# FATTY ACIDS, PART 54\*. SOME REACTIONS OF LONG-CHAIN OXYGENATED ACIDS WITH SPECIAL REFERENCE TO THOSE FURNISHING FURANOID ACIDS

F.D. GUNSTONE and R.C. WIJESUNDERA

Department of Chemistry, The Purdie Building, The University of St. Andrews, Scotland, KY16 9ST (United Kindom)

Received October 15th, 1978 accepted January 2nd, 1979

 $C_{18}$  furanoid acids are prepared from natural oxygenated acids by palladium (II)-catalysed cyclodehydrogenation, by rearrangement of epoxides with iodopropane-sodium iodide-dimethylsulphoxide, and by dehydration of endoperoxides. Some reactions give mixed products but routes to the individual 10,13-, 9,12-, and 8,11-furans are reported. The endoperoxide route leads to speculation about the biosynthesis of natural furanoid acids.

## I. Introduction

In previous studies of long-chain oxygenated acids we were particularly interested in reactions which furnished 1,4-epoxy acids (tetrahydrofurans) and 1,5-epoxy acids (tetrahydropyans) [1-8]. The furanoid acids then reported were only of minor interest [1,3,8].

Following the recognition of several natural furanoid acids [9-13] – albeit of longer chain-length and with additional branched methyl groups – we have re-examined the conversion of oxygenated acids to furanoid compounds. Our substrates were natural products or were readily prepared from such compounds. We now report: (i) the palladium(II)-catalysed cyclodehydrogenation of unsaturated oxygenated acids; (ii) the rearrangement of mono- and diepoxy acids under the influence of iodopropane-sodium iodide-dimethylsulphoxide: and (iii) the formation and subsequent dehydration of endoperoxides. Some of our work overlaps with that recently reported be Lie Ken Jie and Lam [14] though most of it is novel in some respect.

# **Results and discussion**

# A. Palladium(II)-catalysed reactions

Palladium(II) chloride interacts with a double or triple bond by  $\pi$ -bonding making the olefinic or acetylenic carbon atoms prone to inter- or intra- molecular attack by

<sup>\*</sup>Part 53, ref. 13.

a nucleophile. In contrast to mercurinium compounds the resulting palladium complex loses PdHCl so that the overall reaction is cyclisation accompanied by dehydrogenation thus:



With some substrates competitive isomerisation was observed and with others dehydrogenation was accompanied by dehydration. Palladium(II) chloride has been little used in fatty acid reactions [15].

Our reactions were generally effected at approx.  $90^{\circ}$ C on 1-2 mmol of ester in dimethylformamide solution. Palladium chloride is required only in catalytic amount with cupric chloride and a stream of air passing through the reaction mixture to continually regenerate the catalyst. Reaction times varied from minutes to hours. Individual components, separated from the reaction products by preparative thin layer chromatography, were examined by gas liquid chromatography and identified by one or more spectroscopic procedures (ultraviolet, infrared, proton magnetic resonance, and mass spectrometry).

(i) Unsaturated epoxy esters. Methyl vernolate (1, cis-12, 13-epoxyoleate) was completely changed after 18 h reaction to the 10,13-furan\* (3, 52%) accompanied by unidentified polar products (36%), and compounds of intermediate polarity (12%). The furanoid ester contained none of the 9,12-isomer so that this reaction provides a convenient preparative procedure involving a 5-exo-trig process [16]. The products of intermediate polarity may be *cis* and *trans* isomers of 9,10-methylene-12-oxoheptadecanoate and the bicyclic ether (4) all of which were previously recognised among the products of reaction of this epoxide with boron trifluoride etherate. [17].



