrogenation

IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 2010 cm^{-1} (alkene).

NMR spectrum: 4.75 τ (olefinic protons) and 6.77 τ (O.CH_3)

Von-Rudloff oxidation: hexanoic acid and (presumably)

4-methoxy dodecanedioic acid (DEGS, 23.3)

Fraction C:

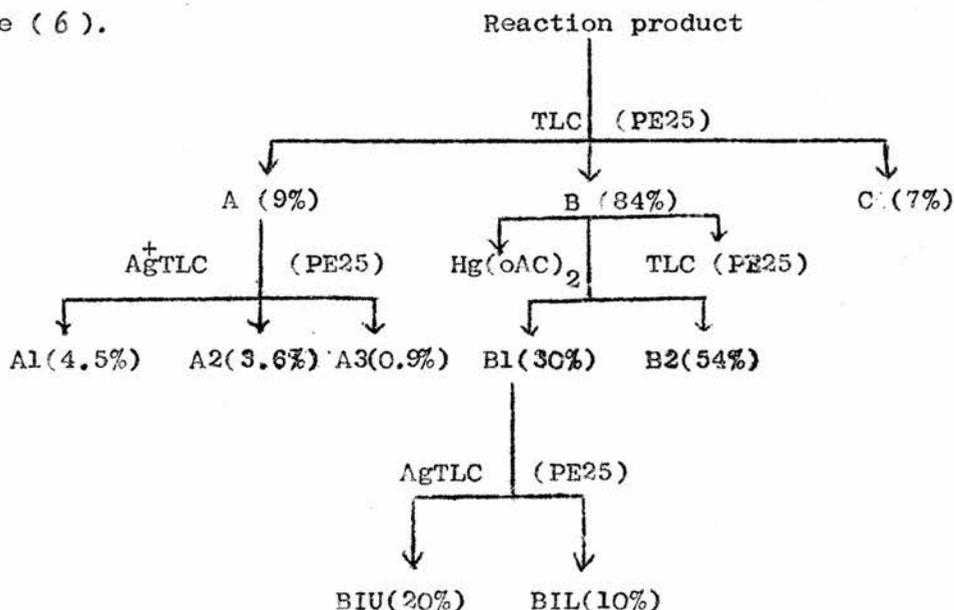
GLC: (DEGS) 19.4 and 26.0

IR spectrum: 920, and 1180 cm^{-1} (mesyloxyester)

The reaction of methyl 12-mesyloxyoleate with acetic acid and sodium acetate:

The mesyloxyester (100 mg) was heated (100°C) for four hours with acetic acid (10 ml) and sodium acetate (10 mg). The product (90 mg) recovered by addition of water and extraction with ether, was separated as shown in scheme (6). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (6).



Reaction product:

GLC: (DEGS) two series of peaks 19.4, 20.4, 20.8 and 21.2 (10-15%) and 23.3, 24.1 and 24.6 (85-90%)

IR spectrum: 975 cm^{-1} (trans alkene), 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1250 cm^{-1} and 1370 cm^{-1} (acetate), and 1740 cm^{-1} (ester).

NMR spectrum: 4.65 τ (olefinic protons), 80.5 τ (OCOCF_3), and 9.4 τ (cyclopropane protons).

Fraction A and subfractions A1 A2 and A3:

The following results apply to fraction A except where otherwise stated.

GLC: (DEGS) 19.2, 19.4 (major), 20.4, 20.8, 21.2, 22.7 and 23.2

A1: 19.2, 20.4, 20.8, 21.1 and 23.2

A2: 19.4

A3: 19.4

IR spectrum: 975 cm^{-1} (trans alkenes) and 1740 cm^{-1} (ester).

NMR spectrum: 4.65 τ (olefinic protons) and 7.2 (non-conjugated diene protons).

Von-Rudloff oxidation: nonanedioic acid as the only dibasic acid

Fraction B:

GLC: (DEGS) before hydrogenation 19.0, 19.4 (5%), 24.1 (27%) and 24.6 (66%)

after hydrogenation 18.0, 19.4, 21.2, 23.0, 24.1 and 24.3 (major)

(ApL) 17.4, 17.7, 17.9 and 19.55

IR spectrum: 975 cm^{-1} (trans alkene), 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane) 1250 cm^{-1} and 1370 cm^{-1} (acetate) and 1740 cm^{-1} (ester).

NMR spectrum: 4.65τ (olefinic protons), 8.04τ (OCOCH_3) and 9.4τ (cyclopropane protons)

Von-Rudloff oxidation: products of ECL (DEGS): 15.4, 17.6, 19.2, 20.4 and 23.2.

Fraction BL (BIU and BIL): Although the subfractions BIU and BIL separate on TLC as shown in Scheme (6), they did not show other significant chromatographic or spectroscopic differences.

GLC: (DEGS) 24.1 (85-90%) and 19.4, 23.2, 24.6 (10-15%)

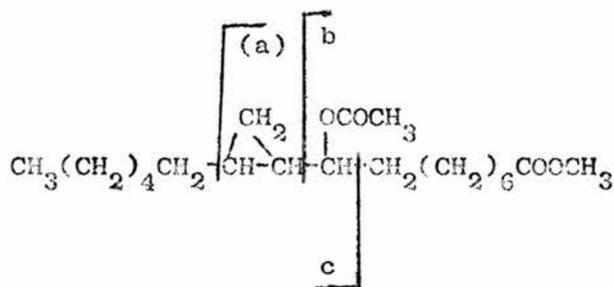
(ApL) overlapping wide peaks 17.4, 17.7, 17.9 and 19.55

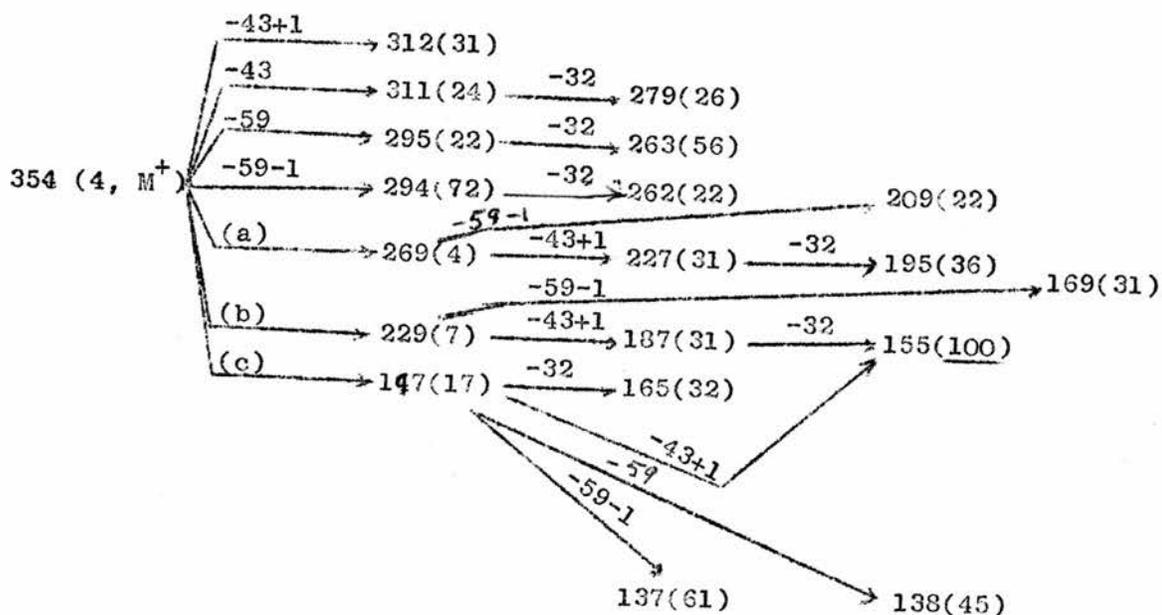
(decomposition probably occurring)

IR spectrum: 1030 cm^{-1} (cyclopropane) 1250 cm^{-1} and 1370 cm^{-1} (acetate) and 1740 cm^{-1} (ester).

NMR spectrum: 8.05τ (OCOCH_3), and 9.4τ (cyclopropane protons)

Mass spectrum:



major peaks:

Fragment (a) result from cleavage α to the cyclopropane ring and fragments (b) and (c) result from cleavage α to the acetoxy group. These fragments and the molecular ion peaks readily lose one or more smaller fragments of (-32, -43, -59).

In addition, peaks occur at 169(31), 164(28), 150(61), 149(100), 141(39) and 136(39).

