FATTY ACIDS, PART 38 *

NEIGHBOURING GROUP PARTICIPATION IN THE OXYMERCURATION-DEMERCURATION REACTION. ANOTHER ROUTE TO 1,4- AND 1,5-EPOXIDES

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Oxymercuration-demercuration of hydroxy alkenes follows an intramolecular pathway to furnish 1,4-epoxides (tetrahydrofurans) when the hydroxyl group is β (*trans* only) or γ to a double bond and 1,5-epoxides (tetrahydropyrans) when the hydroxyl group is δ to the double bond. The *cis* and *trans* isomers of methyl ricinoleate and methyl 9-hydroxyoctadec-12-enoate, and a series of *cis* and *trans* octadecenols ($\Delta 2 - \Delta 6$) are used to establish these relationships.

1,4- and 1,5-Epoxides are also formed during the oxymercuration of methyl densipolate and methyl 12,13-dihydroxyoleate and during the hydroxymercuration of methyl octadeca-9,12 and 8,12-dienoates.

1. Introduction

In the previous paper [1] we described the application of the oxymercurationdemercuration reaction to long-chain alkenoates and showed (a) that the reaction occurred in high yield with methanol and a range of other participating solvents (mainly those containing a hydroxyl group), and (b) how the methoxymercuration process is influenced by neighbouring non-participating substituents (OAc, OMe, CO_2Me). In this paper we show that the hydroxyl group, when present in an appropriate position with respect to the double bond, can participate in the oxymercuration process and furnish cyclic ethers by intramolecular reaction even in the presence of a participating solvent such as methanol. This observation is checked through a range of hydroxy alkenes. Its application to a number of problems is discussed in the following paper. The possibility of the carboxyl group, the epoxy group, or the oxo group behaving as a participating substituent is also examined.

* Part 37: Preceding paper.

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The intramolecular oxymercuration reaction is already well documented [2] and the effect of double bond configuration has been discussed [3].

2. Reactions of hydroxyoctadecenoates

The oxymercuration-demercuration of some natural hydroxyoctadecenoates was first examined. These had a hydroxyl group in the β or γ position with respect to the double bond which had the *cis* configuration in the natural acid but was converted, in some cases, to the *trans* configuration.

Using methanol as solvent, methyl 12-hydroxyelaidate (1, a β -hydroxy alkene) and the *cis* and *trans* isomers of methyl 9-hydroxy-octadec-12-enoate (3, γ -hydroxy alkenes) react entirely in an intramolecular manner giving mixtures of the *cis* and *trans* 9,12-epoxystearates (2, a tetrahydrofuran derivative). One isomer predominated in all three reactions but we do not know whether this is the *cis* or *trans* form. The γ -hydroxy alkene could conceivably produce a 1,5-epoxide (4, a tetrahydropyran derivative) but this is formed as a minor product only with the *trans* isomer (see table 1). A greater difference is apparent between the *cis* and *trans* β hydroxy alkenes: the former gives very little epoxide (2) and the major reaction product results from intermolecular reaction between the alkenoate and methanol. As with the methoxy and acetoxy octadecenoates reported in the previous paper, the incoming methoxyl group is attached preferentially to the unsaturated carbon atom further from the substituent. Methyl ricinoleate and water (in the presence of THF) react in a similar manner giving a little epoxide (17%) and a larger proportion of the dihydroxystearates (79%).

Substrate ester	Solvent	Products of intermolecular reaction % (ECL)		9, 12-epoxy- stearates	
		10, 12-	9,12-	(21.3)	(21.6)
12 OH 9c	H ₂ O	9% (20.4) ^a	70% (20.7) ^{a,b}	16%	1%
12 OH 9c	MeOH	18% (28.0) ^b	66% (29.0) ^b	8%	2%
12 OH 9t	MeOH			20%	7 9 %
9 OH 12c	MeOH			33%	67%
9 OH 12t	MeOH			35%	57% ^c

 Table 1

 Oxymercuration-demercuration of some methyl hydroxyoctadecenoates

^a ECL of bis-TMS ether.