Methyl cis-9,10-epoxyocatadec-12-ynoate gave only polar products which were not examined but the isomeric methyl trans-11,12-epoxyoctadec-9-ynoate (5) furnished the 9,12-furan (6, 57%) rather than the unsaturated furanoid ester which

<sup>\*</sup>The  $C_{18}$  furanoid esters obtained in this study are described as 9,12- or 10,13-furan etc. The numbers indicate which carbon atoms within the  $C_{18}$  chain are linked to the ether oxygen.

might have been expected. This reaction occurred at room temperature and is a rearrangement similar to that already observed with Hg(II) compounds [3].



(ii) Unsaturated dihydroxy ester. The 10,13-furan (64%) is more conveniently prepared in a quicker reaction (20 min) from methly *threo*-12,13-dihydroxyoleate (2) itself obtained from the natural epoxy ester. Again there is no evidence of any 9,12-furan. Cyclisation is confined to the  $\gamma$ -hydroxyl group – rather than the  $\beta$ -hydroxyl group also present – and the double bond is involved in an exo manner. Differences between the reactivity of  $\beta$ - and  $\gamma$ -hydroxyl groups were previously reported in reactions leading to tetrahydrofuranoid esters [5]. The  $\beta$ -hydroxyl is nevertheless an important requirement for this reaction since dehydration is an essential part of the overall reaction. The reaction follows a different course when only one hydroxyl group ( $\beta$  or  $\gamma$ ) is present (see below).

(iii) Unsaturated monohydroxy esters. Following this result with a dihydroxy ester it was of interest to discover what happens to substrates such as methyl ricinoleate (13) and methyl 9-hydroxyoctadec-cis-12-enoate (7) each of which have one hydroxyl group, in the  $\beta$ - and  $\gamma$ -position respectively.

The product(s) obtained from methyl 9-hydroxyoctadec-*cis*-12-enoate (7) was not easy to identify. We concluded that the vinyl ether (8) was formed quickly in a favoured 5-exo-trig process but that this was subsequently converted to the ketol (10) via the hemiketal (9). Ketol (10), however, eluted from a GLC column (DEGS) as a vinyl ether of ECL 21.3. Catalytic hydrogenation of the reaction product furnished the 9,12- (and some 9,13-) epoxide (11) whereas reduction with sodium borohydride gave the diol (12) which did not cyclise on subsequent treatment with palladium charcoal.



Methyl ricinoleate (13) reacted much more slowly and gave a dihydro-9,12-furan (14, 61%) as major product along with some 9,12-furan (6, 16%) and unidentified

### 196 F.D. Gunstone and R.C. Wijesundera, Reactions of long-chain oxygenated acids

polar products. This cyclisation involves a kinetically-disfavoured 5-endo-trig process. Mass spectrometry confirms the dihydrofuranoid structure without indicating the double bond position. The <sup>1</sup>H NMR spectrum, however, showed a one-proton



olefinic signal and a one-proton signal for the hydrogen next to the ether-oxygen in accord with structure (14). The minor furanoid product must be formed by further dehydrogenation or, more likely, by modification of the ricinoleate before cyclo-dehydrogenation.

The *trans* isomer of methyl ricinoleate gave only polar products which were not further examined but the acetylenic analogue (15) quickly furnished the 9,12-furan (6, 61%) and a second product which may be a ketol (16). The furan is now the product of a favoured 5-endo-trig ring closure and this reaction is a convenient route to the 9,12-furan. The ketol may be formed by a catalysed hydration of the triple bond similar to the well-known Hg(II)-catalysed reaction.



(iv) Unsaturated oxo ester. Methyl 12-oxo-oleate (17), at the same oxidation level as methyl 12-hydroxyocatadec-9-ynoate, reacted quickly but no furanoid ester was produced. The polar products may result from a rapid autoxidation process.



 $R' = (CH_2)_7 CO_2 CH_3$ 

### B. Epoxide rearrangements

Boron trifluoride etherate catalyses the conversion of epoxides to ketones but the reaction is more complex in the presence of a second functional group. Unsaturated epoxides furnish cyclopropanoid ketones [17] and diepoxides give furans and other products [3,8]. Iodopropane-sodium iodide-dimethylsulphoxide also converts epoxides to ketones [18] and Lie Ken Jie and Lam [14] obtained the mixed 9,12- and 10,13-furans from methly linoleate diepoxide by this method.