Fraction B2:

GLC: (DEGS) before hydrogenation 24.6 and after hydrogenation 24.3

(ApL) 19.6

IR spectrum: 980 cm^{-1} (trans alkene), 1250 cm^{-1} and 1380 cm^{-1} (acetate) and 1740 cm^{-1} (ester).

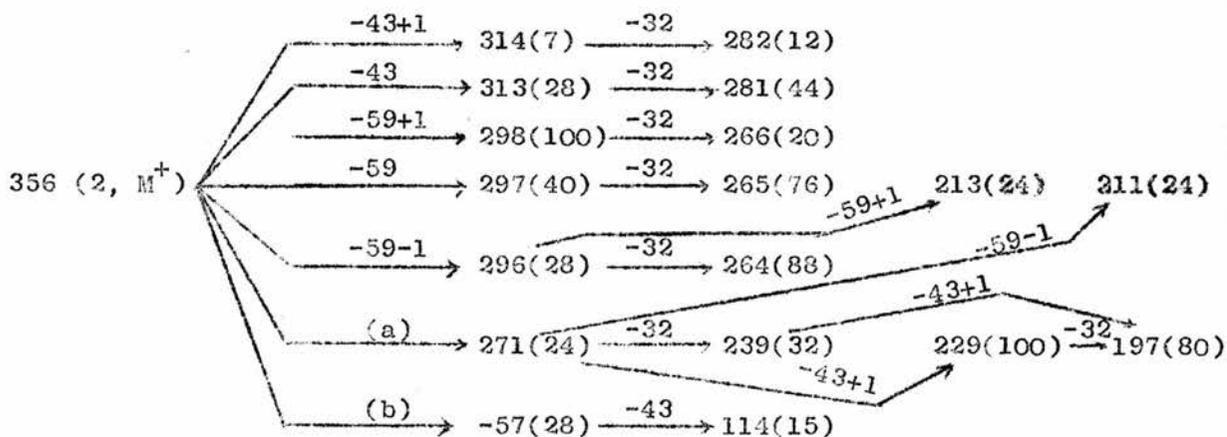
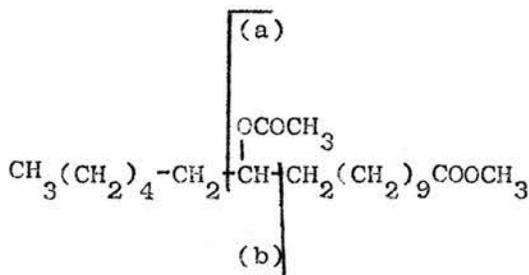
NMR spectrum: 4.65 τ (olefinic protons), and 8.05 τ (O.OCH₃).

Von-Rudloff oxidation: nonanedioic acid and (presumably)

3-acetoxynonanoic acid (DEGS, 15.2)

Mass spectrum: (after hydrogenation)

major peaks:



Fragments (a) and (b) result from cleavage α to the acetoxy group. These fragments and the molecular ion peaks readily lose one or more smaller fragments of (-32, -43, -59).

In addition peaks occur at: 255(40), 199(40), 149(100), 141(32).

Methyl 12-acetoxyelaidate: An authentic sample of methyl 12-acetoxy elaidate was prepared from methyl ricinelaidate (100 mg) by refluxing with acetic anhydride (10 ml) for 10 hours. After recovery, the product was purified by preparative TLC (PE25), and compared with fraction B₃

GLC: (DEGS) 24.6 (ApL) 19.6 before hydrogenation and (DEGS) 24.2, (ApL) 19.3 after hydrogenation.

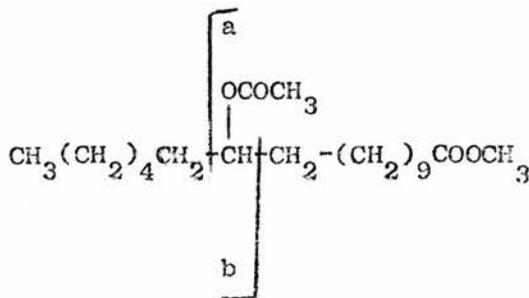
IR spectrum: 1250 cm^{-1} and 1380 cm^{-1} (acetate), and 1740 cm^{-1} (ester) and 980 cm^{-1} (trans alkene)

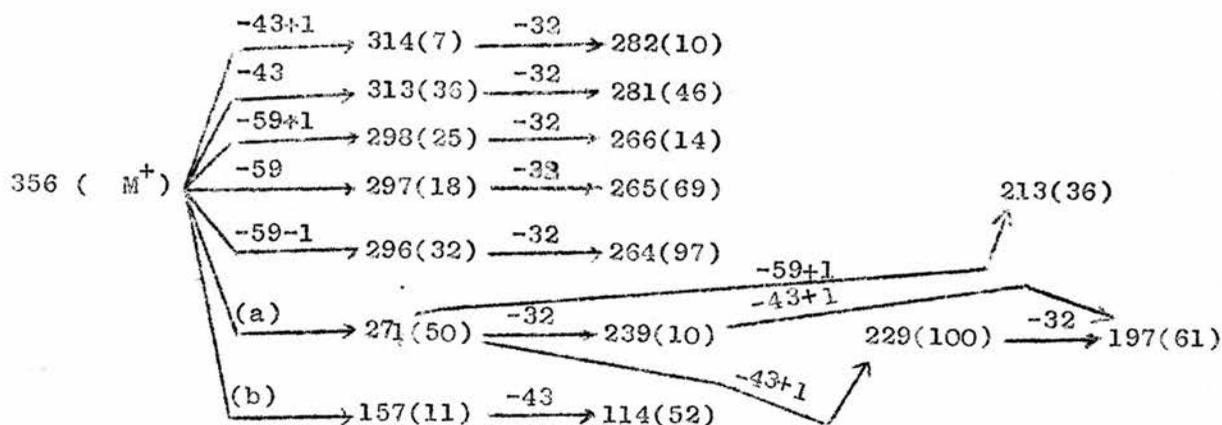
NMR spectrum: 4.65 \uparrow (olefinic protons), and 8.05 \uparrow (OCOCH_3).

Von-Rudloff oxidation: nonanedioic acid and (presumably)

3-acetoxynonanoic acid (DEGS 15.2)

Mass spectrum: (after hydrogenation)





Fragments (a) and (b) result from cleavage α to the acetoxy group. These fragments and the molecular ion peak readily lose one or more smaller fragments of (-32, -43, -59).

Fraction C:

GLC: (DEGS) 19.4, 20.4, 20.8, 21.1 and 23.3 (30%) [^{*}decomposition of unreacted mesyloxy ester] and 25.7 and 26.0 (70%).

IR spectrum: 920 cm^{-1} and 1180 cm^{-1} (mesyloxy ester), 980 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 3500 cm^{-1} (hydroxyl group).

NMR spectrum: 4.65τ (olefinic protons), 7.14τ (mesyloxy protons)

Von-Rudloff oxidation: nonanedioic acid and (presumably)

3-hydroxy nonanoic acid (DEGS, 16.0) along with minor peaks at 19.0, 20.4, 21.0, 21.4 and 23.2 (which are probably from the mesyloxy ester).

* The mesyloxy ester always decomposes on (DEGS) giving this pattern of ECL's.

The reaction of methyl 12-mesyloxyoleate with acetic acid and sodium acetate for different periods of time:

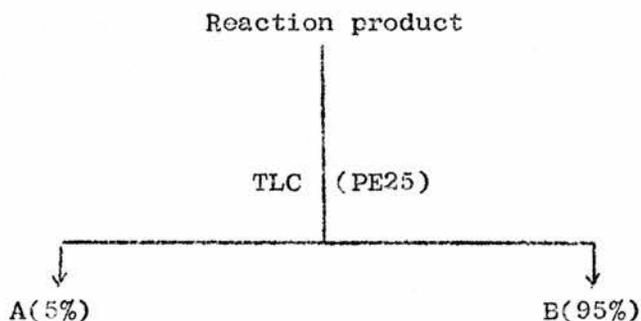
This reaction has been carried under the same conditions as in 1a but for different periods of time and the table below shows the changes in the relative amounts of the three major peaks.

Time	area (%) under major peaks (DEGS)		
	23.2	24.1	24.6
5 min	33	30	36
10 min	17	43	40
15 min	10	52	38
30 min	0	52	48
2 hr	15	31	54
4 hr	4	29	67
6 hr	10	13	77
8 hr	6	9	85

The reaction of methyl 12-mesyloxy oleate with formic acid and sodium formate:

The mesyloxy ester (100 mg) was heated (100°) for four hours with formic acid (98%, 8 ml) and sodium formate (50 mg). The product (85 mg), recovered by addition of water and extraction with ether, was separated as shown in Scheme 7.