^b ECL of dimethoxystearates: 10, 12 (23.3); 9, 12 (23.9).

^c Also formed: methyl 9, 13-epoxystearate (8%, 20.0).

These differences probably arise on steric grounds. The conformation of the intermediate mercury compound required for intramolecular reaction will be restricted only for the $cis \beta$ -hydroxy alkene.



The greater facility with which γ -hydroxy alkenes undergo intramolecular reaction compared with β -hydroxy alkenes and the preference of the former to give five-membered rather than six-membered rings is illustrated in the oxymercurationdemercuration of methyl densipolate (5, 12 OH 18 : 2 9c15c) and of methyl *threo*-12,13-dihydroxyoleate (6, prepared from methyl vernolate). These esters give the 1,4-epoxides shown below:





When intramolecular reaction is possible it usually supersedes the intermolecular reaction with a participating solvent. The reaction follows a similar course when conducted in a non-participating solvent except that additional double bonds do not then react. This is sometimes advantageous as will be discussed in the following paper.

3. Reactions of the octadecenols and of arachidonyl alcohol

The reactions described in the previous section are restricted to β - and γ -hydroxy alkenes because only these are conveniently available. To extend this study we have examined a series of octadecenols ($\Delta 2-\Delta 6$) prepared by lithium aluminium hydride reduction of synthetic methyl octadecenoates [4, 5]. The results, summarised in table 2, confirm and extend those already reported. Even in methanol solution intramolecular reaction is dominant for the 3t (β), 4c and 4t (γ), and 5c and 5t (δ) octadecenols. These furnish 2-tetradecyltetrahydrofuran (1,4-epoxyoctadecane) or 2-tridecyltetrahydropyran (1,5-epoxyoctadecane). With the 2c, 2t, 3c, and 6c octadecenols, cyclic ethers are not formed or are present in insignificant amounts: instead there is addition of methanol across the double bond in the usual way with the hydroxyl group exerting an orientating influence in the 2c, 2t, and 3c alcohols. The 4t alcohol gives the same cyclic ethers in a non-participating solvent (DMF) but the 6c alcohol does not react under these conditions and the octadecenol is recovered unchanged.

The 2t octadecenol gave only a moderate yield (43%) of 2(3)-methoxyoctadecanols along with appreciable amounts (36%) of an additional compound which is formed in even larger proportions (73%) during the attempted regeneration of the alcohol by halogen acid. This compound is shown to be 3-methoxyoctadec-1-ene (8) which must arise from an alternative and preferred regeneration pathway:



Arachidonyl alcohol is typical of a range of polyene alcohols which have a double bond γ or δ to the primary alcohol function and might therefore be expected to give cyclic ethers by this oxymercuration reaction. In methanol solution the product would be a mixture of several trimethoxypentadecyltetrahydropyrans: in DMF solution reaction is confined to the 5c double bond and the product is a pentadecatrienyltetrahydropyran (9) which can be reduced to 2-pentadecyltetrahydropyran (10).

$$CH_{3}(CH_{2})_{4}(CH=CHCH_{2})_{3}CH=CH(CH_{2})_{3}CH_{2}OH \xrightarrow{Hg(OAc)_{2}, DMF;}{NaBH_{4}}$$



Alkyltetrahydrofurans are more polar than the isomeric alkyltetrahydropyrans on TLC. They also differ in their GLC behaviour (see table 2) and can be distinguished by mass spectrometry.

4. Examination of compounds with other substituents

Having shown that appropriately placed hydroxy substituents are involved in the oxymercuration procedure and furnish cyclic products, we examined the behaviour of octadecenoic acids, of epoxy and oxo alkenoates, and the hydroxymercuration of octadecadienoates which should proceed through intermediate hydroxy octadecenoates.