We have confirmed this result but in contrast to the Hong Kong study our furans (42%) were accompanied by dioxostearates (41%). There was spectroscopic evidence for the presence of the 10,12- and 9,13-dioxo esters but the existence of 9,12- and 10,13-isomers could not be precluded. The signal at  $\delta$  2.45 (-COCH<sub>2</sub>CO-) in the <sup>1</sup>H NMR spectrum confirmed the presence of a  $\beta$ -diketone (the 10,12-isomer). These products probably arose from intermediate oxo epoxides thus:



To obtain unsaturated furans we studied the rearrangement of the mixed unsaturated diepoxides (18a-c) resulting from partial epoxidation of methyl  $\alpha$ -linolenate and identified unsaturated furans (19a, 19b, 31%), oxo furans (20a, 20b, 36%), and unsaturated diketones (33%). From spectroscopic evidence we concluded that this





10,13-furan –  $\Delta 15c$  from 18c 12,15-furan –  $\Delta$  9c from 18a 19a



10-oxo-12,15-furan 15-oxo-10,13-furan 20a

9,12-furan –  $\Delta 15c$  from 18c 13,16-furan –  $\Delta$  9c from 18a 19b

9-oxo-12,15-furan 16-oxo-10,13-furan 20b

last group could include dioxo-octadec-9-enoates from 18a (12,15-, 12,16-, 13,15and 13,16-), dioxo-octadec-12-enoates from 18b (9,15-, 10,15-, 9,16-, and 10,16-), and dioxo-octadec-15-enoates from 18c (9,12-, 9,13-, 10,12-, and 10,13-). Whilst some of these diketones could cyclodehydrate to give furans we cannot be sure of their absence from this fraction.

The oxo furans (20a and 20b) were of special interest because the occurrence of these unexpected products, containing a keto function instead of the expected double bond in addition to the furan system, suggested that this heterocyclic system could result from interaction of epoxide and double bond. This had not previously been appreciated. In the light of evidence presented below the four oxo furans probably arise from the diepoxide (18b) which cannot furnish the unsaturated furans (19).

In support of this hypothesis we showed that methyl vernolate (1), containing only one epoxide function and one double bond, gave the 9,12-furan (6, 37%) along with a 3:1 mixture of 12- and 13-oxo-oleates (38%) and more polar products which were not identified. The furan appeared to be only the 9,12-isomer resulting from a disfavoured 5-endo-trig cyclisation. It is of interest that this same epoxy ester (1)



gave the 10,13-furan with palladium chloride (where the catalyst exerts its influence on the double bond) and the 9,12-furan with iodopropane-sodium iodide-dimethylsulphoxide (where the catalyst exerts its influence on the epoxide group).

Since it is possible that this reaction might proceed via oxo-oleate we submitted methyl 12-oxo-oleate to the same reaction. The 9,12-furan was indeed produced in low yield (19%) but we have already commented on the instability of the starting material resulting from its easy oxidation.

# C. Formation and dehydration of endoperoxides

It is known that furans can be formed by dehydration of endoperoxides [19] and we have exploited this procedure to obtain long-chain furanoid acids.