Scheme 7.



Reaction product:

GLC: (DEGS) 19.4, 20.4 and 21.1 (3%) and 25.3 (97%).

IR spectrum: 975 cm^{-1} (trans alkene), 1730 cm^{-1} (ester) and 1185 cm^{-1} (formate).

NMR spectrum: 2.04 τ (O.CO \underline{H}), 4.65 τ (olefinic protons).

Fraction A:

GLC: (DEGS) 19.4 (70%) 20.4 and 21.1 (30%).

Fraction B:

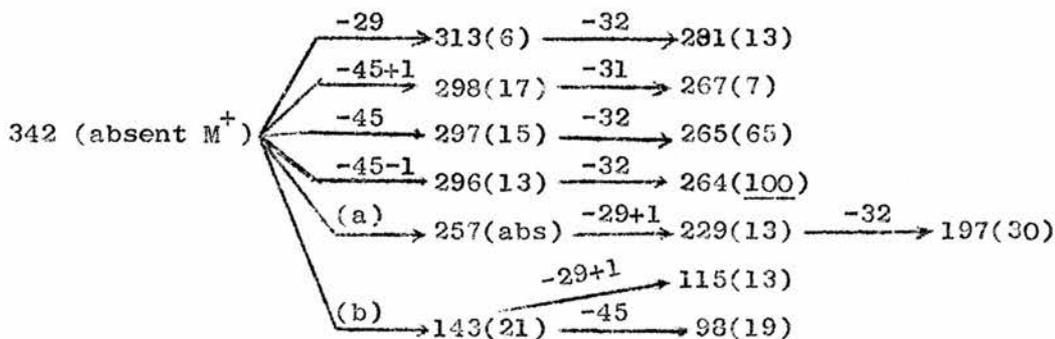
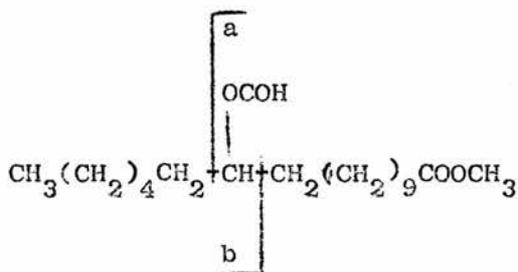
GLC: Before hydrogenation (DEGS) 25.3; (ApL) 19.4.

After hydrogenation (DEGS) 18.0 and 24.8; (ApL) 19.0 and 19.7

IR spectrum: 980 cm^{-1} (trans alkene), 1180 cm^{-1} (formate) and 1730 cm^{-1} (ester).

NMR spectrum: 2.05τ (O.CO \bar{H}) and 4.65τ (olefinic protons).

Mass spectrum: (after hydrogenation).

Major peaks:

Fragments (a) and (b) result from cleavage α to the acetoxy group. These fragments and the molecular ion peak readily lose one or more smaller fragments of (-29, -31, -32, -45).

Reaction of fraction B with methanol and sodium methoxide:

Fraction B (20 mg) was refluxed with methanol (5 ml) and sodium methoxide (5 mg) for one hour. The product had the following properties.

GLC: (DEGS) 25.7 (19.7 after silylation)

IR spectrum: 980 cm^{-1} (trans olefin), and 3500 cm^{-1} (hydroxyl group).

The reaction of methyl 12-mesyloxyoctadec-9-ynoate with acetic acid and sodium acetate:

The mesyloxy ester (100 mg) was heated (160°) for four hours with acetic acid (10 ml) and sodium acetate (50 mg). The product recovered by neutralization with sodium bicarbonate (5% solution), addition of water and extraction with ether, was separated by preparative TLC (PE25) into three fractions: A (22%), B (28%) and C (50%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 21.1, 21.7, 22.9, 26.0 (major) and 27.1

IR spectrum: 920, 1180 and 1370 cm^{-1} (mesyl ester), 1250 cm^{-1} (acetate), 1740 cm^{-1} (ester) and 980 cm^{-1} (small trans alkene).

Fraction A:

GLC (DEGS) 21.1 (36%), 21.7 (57%) and 22.9 (7%)

IR spectrum: 980 cm^{-1} (trans alkene), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

Fraction B:

GLC: (DEGS) 26.0

IR spectrum: 1035, 1250 and 1370 cm^{-1} (acetate) and 1740 cm^{-1} (ester).

Fraction C:

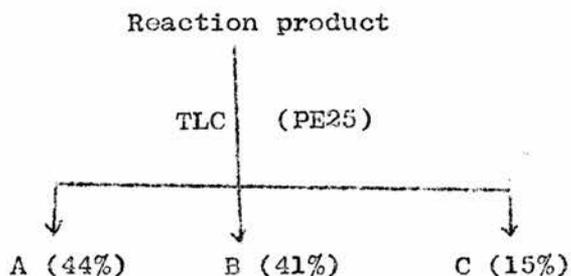
GLC (DEGS) wide overlapping peaks around 21.3, 21.9, 23.0 and 24.4.

IR spectrum: 920 cm^{-1} and 1360 cm^{-1} (very strong, mesyloxy ester), and 1740 cm^{-1} (ester).

The reaction of methyl 9-mesyloxyoctadec-cis-12-enoate with acetic acid and sodium acetate:

The mesyloxy ester (200 mg) was heated (100°) for four hours with acetic acid (15 ml) and sodium acetate (20 mg). The product (185 mg) after addition of water and extraction with ether was separated as shown in Scheme 8 .

Chromatographic and spectroscopic information about each fraction is presented.

Scheme 8 .

Reaction product:

GLC: (DEGS) 19.4 (58%) and 24.9 (42%); (ApL) 17.6 and 19.6

IR spectrum: 980 cm^{-1} (trans alkenes), 1030 cm^{-1} , 1250 cm^{-1}
and 1375 cm^{-1} (acetate), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes).

Fraction A:

GLC (DEGS) 19.4

IR spectrum: 980 cm^{-1} (trans alkene) and 3020 cm^{-1} (alkene).

Fraction B:

GLC: (DEGS) 24.6; (ApL) 19.6

IR spectrum: 1030 cm^{-1} , 1250 cm^{-1} and 1380 cm^{-1} (acetate),
1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

Fraction C:

GLC 26.0

IR spectrum: 1740 cm^{-1} (ester), 3020 cm^{-1} (alkene) and
3500 cm^{-1} (hydroxyl group).

The reaction of methyl 12-mesyloxyoleate with lithium aluminium hydride in tetrahydrofuran

The mesyloxy ester (100 mg) was refluxed with LiAlH_4 (100 mg) and tetrahydrofuran (20 ml). After 20 hours ethyl acetate (\sim 4 ml) was added through the condenser and refluxed for five minutes. The product, recovered by addition of dilute sulphuric acid (6 ml) and extraction with ether, was separated by preparative TLC into three fractions_ A (4%), B (37%) and C (9%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.4 and 20.6 (major)

IR spectrum: 1060 cm^{-1} (alcohol), 3020 cm^{-1} (alkene) and 3350 cm^{-1} (hydroxyl) (ester carbonyl absorption is absent).

Fraction A:

GLC: (DEGS) 19.3

Fraction B:

GLC: (DEGS) 20.6 [14.1 as a trimethyl silyl derivatives and 15.1 as methyl ethers].

IR spectrum: 1060 cm^{-1} and 3350 cm^{-1} (hydroxyl group) and 3020 cm^{-1} (alkene).

NMR spectrum: 4.7 \uparrow (olefinic protons) and 6.4 - 6.7 \uparrow (alcohol protons)

Von-Rudloff oxidation: gave ECL's of (DEGS) 19.4 (13.0 as TMSI derivatives and 13.9 as ethers).

An authentic sample of oleyl alcohol showed the same chromatographic and spectroscopic behaviour.