Henbest and Nicholls [3] have shown, for a bicycloheptene carboxylic acid, that oxymercuration furnishes a lactone but we have not yet succeeded in producing lactones from octadecenoic acids. As expected, oleic acid reacted like its methyl

ester and gave 9(10)-methoxystearic acids with methanol and mercuric acetate. The 4t acid did not seem to react at all and the 5t acid gave, after methylation, methyl 5- and 6-methoxystearates (64%) and methyl 5-hydroxystearate (12, 23%). The hydroxy ester is a single isomer and may have been formed during methylation of the lactone (11). When the reaction was conducted in DMF in place of methanol only starting material was obtained. These reactions are being examined further.

$$RCH=CH(CH_2)_3CO_2H \xrightarrow{Hg(OAc)_2, MeOH,}_{NaBH_4} \xrightarrow{RCH_2} RCH_2CH(OH)(CH_2)_3CO_2H$$
(11)
(12)

With methyl 12,13-epoxyoleate the major product (methyl 12,13-epoxy-9(10)methoxystearates, 78%) was accompanied by a cyclic ether (22%) which was mainly methyl 10,13-epoxy-12-methoxystearate (13). The same product was obtained by methylation of the corresponding hydroxy ester (7) already prepared and identified.



Oxymercuration studies on methyl 12-oxo-oleate and on methyl 9-oxo-octadec-12-enoate in methanol and in DMF were abandoned because of the multiplicity of the products.

In the oxymercuration of methyl linoleate it is possible that the mercurinium ion (14) might have sufficient carbonium ion character to react as shown below furnishing a cyclopropane ester [6] but we have found no evidence of any cyclopropane derivative in the reaction with methanol or with water.



Table 2

Octadecenol	Methoxyoctadecanols ^b	1,4 and/or 1,5- epoxyoctadecanes (%, ECL)		
	(%, ECL)			
Reaction in methanol	solution :			
2 <i>c</i>	{ 2MeO (11%, 21.8) 3MeO (83%, 22.0)			
2t ^c	{2MeO (8%, 21.9) 3MeO (35%, 22.2)			
3 <i>c</i>	{3MeO (18%, 22.5) {4MeO (72%, 22.9)	1,4-epoxy (7%, 15.8)		
3 <i>t</i>		1,4-epoxy (100%, 15.7)		
4 <i>c</i>		1,4-epoxy (92%, 15.8)		
4 <i>t</i>		(1,4-epoxy (88%, 15.8) (1,5-epoxy (12%, 15.2)		
5 <i>c</i>		1,5-epoxy (100%, 15.1)		
5 <i>t</i>		1,5-epoxy (100%, 15.1)		
6 <i>c</i>	6 + 7 MeO (95%, 22.7)			
Reaction in DMF solu	tion :			
4 <i>t</i>		(1,4-epoxy (90%, 15.8) (1,5-epoxy (8%, 15.2)		
6 <i>c</i>	only starting material recovered			
20 : 4 (5c8c11c14c)		1,5-epoxy (97%, 18.6) ^d		

Oxymercuration-demercuration of isomeric octadecenols and of arachidonyl alcohol^a

^a Small amounts of starting material are also present in most reaction products.

^b Identified by mass spectrometry of the dimethoxyoctadecanes (ECL 17.8).

^c 3-Methoxyoctadec-1-ene (36%, 14.1) is also formed, see text.

^d This product (2-pentadeca-3', 6', 9'-trienyltetrahydropyran) is hydrogenated to 2-pentadecyltetrahydropyran (ECL 17.0).

In hydroxymercuration of appropriate methyl octadecadienoates the product of reaction at one double bond is a mixture of hydroxy monoenoates which may react in an intramolecular fashion during reaction at the second alkene centre. This has been shown to occur with the 9c12c (linoleate) and 8c12c octadecadienoates.