Fraction C:

GLC: (DEGS) 27.7

The reaction of methyl 12-mesyloxyoleate with methanol and sodium borohydride:

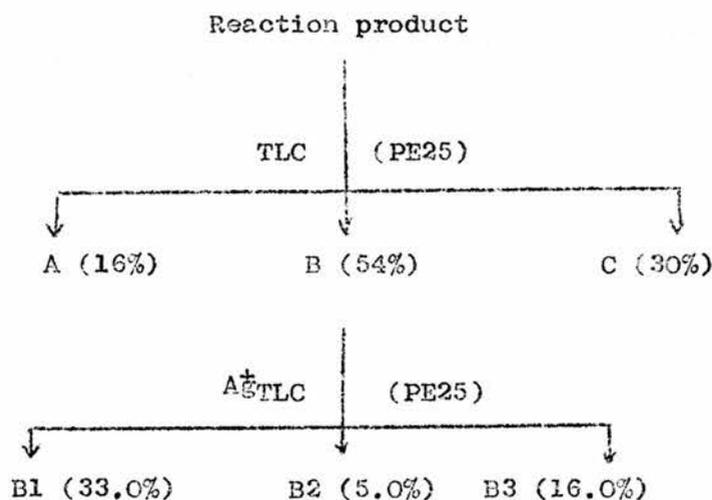
The mesyloxy ester (100 mg) was refluxed with methanol (20 ml) and sodium borohydride (50 mg) for four hours. The product recovered as usual and examined on GLC (DEGS) which showed ECL's of 19.4 (7%) 20.4 (3%), 20.9 (1%), 21.2 (60%) and 21.4 (29%).

The infra-red spectrum showed absorption bands at 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

The reaction of methyl 12-mesyloxyoleate with water and calcium carbonate in acetonitrile:

The mesyloxy ester (100 mg) was refluxed with acetonitrile (15 ml) water (0.2 ml), and calcium carbonate (100 mg) for 12 hours. The product (93 mg) recovered by addition of water and extraction with ether, was separated as shown in scheme (9). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (9)



Reaction product:

GLC: (DEGS) 19.3, 20.4, 20.8, 21.0, 25.6 and 26.0

IR spectrum: 1030 cm^{-1} and 3000 cm^{-1} (cyclopropane) and 3500 cm^{-1} (hydroxyl).

Fraction A:

GLC: (DEGS) 19.3, 20.4, 20.8 and 21.0.

IR spectrum: 980 cm^{-1} (trans alkene) 1740 cm^{-1} (ester) and 960 and 995 cm^{-1} (small, conjugated cis-trans dienes).

Fraction B:

GLC: (DEGS) 25.6 and 26.0

IR spectrum: 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1740 cm^{-1} (ester), 3010 cm^{-1} (alkene) and 3500 cm^{-1} (hydroxyl).

Fraction B1:

GLC: (DEGS) 25.75 (99%) and 20.0 and 20.4 (1%)

(ApL) 17.5, 17.85, 18.25, 18.70 and 19.4 (probably decomposition).

IR spectrum: 1030 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1740 cm^{-1} (ester) and 3500 cm^{-1} (hydroxyl).

NMR spectrum: 9.6 \uparrow (cyclopropane protons).

Von-Rudloff oxidation: this product remained unchanged (GLC, IR spectrum).

Fraction B2:

GLC: (DEGS) 26.0 (90%) and 26.4 and 25.75 (10%).

(ApL) 19.35 (major) and 17.7, 19.15 and 18.6 (very small).

Fraction B3:

GLC: (DEGS) 26.0, (ApL) 19.4.

IR spectrum: 980 cm^{-1} (small, trans alkene), 1740 cm^{-1} (ester), 3020 cm^{-1} (cis alkene) and 3500 cm^{-1} (hydroxyl).

NMR spectrum: 4.6 \uparrow (olefinic protons).

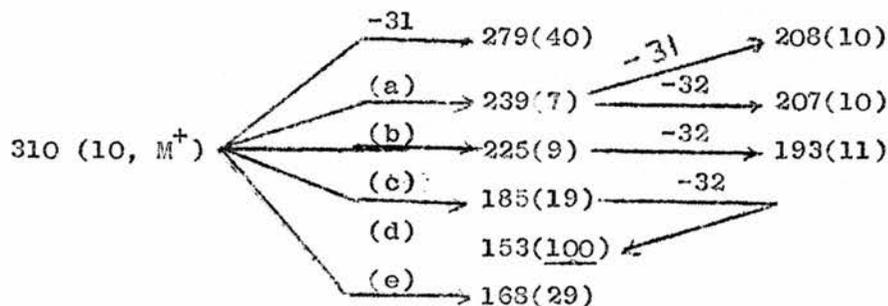
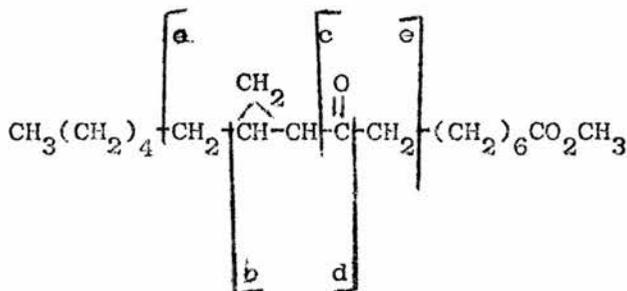
Fraction C:

GLC: (DEGS) 25.6 (major) and small peaks at 19.2, 20.3 and 25.8.
(ApL) 17.5, 17.75, 18.15, 18.75 and 19.45 (decomposition occurring).

IR spectrum: 1035 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1740 cm^{-1} (ester) and 3500 cm^{-1} (hydroxyl).

NMR spectrum: 9.55 and 9.75 τ (cyclopropane protons).

Mass spectrum: (of B1 and C) (after conversion to oxo-cyclopropane, see 158).

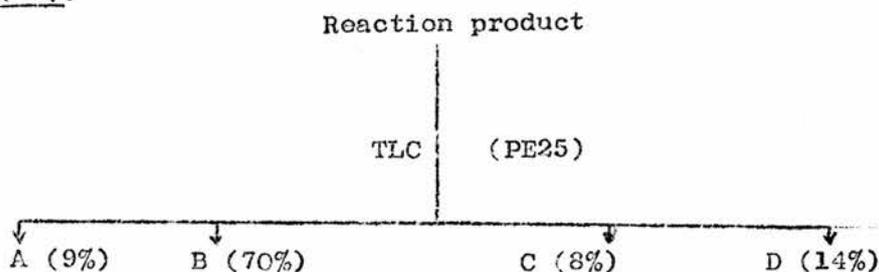


Fragments (c) and (d) result from cleavage α to the carbonyl group, fragment (e) results from cleavage β to the carbonyl group (Mc Lafferty rearrangement) and fragments (a) and (b) result from cleavage α and β respectively to the cyclopropane ring. These fragments and the molecular ion peak readily lose smaller fragments of (-31, and -32).

The reaction of methyl 12-mesyloxy oleate with sodium methoxide and calcium carbonate in acetonitrile:

The mesyloxy ester (100 mg) was refluxed for 12 hours, with sodium methoxide (10 mg) and calcium carbonate (20 mg) in acetonitrile (15 ml). The product recovered by addition of water and extraction with ether, was separated as shown in scheme (10). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (10).



Reaction product:

GLC: (DEGS) 19.3, 19.6, 20.6, 20.8, 21.0, 21.4 and 25.8.

IR spectrum: 960 cm^{-1} and 990 cm^{-1} (conjugated cis-trans dienes), and 1740 cm^{-1} (ester).

Fraction A:

GLC: (DEGS) 19.6

Fraction B:

This was examined before and after treatment with a 5% solution of iodine in carbon disulphide.

GLC: (DEGS) Before treatment: 19.3, 20.4 (56%), 20.8% and 21.0 (14.0%).

After treatment: 20.4 (30%) and 21.0 (70%)

(ApL) Before treatment 17.6, 18.15 (major), 18.4 and 18.65

After treatment 17.6, 18.15 and 18.65 (major)

IR spectrum: Before treatment 960 cm^{-1} and 995 cm^{-1} (conjugated cis-trans diene) and 1740 cm^{-1} (ester).

After treatment 995 cm^{-1} (conjugated trans-trans dienes), 1740 cm^{-1} (ester) and 960 cm^{-1} (very small conjugated cis-trans dienes).

Fraction C:

GLC: (DEGS) 21.4

IR spectrum: 980 cm^{-1} (transalkene), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

Fraction D:

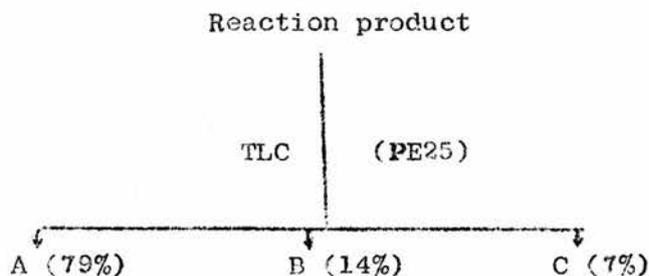
GLC: (DEGS) 25.8

IR spectrum: 980 cm^{-1} (small, trans alkene), 1740 cm^{-1} (ester), 3020 cm^{-1} (alkenes) and 3500 cm^{-1} (hydroxyl).