	Hydroxy- octadecenoates	Dihydroxy- stearates ^a		Epoxy- stearates ^a	
	$(9 \text{ OH } 12c(\gamma) \rightarrow$	[9,12 + 9,13]	+	9,12	[9,13]
$18 \cdot 28c12c$ - >	10 OH 12c (β) \rightarrow	10,12 + 10,13	+	[10,13]	_
	12 OH 9c (β) \rightarrow	9,12 + 10,12	+	[9,12]	
	$\left(\begin{array}{cc} 13 \text{ OH} & 9c\left(\gamma\right) \end{array}\right) \rightarrow$	[9,13 + 10,13]	+	10,13	[9,13]
Yield		52%		48%	0
	$\left(\begin{array}{c} 8 \text{ OH } 12c\left(\delta\right) \rightarrow \end{array}\right)$	[8,12 + 8,13]	+	_	8,12
$18 \cdot 29c12c$	$\int 9 \text{ OH } 12c(\gamma) \rightarrow$	[9,12 + 9,13]	+	9,12	[9,13]
10.290120	12 OH 8c $(\gamma) \rightarrow$	[8,12+9,12]	+	9,12	[8,12]
	$(13 \text{ OH } 8c(\delta) \rightarrow$	[8,13 + 9,13]	+	~	9,13
Yield		14%		23%	36%

Table 3

Hydroxymercuration-demercuration of methyl 9c12c- and 8c12c-octadecadienoates

^a Expected minor products are indicated in brackets.

Methyl linoleate furnishes 9,12- and 10,13-epoxystearates and various dihydroxystearates (table 3). These results are consistent with our earlier observations that β -hydroxyalkenes (*cis*) gave little intramolecular reaction whilst this is the major reaction pathway for the γ -hydroxy alkenes. In a larger scale experiment 21 g of methyl linoleate gave 8 g of the epoxystearates which were subsequently shown not to act as stabilisers for PVC. (We are indebted to Dr. G. Silverstone for this observation.) The yield of cyclic ether was increased to \sim 70% by cyclodehydration of the total reaction product when 9,12- and 10,13-dihydroxystearates are cyclised to form more epoxy esters.

A similar reaction with methyl octadeca-8,12-dienoate gave starting material (18%), acetoxyoctadecenoates (9%), dihydroxystearates (14%), 9,12-epoxystearates (23%), and 8,12- and 9,13-epoxystearates (36%).

5. Experimental

5.1. General procedures

Most of the spectroscopic, chromatographic, and general chemical procedures are detailed in the preceding paper.

Starting materials. – Methyl 12,13-epoxyoleate (vernolate) was obtained (99% pure) from Cephalocroton cordofanus seed oil by methanolysis and subsequent chromatography of the methyl esters [7]. Methyl threo-12,13-dihydroxyoleate was obtained by esterification of the pure dihydroxy acid isolated from Vernonia an-

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thelmintica seed oil by acetolysis, hydrolysis, and crystallisation of the mixed acids from ethyl acetate at 0° [8]. Methyl densipolate was supplied by Dr. G. Fuller (Albany, Calif., U.S.A.).

5.2. Reaction products

(i) Methyl ricinoleate (105 mg), water (5 ml) and THF (5 ml) [table 1] : (a) Methyl ricinoleate (4%). (b) Methyl cis and trans-9,12-epoxystearates [17%, ECL 21.1 (94%) and 21.4 (6%)] identified as indicated in § (ii). (c) Methyl dihydroxystearates [79%, ECL of bis-TMS ethers 20.4 (12%) and 20.7 (88%)] separated on TLC (PE70) with the less polar ester being the minor component. The mixed dihydroxystearates, after refluxing with methanolic sulphuric acid (2M, 6 hr), were separated into methyl 9,12-epoxystearate [84%, ECL 21.1 and 21.4) and a concentrate of methyl 10,12-dihydroxystearate [16%, ECL of bis-TMS ether 20.4 (78%) and 20.7 (22%)]. This dihydroxystearate was methylated (ECL identical with those of authentic samples of the 10,12(23.3) and 9,12(23.9) dimethoxystearates) and examined by MS which showed the presence of OMe groups on C(12), C(10), and to a minor extent on C(9).

(ii) Methyl hydroxyoctadecenoates (65-125 mg) and methanol (10 mg): The products from these reactions along with the yields and ECL are summarised in table 1. Structures were determined by MS (table 4).

In THF solution, in the absence of methanol, methyl ricinoleate gave some 9,12-epoxystearate (ECL 21.3, 7%; ECL 21.6, 2%) and methyl 9-hydroxyoctadeccis-12-enoate gave 9,12-epoxystearate (ECL 21.3, 28%; ECL 21.6, 61%) as the major reaction product.

(iiia) Methyl densipolate (18 mg) and DMF (10 ml): Unchanged methyl densipolate (14%; ECL 26.1, 20.8 for TMS ether) was accompanied by methyl cis and trans-12,15-epoxyoctadec-9-enoates (ECL 21.9, 28% and ECL 22.1, 58%). The GC-MS of these two epoxy esters were almost identical (table 4). Von Rudloff oxidation gave methyl nonanedioate along with compounds of ECL 12.3 (12%) and 12.6 (22%).

(iiib) Methyl densipolate (20 mg) and methanol (2 ml): The following compounds were identified on the basis of GLC and MS behaviour (table 4): methyl 10-methoxy-cis and trans-12,15-epoxystearates (ECL 23.7, 2% and ECL 23.9, 14%) and the 9-methoxy isomers (ECL 24.3, 20% and ECL 24.6, 62%). The 9- and 10-methoxy esters separated into two bands on TLC.

(*iv*) Methyl threo-12,13-dihydroxyoleate (100 mg) and methanol (10 ml): The major product of this reaction, methyl cis- and trans-10,13-epoxy-12-hydroxystearates [92%; ECL 29.3 (10%) and 29.9 (90%) as hydroxy esters, 24.3 (12%) and 24.8 (88%) as methoxy esters, and 22.5 (14%) and 22.9 (86%) as TMS ethers] was identified from the MS (table 4) of the methoxy ester.

(v) Octadecenols and arachidonyl alcohol with methanol or DMF (table 2): The reaction with mercuric acetate was carried out by the general procedure already

Table 4 Mass spectra (70 eV) of various oxymercuration-demercuration products

Values quoted are m/e, origin of fragment, and intensity relative to the base peak = 100. Most of the proposed transitions were confirmed by the presence of a metastable peak with the expected m/e value. Peaks are quoted in decreasing values of m/e except for mixtures where the fragments are separated into groups relating to each component of the mixture. Those marked with an asterisk may result from more than one component. The roman numerals attached to each name are cross-references to § 2 in § 5. Experimental

methyl 9,12-epoxystearate (ii) and (ix) [9, 10] : $CH_{3}(CH_{2})_{5a} \xrightarrow{[a]{0}{b}} (CH_{2})_{7}CO_{2}Me$ major peaks: 313 (M+1, 1) 312 (M, 2) 311 (M-1, 1) 294 (M-18, 1) 281 (M-31, 2) 263 (M-49), 2) 227 (a, 48) 209 (a-18, 12) 195 (a-32, 50) 177 (a-50, 15) 155 (b, 100) 137 (b-18, 38)

[The above figures refer to the product from experiment (ii), similar results were obtained with the product from experiment (ix).]

methyl 9,13-epoxystearate (ii) [9, 10] : $CH_3(CH_2)_4 = 0$ (CH₂)₇CO₂Me major peaks : 313 (M+1, 1) 312 (M, 3) 311 (M-1, 1) 294 (M-18, 2) 281 (M-31, 2) 263 (M-49, 2) 241 (a, 15) 223 (a-18, 25) 209 (a-32, 27) 191 (a-50, 13) 155 (b, 100) 137 (b-18, 58)

methyl 9,12-dimethoxystearate (ii) [1, 9] :