The reaction of methyl 12-mesyloxyoleate with lithium chloride and calcium carbonate in acetonitrile:

The mesyloxy ester (100 mg) was refluxed for 12 hours with lithium chloride ($\text{LiCl} \cdot \text{H}_2\text{O}$, 50 mg), calcium carbonate (50 mg) and acetonitrile (15 ml). The product (95 mg), recovered by addition of water and extraction with ether, was separated into three fractions as shown in Scheme (11). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (11)



Reaction product:

GLC: (DEGS) 19.2, 19.4, 20.4, 20.6, 21.0, 22.9, 23.3 (major) and 25.6 and 25.9.

IR spectrum: 980 cm^{-1} (trans alkenes), and 920 cm^{-1} , 1180 cm^{-1} and 1370 cm^{-1} (small, probably due to unreacted mesyloxy ester), and 1740 cm^{-1} (ester).

Fraction A:

GLC: (DEGS) 19.2, 19.4, 20.4, 20.6, 21.0 and 22.9 (25%) and 23.3 (75%).

IR spectrum: 980 cm^{-1} (trans alkenes), 1740 cm^{-1} (ester).

Von-Rudloff oxidation: nonanedioic acid and (presumably)

3-chlorononanoic acid (DEGS, 13.8).

Fraction B:

GLC: (DEGS) 19.3, 20.4, 21.0 and 23.3 (30%) and 25.6 and 25.9 (70%).

IR spectrum: 970 cm^{-1} (trans alkene), 1720 cm^{-1} (oxo), 1740 cm^{-1} (ester) 3070 cm^{-1} (cyclopropane), and 3400 cm^{-1} (hydroxyl).

Fraction C:

GLC: (DEGS) 19.7, 20.3 and 25.6 (major).

IR spectrum: 970 cm^{-1} (trans alkene), 1640 cm^{-1} and 1720 cm^{-1} (small, possibly free acid), 1740 cm^{-1} (ester), 3400 cm^{-1} (hydroxyl) and possibly 3070 cm^{-1} (cyclopropane).

The reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide:

Methyl 12-mesyloxyoleate (50 mg) was heated (100°) for four hours with dimethyl sulphoxide (10 ml). The product (45 mg), recovered by addition of water and extraction with ether was separated by preparative TLC (PE25) into two fractions: A (74%) and B (20%). Chromatographic and spectroscopic informations about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.4, 20.4, 21.0 and 26.0.

IR spectrum: 960 cm^{-1} (very small) and 996 cm^{-1} (very strong, conjugated cis-transdiene and conjugated trans-transdiene), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

Fraction A:

GLC: (DEGS) 19.4, 20.4 and 21.0 (31%, 28% and 41% respectively)

IR spectrum: 960 cm^{-1} and 996 cm^{-1} (conjugated cis-transdiene and conjugated trans-transdiene, major). 1740 cm^{-1} (ester), and 3020 cm^{-1} (alkene)

Fraction B:

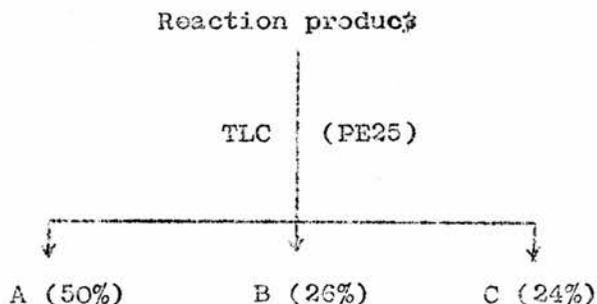
GLC: (DEGS) 19.4, 20.4, 20.8, 21.0 (5%, probably mesyloxy ester decomposition), and 25.8 and 26.0 (major).

IR spectrum: 920 cm^{-1} and 1180 cm^{-1} (mesyloxy ester), 980 cm^{-1} (small, trans alkene), 1740 cm^{-1} (ester), and 3450 cm^{-1} (hydroxyl).

The reaction of methyl 12-mesyloxy oleate with dimethyl sulphoxide and calcium carbonate

The mesyloxy ester (50 mg) was heated (100°C) for four hours with dimethyl sulphoxide (10 ml) and calcium carbonate (50 mg). The product (47 mg), recovered by addition of water and extraction with ether, was separated as shown in scheme/2. Chromatographic and spectroscopic information about each fraction is presented.

Scheme 2



Reaction product:

GLC: (DEGS) two series of peaks 19.4, 20.4, 20.6, 21.0 and 23.2 (50%) and 25.0, and 25.6 (50%).

IR spectrum: 960 cm^{-1} and 995 cm^{-1} (conjugated cis-transdienes), 975 cm^{-1} (trans alkene), 1720 cm^{-1} (oxo group), 1740 cm^{-1} (ester), 3020 cm^{-1} (alkenes) and 3500 cm^{-1} (hydroxyl)

Fraction A:

GLC: (DEGS) 19.4 (31%), 20.4 (39%), 20.6 (12%), 21.0 (12%) and 23.3 (6%).

IR spectrum: 960 cm^{-1} and 995 cm^{-1} (conjugated cis-trans dienes), 980 cm^{-1} (small, trans alkene), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

Fraction B:

GLC: (DEGS) Before hydrogenation 25.0

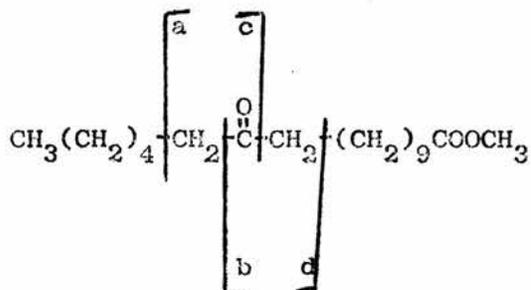
After hydrogenation 24.9

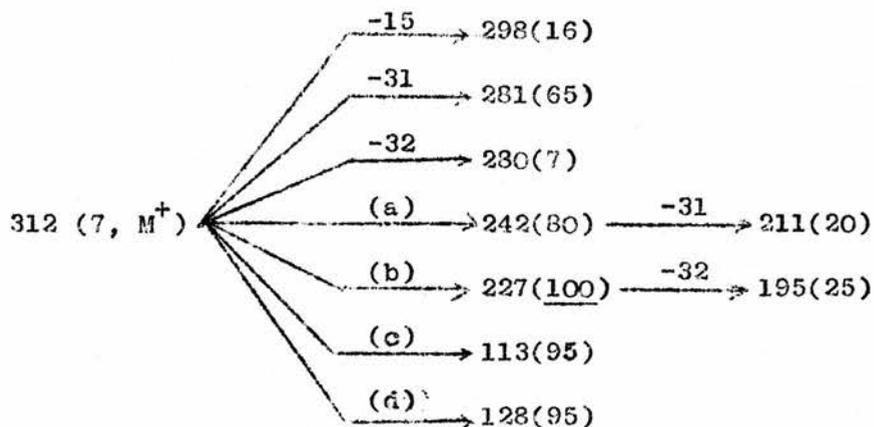
IR spectrum: 1720 cm^{-1} (oxo), 1740 cm^{-1} (ester), 980 cm^{-1} (small, trans-alkene) and 3030 cm^{-1} (alkene)

Von-Rudloff oxidation: nonanedioic acid.

Mass spectrum: (after hydrogenation)

Major peaks:





Fragments (b) and (c) result from cleavage α to the carbonyl group, and fragments (a) and (d), result from cleavage β (McLafferty rearrangement) to the carbonyl group. These fragments and the molecular ion peak readily lose smaller fragments of (-15, -31, and -32).

Methyl 12-oxo oleate: An authentic sample of methyl 12 oxo oleate was prepared from methyl ricinoleate (see 158) for comparison with fraction B.

GLC: (DEGS) Before hydrogenation 25.0

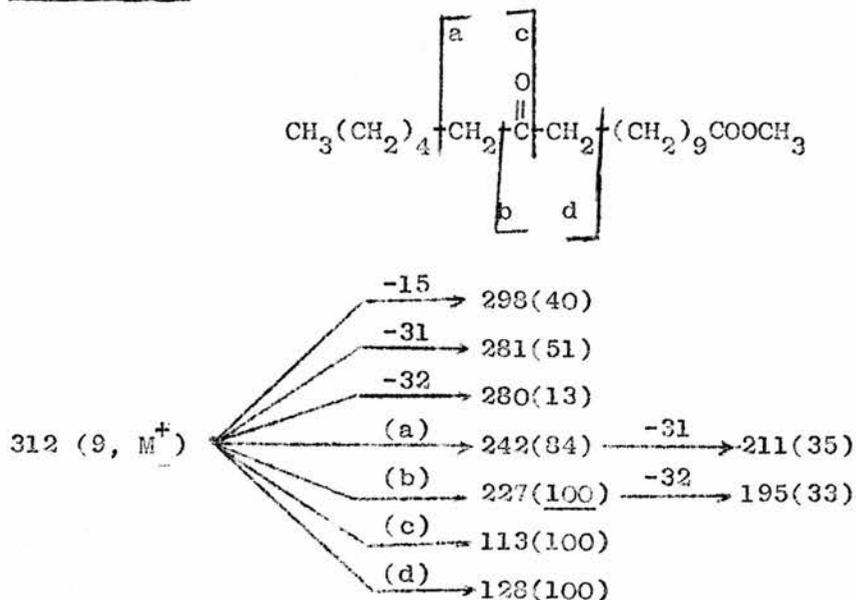
After hydrogenation 24.9

IR spectrum: 1720 cm^{-1} (oxo), 1740 cm^{-1} (ester) and 3030 cm^{-1} (alkene)

Von-Rudloff-oxidation: nonanedioic acid.

Mass spectrum: (after hydrogenation)

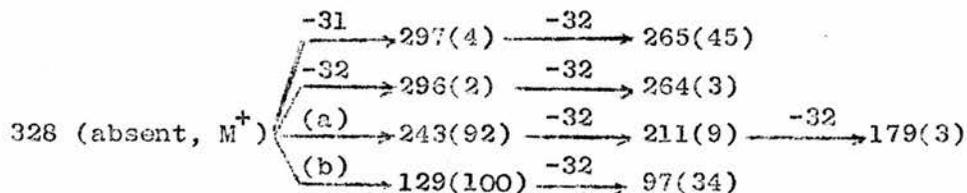
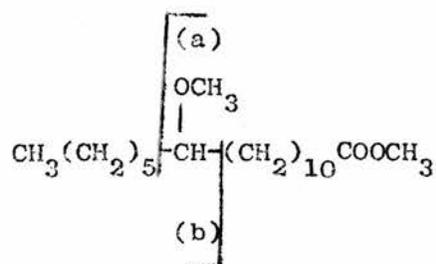
Major peaks:



Fragments (b) and (c) result from cleavage α to the carbonyl group, and fragments (a) and (d) result from cleavage β (McLafferty rearrangement) to the carbonyl group. These fragments and the molecular ion peak readily lose smaller fragments of (-51, -31, -32).

Methyl 12-methoxyoleate: An authentic sample of methyl 12-methoxyoleate was prepared from methyl ricinoleate (see p. 81) and its mass spectrum compared with that of fraction (C).

The mass spectrum: (after hydrogenation)



Fragments (a) and (b) result from cleavage α to the methoxy group. These fragments and the molecular ion peak readily lose one or more smaller fragments of (-31 and -32).

The reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide and sodium methoxide.

The mesyloxy ester (50 mg) was heated (100°) for four hours with dimethyl sulphoxide (10 ml) and sodium methoxide (10 mg). The product recovered by neutralization with acetic acid, addition of water, and extraction with ether, gave the following chromatographic and spectroscopic information.

GLC: (DEGS) 20.4 (22%) and 21.0 (78%)

(ApL) 18.15 (35%) and 18.6 (65%)

IR spectrum: 960 cm^{-1} and 995 cm^{-1} (conjugated cis-trans dienes), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkenes).

When heated with iodine in Carbon disulphide the infra-red spectrum showed strong absorption at 995 cm^{-1} (conjugated trans-trans dienes).

The reaction of methyl 12-mesyloxy oleate with lithium chloride and dimethyl sulphoxide:

Methyl 12-mesyloxyoleate (50 mg) was heated (100°) with lithium chloride (hydrated, 20 mg) in dimethyl sulphoxide solution (10 ml) for four hours. The product recovered by addition of water and extraction with ether, was separated by preparative TLC (PE25) into two fractions: A (90%) and B (10%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.3, 20.4, 20.8, 21.0 (major) and 25.9

IR spectrum: 960 cm^{-1} and 995 cm^{-1} (very small, conjugated cis-trans diene), 1025 cm^{-1} and 3020 cm^{-1} (alkene) 1740 cm^{-1} (ester) and 3450 cm^{-1} and 3520 cm^{-1} (hydroxyl).

Fraction A:

GLC: (DEGS) 19.3, 20.4, 20.8 and 21.0 (25%) and 23.3 (75%)

IR spectrum: 960 cm^{-1} (conjugated cis-trans diene), 1025 cm^{-1} and 3020 cm^{-1} (alkene) 1740 cm^{-1} (ester).

Fraction B:

GLC: (DEGS) 25.9

IR spectrum: 1740 cm^{-1} (ester), 3020 cm^{-1} (alkene) and 3500 cm^{-1} (hydroxyl).

The reaction of methyl 12-mesyloxy oleate with dimethyl sulphoxide, lithium chloride and calcium carbonate:

The mesyloxy ester (50 mg) was heated (100°C) for four hours with dimethyl sulphoxide (10 ml), lithium chloride (hydrated, 20 mg) and calcium carbonate (30 mg). The product recovered by addition of water and extraction with ether, was separated by preparative TLC (PE25) into two fractions: A (87%) and B (13%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.4, 20.4, 20.8, 21.0, 23.3 (major) and 25.9.

IR spectrum: 1740 cm^{-1} (ester), 3020 cm^{-1} (alkene) and 3500 cm^{-1} (hydroxyl).

Fraction A:

GLC: (DEGS) 19.4, 20.4, 20.8 and 21.1 (15%) and 23.3 (85%).

These appeared at 18.0, 18.6 and 22.9 after hydrogenation.

IR spectrum: 800 cm^{-1} (small, probably chloro-group), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

NMR spectrum: 4.60 τ (olefinic protons).

Von-Rudloff oxidation: nonanedioic acid and (presumably) 3-chlorononanoic acid (DEGS, 13.9).

Fraction B:

GLC: (DEGS) 25.9

IR spectrum: 1740 cm^{-1} (ester) and 3500 cm^{-1} (hydroxyl)

The reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide, magnesium bromide and calcium carbonate:

The mesyloxy ester (100 mg) was heated (100°C) for four hours with dimethyl sulphoxide (15 ml), magnesium bromide (hydrated, 50 mg) and calcium carbonate (50 mg). The product recovered by addition of water and extraction with ether was separated by reparaive TLC (PE25) into two fractions; A (75%) and B (25%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction product:

GLC: (DEGS) 19.3, 20.4 (major), 20.8, 23.3, 24.6 and 26.0

IR spectrum: 960 cm^{-1} and 990 cm^{-1} (conjugated cis-trans dienes), 1740 cm^{-1} (ester), 3020 cm^{-1} (alkene) and 3500 cm^{-1} (hydroxyl group).

Fraction A:

GLC: (DEGS) 19.3 (22%), 20.4 (49%) (major), 20.8 (12%), 21.1 (9%), 24.5 (8%).

IR spectrum: 960 cm^{-1} and 990 cm^{-1} (conjugated cis-trans dienes), and 1740 cm^{-1} (ester).

Fraction B:

GLC: (DEGS) 25.9

IR spectrum: 1740 cm^{-1} (ester), and 3500 cm^{-1} (hydroxyl group).

The reaction of methyl 12-mesyloxyoleate with dimethyl sulphoxide potassium iodide and calcium carbonate:

The mesyloxy ester (100 mg) was heated (100°C) for four hours with dimethyl sulphoxide (10 ml), potassium iodide (50 mg) and calcium carbonate (50 mg). The product, recovered as usual by addition of water and extraction with ether, was separated by preparative TLC (PE25) into two fractions A (78%) and B (22%). Chromatographic and spectroscopic information about each fraction is presented.

Reaction Product:

GLC: (DEGS) 19.4 (22%), 20.4 (20%), 21.1 (30%) and 26.0 (20%)

IR spectrum: 960 cm^{-1} very small, and 995 cm^{-1} very strong (conjugated cis-trans, and conjugated trans-trans dienes), 1740 cm^{-1} (ester), 3020 cm^{-1} (alkenes), and 3500 cm^{-1} (hydroxy).

Fraction A:

GLC: (DEGS) 19.4 (23%), 20.4 (25%) and 21.1 (46%).