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} & \overline{b} \\ CH_{3}(CH_{2})_{5} & \overline{c} \\ CH \\ CH_{1}(CH_{2})_{2} & \overline{c} \\ CH \\ CH_{1}(CH_{2})_{2} & \overline{c} \\ CH \\ OMe & OMe \end{array} \\ \end{array} \\ \begin{array}{c} \begin{array}{c} major \ peaks : & 327 \ (M-31, 2) \\ 294 \ (M-64, 4) \\ 294 \ (M-64, 4) \\ 209 \ (a-64, 13) \end{array} \\ \begin{array}{c} 326 \ (M-32, 5) \\ 201 \ (c \ and \ d, 100) \\ 169 \ (c-32 \ and \ d-32, 86) \\ 129 \ (b, 64) \\ 97 \ (b-32, 46) \end{array} \\ \end{array} \\ \begin{array}{c} methyl \ 10, \ 12-dimethoxystearate \ (ii) : \\ \hline \\ CH_{3}(CH_{2})_{5} & \overline{c} \\ CH \\ CH_{2} & CH \\ CH_{2}$$

methyl 12,15-epoxyoctadec-9-enoate (iiia) [9, 10] : $CH_3CH_2CH_2 H_a O_h CH_2CH=CH(CH_2)_7CO_2Me$ major peaks (from GLC peak of ECL 21.9) : 310 (M, 0.5) 279 (M-31, 1) 249 (a-18, 0.4) 235 (a-32, 0.4) 113 (b, 100) 95 (b-18, 86) major peaks (from GLC peak of ECL 22.1) : 310 (M, 0.7) 279 (M-31, 1.1) 235 (a-32, 0.4) 113 (b. 100) 249 (a-18, 0.4) 95 (b-18, 85) methyl 12,15-epoxy-9(10)-methoxystearate (iiib): ď ÒМе 310 (M-32, 5) 299 (a, 4) 342 (M, 01) 311 (M-31, 3) major peaks : 267 (a-32, 4) 279 (M-63, 2) 293 (M-49, 1) 249 (a-50, 5) 235 (a-64, 5) 113 (b, 100) 95 (b-18, 77) 215 (c, 14) 183 (c-32, 3) 171 (d, 3) $153^{*}(d-18, 25)$ 151(c-64, 4)139 (d-32, 19) 121 (d-50, 5) 167 (d-18, 2) 201 (c, 34) 185(d, 42)169 (c-32, 6) 153*(d-32, 25) 137 (c-64, 11) 135 (d-50, 7) methyl 10,13-epoxy-12-methoxystearate (IV) and (VII) [11] : MeO

major peaks :	343 (M+1, 0.2)	341 (M~1, 0.2)	324 (M-18, 04)
	311 (M-31, 6)	310 (M-32, 2)	293 (M-49, 04)
	279 (M-63, 4)	271 (a, 1.2)	253 (a-18, 2.5)
	242(c, 3)	239 (a-32, 1.9)	210 (c-32, 12)
	178 (c-64, 25)	171 (b, 20)	139 (b-32, 10)
	129 (53)	71 (100)	

fragment c is considered to be $Me\dot{O} = CHCH_2\dot{C}H(CH_2)_8CO_2Me$

[The above figures refer to the product from experiment (IV), similar results were obtained with the product from experiment (VII).]