IR spectrum: 960 cm^{-1} and 995 cm^{-1} (conjugated cis-trans dienes). 980 cm^{-1} (trans alkene), 995 cm^{-1} (conjugated trans-trans dienes), and 1740 cm^{-1} (ester).

Fraction B:

GLC: (DEGS) 26.0

IR spectrum: 1740 cm^{-1} (ester), 3010 cm^{-1} (cis alkene), and 3500 cm^{-1} (hydroxy).

The reactions of methyl 12-mesyloxyoleate with different reagents
in acetone:

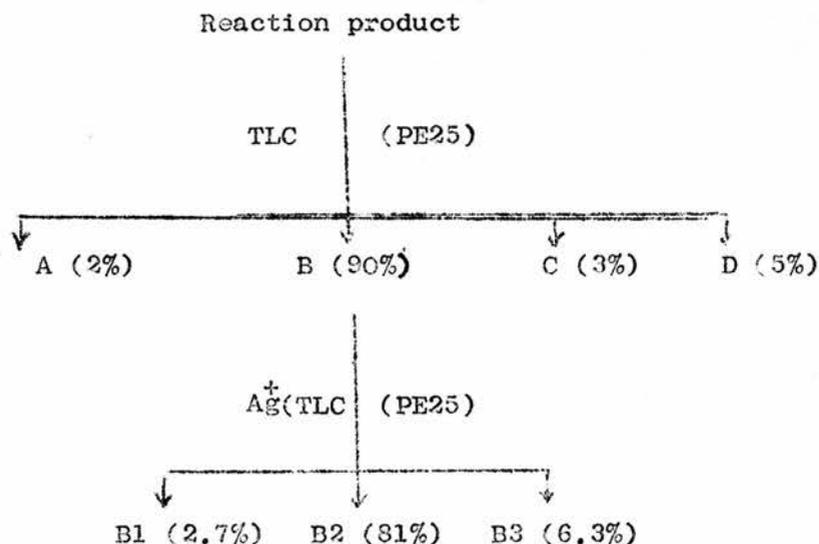
The mesyloxy ester was refluxed for 12 hr. in acetone with different reagents, with the results shown in the following table.

Reagents	GLC (DEGS) of the products	I.R. spectrum of the products
NaOMe/CaCO ₃	19.3 and 19.5 (19%), 20.3 (22%), 20.7 (20%), 21.4 (33%) and 25.7 (6%)	920 cm ⁻¹ , 1180 cm ⁻¹ (mesyloxy ester), 1740 cm ⁻¹ (ester) and 3500 cm ⁻¹ (small, OH).
NaOAc/CaCO ₃	19.4, 20.4 and 20.8 (probably mesyloxy ester decomposition).	920, 1180 and 1370 cm ⁻¹ (very strong, mesyloxy ester), 1740 cm ⁻¹ (ester).
H ₂ O/CaCO ₃	19.4, 20.4, 20.6 and 21.0 (66%), (probably elimination and mesyloxy ester decomposition), 25.6 and 25.9 (34%).	920, 1180 and 1370 cm ⁻¹ (mesyloxy ester), 1030 and 3070 cm ⁻¹ (cyclopropane), 1740 cm ⁻¹ (ester) and 3500 cm ⁻¹ (hydroxyl).
LiCl.H ₂ O/CaCO ₃	19.4, 20.4 and 20.8 (84%) mesyloxy ester decomposition) and 23.3 (16%)	920, 1180, 1370 cm ⁻¹ (mesyloxy ester), 1740 cm ⁻¹ (ester) and 3020 cm ⁻¹ (alkene).
CaCO ₃	mesyloxy ester decomposition only 19.4, 20.4, 20.8	mesyloxy ester absorption bands only.

The thermal decomposition of methyl 12-mesyloxy oleate in boiling triglyme:

The mesyloxy ester (80 mg) was refluxed for 20 minutes in triglyme (10 ml). The product, recovered by addition of water and extraction with ether, was separated as shown in Scheme (13). Chromatographic and spectroscopic information about each fraction is presented.

Scheme (13).



Fraction B:

GLC: (DEGS) 19.4 (major), 20.4, 20.8 and 21.0

IR spectrum: 960 cm^{-1} , 980 cm^{-1} and 995 cm^{-1} (a mixture of conjugated cis-trans, and conjugated trans-trans dienes, and nonconjugated trans alkene), 1740 cm^{-1} (ester) and 3020 cm^{-1} (alkene).

Fraction B2:

GLC: (DEGS) 19.4 (major), 20.4, 20.8 and 21.0

IR spectrum: The same as B

Fraction B3:

GLC: (DEGS) 19.4

The reaction of methyl 12-mesyloxy oleate with lithium chloride and calcium carbonate in tetrahydrofuran

The mesyloxy ester (50 mg) was refluxed with tetrahydrofuran (10 ml) containing lithium chloride (hydrated, 20 mg) and calcium carbonate (20 mg) for four hours. The product recovered as usual, showed the following chromatographic and spectroscopic information.

GLC: (DEGS) 19.4, 20.4, 20.8 and 21.0 (75%, probably decomposition of unreacted material), and 23.3 (18%) and 27.4 (7%).

IR spectrum: 920 cm^{-1} , 1180 cm^{-1} and 1370 cm^{-1} (mesyloxy ester), 1740 cm^{-1} (ester), 3030 cm^{-1} (alkene) and 3450 cm^{-1} (hydroxyl).

The reaction of the methoxy cyclopropane ester with methanol and sulphuric acid.

The methoxy cyclopropane ester (20 mg) was refluxed for two hours with methanol (5 ml) and concentrated sulphuric acid (0.1 ml). The product recovered by neutralization with sodium bicarbonate, addition of water, and extraction with ether, showed the following characteristics when ^{by} examined chromatography~~es~~ and spectroscopy~~es~~.

GLC: (DEGS) 21.4

IR spectrum: 978 cm^{-1} (trans alkene), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and complete disappearance of the cyclopropane absorption bands.

NMR spectrum: 4.65 τ (olefinic protons), 6.78 τ (ether, O.CH₃) and complete disappearance of the cyclopropane protons.

Von-Rudloff oxidation: nonanedioic acid and (presumably) 3-methoxynonanoic acid (ECL of methyl ester, 12.0, DEGS).

When the methoxy cyclopropane ester (50 mg) was refluxed for four hours with methanol (20 ml), the product gave the following chromatographic and spectroscopic information.

GLC: (DEGS) 21.2.

IR spectrum: 1030 and 3070 cm^{-1} (cyclopropane), 1100 cm^{-1} (ester) and 1740 cm^{-1} (ester).

The reaction of methyl 12-methoxy oleate with methanol and sulphuric acid:

Methyl 12-methoxyoleate (50 mg) was refluxed for four hours with methanol (10 ml) and concentrated sulphuric acid (0.5 ml). The product, recovered by extraction as usual, had the following properties:

GLC: (DEGS) 21.4

IR spectrum: 1100 cm^{-1} (ether), 1740 cm^{-1} (ester) and 3010 cm^{-1} (alkene).

NMR spectrum: 4.65 \uparrow (olefinic protons), and 6.75 \uparrow (O.CH₃)

Von-Rudloff oxidation: nonanedioic acid and (presumably) 3-methoxy nonanoic acid (ECL of methyl ester 12.0 DEGS).

Attempted Von-Rudloff oxidation of methyl 9-methoxy cyclopropane ester:

Methyl 9-methoxy cyclopropane ester (20 mg) was submitted to Von-Rudloff oxidation. The product after reaction with methanol (5 ml) and methanolic boron trifluoride solution (14, 0.1 ml) for 15 minutes had the following properties:

GLC: (DEGS) 21.4

IR spectrum: 978 cm^{-1} (trans alkene), 1100 cm^{-1} (ether) and 1740 cm^{-1} (ester).

When submitted to Von-Rudloff oxidation this product gave nonanedioic acid and (presumably) 3-methoxy nonanoic acid (ECL of methyl ester 12.0 DEGS).

The reaction of methyl 9-acetoxy cyclopropane ester with methanolic boron trifluoride and methanol.

When refluxed with methanol (5 ml) and methanolic boron trifluoride (14%, 0.1 ml) for 15 minutes, the methyl 9-acetoxy cyclopropane gave a product with the following properties.

GLC: (DEGS) 21.4; (ApL) 18.6

IR spectrum: 980 cm^{-1} (trans alkene), 1100 cm^{-1} (ether), 1740 cm^{-1} (ester), and 3450 and 3520 cm^{-1} (hydroxyl group).

The reaction of methyl 9-acetoxy cyclopropane ester with acetic acid and sodium acetate:

Methyl 9-acetoxy cyclopropane ester (10 mg) was heated (100°) with acetic acid (2 ml) and sodium acetate (5 mg) for 2 hours. The product recovered in the usual way had ECL's of 19.4 (5%), 23.3 (25%), 24.1 (35%) and 24.6 (35%) on DEGS column.

The reaction of methyl 9-acetoxy cyclopropane ester with methanol and hydrochloric acid.

Methyl 9-acetoxy cyclopropane ester (20 mg) was stirred with methanol (5 ml) and concentrated hydrochloric acid (0.5 ml) at room temperature. Samples were withdrawn after various time intervals and examined by GLC (see the table).

The infra-red spectrum showed absorption bands at 1100 cm^{-1} (ether) and 3070 cm^{-1} (cyclopropane).

time (minutes)	Area %	
	22.2 (DEGS)	24.1 (DEGS)
5	35	65
10	44	56
20	46	54
40	55	45
90	70	30
150	86	14

Conversion of methyl 9-acetoxy cyclopropane ester to methyl 9-hydroxy cyclopropane ester.

The acetoxy cyclopropane ester (50 mg) was refluxed for one hour, with methanol (5 ml) and sodium methoxide (30 mg). The product (45 mg) recovered by addition of water and extraction with ether, had the following chromatographic and spectroscopic properties.

GLC: (DEGS) 25.7

IR spectrum: 1035 and 3070 cm^{-1} (cyclopropane), 1740 cm^{-1} (ester) and 3450 cm^{-1} (hydroxyl group) with complete disappearance of the acetoxy group.

Conversion of methyl 9-hydroxy cyclopropane ester to methyl 9-methoxy cyclopropane ester.

The hydroxy cyclopropane ester (20 mg) was refluxed with methyl iodide (0.5 ml) and silver oxide (10 mg) for four hours. The product (18 mg) recovered by addition of ether, filtering and evaporating the solvent ether and the excess of methyl iodide, showed the following characteristics:

GLC: (DEGS) 21.2

IR spectrum: 1020 cm^{-1} and 3070 cm^{-1} (cyclopropane), 1740 cm^{-1} (ester), and 1100 cm^{-1} (ether), with the complete disappearance of the hydroxyl group.

Conversion of methyl 9-hydroxy cyclopropane ester to methyl 9-acetoxy cyclopropane ester.

The hydroxy cyclopropane ester (20 mg) was refluxed with acetyl chloride (5 ml) for 15 minutes. The product recovered by addition of water and extraction with ether, showed the following properties:

GLC: (DEGS) 22.8 (5%), 23.3 (66%), 24.1 (17%) and 24.6 (12%)

IR spectrum: 980 cm^{-1} (trans alkene), 1250 cm^{-1} and 1370 cm^{-1} (acetate), 1740 cm^{-1} (ester) and 3070 cm^{-1} (small, cyclopropane).

In another reaction, the hydroxy cyclopropane ester (20 mg) was refluxed with acetic anhydride (5 ml) and sodium acetate (20 mg) for 8 hours. The product recovered by addition of water and extraction with ether showed the following properties:

GLC: (DEGS) 19.3 and 19.6 (total, 20%) 24.1 (18%), and 24.6 (62%).

IR spectrum: 980 cm^{-1} (trans alkene), 1250 and 1370 cm^{-1} (acetate), 1740 cm^{-1} (ester), 3070 cm^{-1} (small, cyclopropane) and the complete disappearance of the hydroxyl absorption band.

Conversion of methyl 9-hydroxy cyclopropane ester to methyl 9-oxo-cyclopropane ester.

To the hydroxy cyclopropane ester (40 mg) was added at once a solution of sodium dichromate (30 mg), conc. sulphuric acid (2 drops), water (4 drops), and acetic acid (0.3 ml). After 30 seconds, water was added and the mixture was extracted with ether (3 x 5 ml), washed with sodium carbonate solution (5%, 3 x 10 ml) and water (3 x 10 ml) and dried over sodium sulphate. After purification on TLC this product had the following chromatographic and spectroscopic properties:

GLC: (DEGS) 25.0; (ApL) 19.1

IR spectrum: 1700 cm^{-1} (oxo), 1740 cm^{-1} (ester) and 3070 cm^{-1} (cyclopropane), beside the disappearance of the hydroxyl group.

NMR spectrum: 9.35τ and 9.70τ (cyclopropane protons).

Preparation of some methyl cyclopropane esters:1. preparation of methyl cis-9,10-methylenoctadecanoate from methyl oleate

[(W.W. Christie, F.D. Gunstone, I.A. Ismail and (Mrs.) L. Wade)
chem. Phys. Lipids 1968, 2, 196.]

Zinc dust (4.0 g) was added to vigorously stirred, nearly boiling, acetic acid (20 ml) in a 100 ml flask (oil bath temperature 130°C). After 10 minutes cupric acetate (0.3 g) was added and the mixture stirred until the blue colour disappeared. The supernatant liquid was decanted and the residue washed with acetic acid (5 x 30 ml), and ether (5 x 30 ml).

A solution of di-iodomethane (8 ml) and methyl oleate (0.8 g) in ether (10 ml) was added to the zinc copper couple and the mixture was stirred overnight at 60°C in a nitrogen atmosphere. The ether solution was washed with hydrochloric acid (IN, 3 x 20 ml) and with water (4 x 30 ml). After removal of ether and excess of diiodomethane, the cyclopropane ester (~600 mg) was purified on a silica column by elution with petroleum containing increasing proportions of ether (PE10, PE20, PE30), and then on Ag⁺TLC (PE25).

Chromatographic and spectroscopic information is presented:

GLC: (DEGS) 19.5

IR spectrum: 1030 cm⁻¹ and 3070 cm⁻¹ (very strong, cyclopropane) and 1740 cm⁻¹ (ester).

NMR spectrum: 9.4τ and 10.3τ (cyclopropane protons)

2. Preparation of methyl trans 9,10-methyleneoctadecanoate

This was prepared from methyl elaidate as described above and showed the following chromatographic and spectroscopic properties:

GLC: (DEGS) 19.0

IR spectrum: 1025 cm^{-1} and 3070 cm^{-1} (cyclopropane), and 1740 cm^{-1} (ester).

NMR spectrum: 9.6 \uparrow and 9.8 \uparrow (cyclopropane protons).

Hydrogenolysis of some cyclopropane and other esters:

Each ester (50 mg), dissolved in acetic acid (5 ml), was shaken with Adams catalyst (PtO_2 , 5 mg) in a hydrogen atmosphere for one hr. at 40°. After filtration the solution was diluted with water and extracted with ether. The product was examined by GLC and by infra-red spectroscopy:

(VI) Methyl, cis-9,10-methyleneoctadecanoate:

GLC: (DEGS) 18.35

IR spectrum: 1740 cm^{-1} (ester) and complete disappearance of the cyclopropane.

(VII) Methyl-trans-9,10-methyleneoctadecanoate: (6 hours).

GLC: (DEGS) 18.3 (60%) and 19.0 (40%)

IR spectrum: 1740 cm^{-1} (ester) and 3070 cm^{-1} (very small, cyclopropane).

GLC: (DEGS) 17.3 (8%), 18.0 (26%), 24.2 (31%) and 25.6 (34%).

IR spectrum: 1250 cm^{-1} and 1370 cm^{-1} (acetate), 1740 cm^{-1} (ester), and 3500 cm^{-1} (small, hydroxyl).

(III) Methyl 9-hydroxy-10,11-methylene heptadecanoate:

GLC: (DEGS) 17.3 (4%), 18.0 (27%), 22.8 and 23.2 (3%), 24.2 (30%) and 25.5 (36%).

IR spectrum: 1250 cm^{-1} and 1370 cm^{-1} (acetate), 1740 cm^{-1} (ester) and 3500 cm^{-1} (hydroxyl).

(IV) Methyl 12-acetoxyoleate:

GLC: (DEGS) 18.0 (6%), 24.2 (92%) and 24.9 (2%).

(ApL) 18.0 (6%), and 19.8 (94%)

IR spectrum: 1250 cm^{-1} and 1370 cm^{-1} (acetate), and 1740 cm^{-1} (ester).

(V) Methyl ricinoleate:

GLC: (DEGS) 18.0 (24%), 24.2 (4%) and 25.5 (72%).

(ApL) 18.0 (24%) and 19.8 (76%).

IR spectrum: 1740 cm^{-1} (ester) and 3600 cm^{-1} (hydroxyl) and 1250 and 1370 cm^{-1} (small, acetates).

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