1,3-dimethoxyoctadecane (with some 1,2-isomer) (V) :

$$\begin{array}{c|c} b \\ CH_{3}(CH_{2})_{x} & CH_{1}(CH_{2})_{y} & CH_{2} \\ OMe & OMe \\ \end{array}$$
major peaks : 314 (M, 1) 283 (M-31, 3) 269*(c, 10) 255 (b, 33) 103 (a, 100) 71 (a-32, 43) 45* (d, 77) 269*(c, 10) 57 (a-32, 29) 45*(d, 77) \end{array}

1,4- and 1,3-dimethoxyoctadecanes (V) :



major peaks :	313 (M-1, 1)	282 (M-32, 2)	250 (M-64, 6)	
	241 (b, 27)	117 (a, 71)	85 (a-32, 96)	
	255 (b, 10)	103 (a, 40)	71 (a-32, 100)	45 (<i>c</i> , >100)

the base peak at m/e 71 is probably only partly the fragment a-32

1,6- and 1,7-dimethoxyoctadecanes (V) :





[significant peaks for the 6-isomer : 271 (b, 2) 217 (a, 3) 185 (a-32, 0).]

203(a, 84)

171 (a-32, 12)

74 (100)

285 (b, 29)

methyl 12,13-epoxy-9(10)-methoxystearate (VII) $CH_3(CH_2)_4$ CHCH(CH₂)₂CH(CH₂)₂CO₂Me OMe major peaks : 201 (a, 37) 169 (a-32, 8) 137 (a-64, 22) 215 (a. 32) 183 (a-32, 5) 152 (100) methyl acetoxystearates (VIII) [1]: b ſa $\operatorname{CH}_{3}(\operatorname{CH}_{2})_{x}|_{U}^{CH}(\operatorname{CH}_{2})_{y}\operatorname{CO}_{2}\operatorname{Me}$ major peaks : 356 (M, 0.6) 325(M-31, 0.5)313 (M-43, 11) 264 (M-92, 41) 296 (M-60, 8) 265 (M-91, 28) 74 (100) 229* (a, 24) $197^{*}(a-32, 15)$ 199 (b, 10) x = 8 $157^{*}(b-42, 12)$ 187 (a-42, 34) 169*(a-60, 21) 155 (a-74, 38) 139 (*b*-60, 7) $243^{*}(a, 24)$ 211*(a-32, 16) 201 (a-42, 24) x = 7169*(a-74, 21) $143^{*}(b-42, 28)$ 185 (b, 8) 125 (b-60, 16) 229*(a-42, 24) x = 5271 (a, 4) 239 (a-32, 3) 211*(a-60, 16) 197*(a-74, 15) 157*(b,12) 115 (b-42, 9) 97 (b-60, 44) x = 4285 (a, 4) 253 (a-32, 4) 243*(a-42, 24) 211*(a-74, 16) 143*(b, 28) 101 (b-42, 11) 83 (b-60, 58)

methyl 9,12- and 10,13-epoxystearates (VIII) [9, 10] :

$$\begin{array}{c} \mathrm{CH}_{3}(\mathrm{CH}_{2})_{x} \stackrel{[a]{}}{=} 0 \stackrel{[b]{}}{=} (\mathrm{CH}_{2})_{y} \mathrm{CO}_{2} \mathrm{Me} \\ \\ \text{major peaks :} & 313 \ (\mathrm{M}+1, 2.4) & 312 \ (\mathrm{M}, 1.7) & 311 \ (\mathrm{M}-1, 1.1) \\ & 294 \ (\mathrm{M}-18, 1.3) & 281 \ (\mathrm{M}-31, 1.5) & 263 \ (\mathrm{M}-49, 2) \\ & 45 \ (100) \\ \\ & 227 \ (a, 35) & 209^{*}(a\text{-}18, 34) & 195 \ (a\text{-}32, 31) \\ & 177 \ (a\text{-}50, 8) & 155 \ (b, 72) & 137 \ (b\text{-}18, 22) \\ & 241 \ (a, 33) & 223 \ (a\text{-}18, 4) & 209^{*}(a\text{-}23, 34) \\ & 191 \ (a\text{-}50, 4) & 141 \ (b, 80) & 123 \ (b\text{-}18, 42) \end{array}$$

Table 4 (continu	eđ)
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nethyl 8,12- and 9,13	-epoxystearates (IX)	[9, 10] :	
CH ₃ (CH	$a_2)_x \downarrow a \downarrow 0 b \downarrow$ (CH ₂)yCO ₂ Me	
major peaks:	313 (M +1, 3.9)	312 (M, 6.4)	311 (M-1, 1.4)
	294 (M-18, 2.3)	281 (M–31, 3.2)	263 (M-49, 3.4)
	227 (a, 16)	209*(a-18, 41)	195 (a-32, 25)
	177 (a-50, 12)	169 (b, 61)	151 (b-18, 26)
	241 (a, 17)	223 (a-18, 16)	209*(a-32, 41)
	191 (a-50, 8)	155 (b, 100)	137 (b-18, 39)

described. The resulting epoxides and methoxyoctadecanols (after methylation to dimethoxyoctadecanes) were identified by MS (table 4).

Portions of certain reaction products were treated with methanolic hydrochloric acid (0.5 M). Both octadec-3-enols were regenerated stereochemically pure but the octadec-2-enols gave mainly 3-methoxyoctadec-1-ene (> 70%, ECL 14.0) which was identified by MS before and after hydrogenation (table 4).

(vi) Octadecenoic acids (50 or 100 mg) and methanol (5–15 ml): (a) Oleic acid gave a product which after methylation contained methyl oleate (13%) and methyl 9(10)-methoxystearate (87%, ECL 21.0). (b) Octadec-trans-4-enoic acid did not react and only starting material was recovered (84%). (c) Octadec-trans-5-enoic acid gave, after methylation, methyl octadecenoate (14%), methyl 5(6)-methoxystearates (64%, ECL 20.9), and methyl 5-hydroxystearate (22%; ECL 26.1, 20.0 as TMS ether). The reaction product, after silylation, was submitted to GC-MS and the methoxystearates and silyloxystearate identified by MS (table 4).

(vii) Methyl vernolate (85 mg) and methanol (10 ml): Methyl cis-12,13-epoxy-9(10)-methoxystearates (ECL 27.6, 78%) and methyl 10,13-epoxy-12-methoxystearate [22%; ECL 24.3 (11%) and 24.7 (89%)] were identified by MS (table 4).

(viii) Methyl linoleate (table 3): (a) Oxymercuration in DMF gave methyl linoleate (81%) and methyl acetoxyoctadecenoates (ECL 24.4 19%). The latter was reduced to a mixture of methyl 9-, 10-, 12- and 13-acetoxystearates [ECL 24.1, identified by MS (table 4)]. (b) Reaction in water and DMF gave methyl 9,12- and 10,13-epoxystearates [48%, ECL 21.0 (46%) and 21.3 (54%)] and methyl dihydroxystearates [52%; ECL of bis-TMS ethers: 19.9 (5%), 20.1 (13%), 21.5 (17%), and 21.8 (64%)]. In another experiment the reaction product was refluxed with methanolic sulphuric acid (0.5 M, 6 hr) and the methyl epoxystearates (70%) isolated by preparative TLC. (d) Methyl linoleate (21 g), mercuric acetate (50 g), water (100 ml), and DMF (750 ml) gave, after reduction with sodium borohydride (10 g), a petrol extract (23 g) from which pure methyl epoxystearates (8 g) were isolated by elution from a silica column (Sorbsil, 75 X 3 cm) with PE10 after removal of less polar impurities with PE5. Methyl dihydroxystearates (12 g) were subsequently eluted with methanol.

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(ix) Methyl octadeca-8,12-dienoate (120 mg), water (1 ml), and DMF (9 ml) (table 3): The reaction product contained methyl octadecadienoate (18%, ECL 19.2) methyl dihydroxystearates (14%, ECL of bis-TMS ethers 20.2, 21.8, and 22.0), methyl acetoxyoctadecenoate (9%, ECL 24.5), methyl 9,12-epoxystearates [23%, ECL 21.0 (22%) and 21.3 (78%)], and methyl 8,12- and 9,13-epoxystearates [36%, ECL 19.7, MS (table 4)].

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