Methyl octadeca-*trans*-8, *trans*-10-dienoate (21), submitted to photooxidation in the presence of methylene blue, was slowly converted over 5 days to the 8,11-endoperoxide (22) in 74% yield. Its identification was based on its infrared, <sup>1</sup>H NMR, and mass spectra. This interesting compound has not been reported before but we have confined our attention to its dehydration to the 8,11-furan (23, 72%) in the presence of iron (II) sulphate in aqueous tetrahydrofuran. The only other product was unreacted endoperoxide.

$$RCH=CHCH=CHR' \xrightarrow{0_2} R \xrightarrow{0_2} R' \xrightarrow{-R'-} \xrightarrow{Fe(11)S0_4} aq. THF \xrightarrow{R'} 0$$

$$R = CH_3(CH_2)_6 R' = (CH_2)_6C0_2CH_3$$

This preparative procedure leads to an interesting speculation concerning the possible biosynthesis of natural furanoid acids. Autoxidation of linoleate furnishes two conjugated diene hydroperoxides (9-OOH $\Delta$ 10t12c and 13-OOH $\Delta$ 9c11t) whilst photo-oxidation occurs via the ene reaction to give a mixture of 9-OOH  $\Delta$ 10t12c, 10-OOH  $\Delta$ 8t12c, 12-OOH  $\Delta$ 9c13t, and 13-OOH  $\Delta$ 9c11t [20]. Lipoxy-genases promote the formation of specific hydroperoxides similar to those resulting from autoxidation whilst prostaglandin synthetase gives a 1,3-endoperoxide in a reaction which also involves carbon-carbon cyclisation. An alternative scheme set out below leads to a 1,4-endoperoxide and thence a furan. The conversion of intermediate radical to neutral molecule is shown as the last stage in the sequence but it could equally well occur with intermediates (25) or (26).



## D. Recognition and identification of long-chain furanoid acids

Because of the novelty of these compounds it is useful to summarise the chromatographic and spectroscopic properties by which their presence may be detected and their structures completely designated.

Furanoid esters are not very polar and travel along with the more common longchain esters on silica chromatography. Nor are they retarded appreciably by silver ions, travelling between saturated and *cis* monoene esters in silver ion chromatography.

The isomeric  $C_{18}$  furans obtained in this study (8,11-, 9,12-, and 10,13-) were not separated from each other on conventional packed GLC columns and had ECL of approx. 21.0 on polar columns.

The furan system products characteristic ultraviolet absorption at 222 nm ( $\epsilon = 9000$  in hexane). Acyclic conjugated dienes also absorb in this region but they generally have a higher extinction coefficient ( $\epsilon$  approx. 23 000).

In the infrared, 2,5-disubstituted furans absorb at 3100 (C–H stretching in the furan), 1610 (asymmetrical C=C stretch), 1560 (symmetrical C=C stretch), 1010 (ring breathing), and 775 cm<sup>-1</sup> (out-of-plane deformation of the ring). All these are sharp bands and those at 1560, 1010, and 775 cm<sup>-1</sup> are strong.

Signals in the <sup>1</sup>H NMR spectra of 2,5-disubstituted furans at  $\delta$ 5.70, 2.50, and 1.58 are of diagnostic value.



### 200 F.D. Gunstone and R.C. Wijesundera, Reactions of long-chain oxygenated acids

Furan esters produce relatively simple mass spectra with a few intense peaks. The molecular ion and fragment ions a-e are usually apparent. Ions c-e indicate the existence of a furan whilst fragments resulting from cleavage a and b also locate the furanoid ring within the long-chain. The fragment resulting from cleavage b is usually the base peak.



# III. Experimental

# A. Experimental procedures and starting materials

Solvents: Dimethylformamide and dimethylsulphoxide were refluxed with calcium hydride for 2 h before distillation and the dried solvents were stored over molecular sieve type 3 A (0.3 cm pellets).

Thin layer chromatography: Analytical TLC was carried out on 0.25 mm layers (20 cm  $\times$  5 cm plates) and preparative TLC on 1.0 mm layers (20 cm  $\times$  20 cm plates). Plates were usually developed with mixtures of petroleum ether (b.p. 40-60°C) and diethyl ether and an 80:20 mixture (designated PE20) was used unless otherwise stated. To detect the separated components, analytical plates were sprayed with ethanolic phosphomolybdic acid and preparative plates with ethanolic 2',7'-dichlorofluorescein.

Column chromatography was carried out with silica gel (Sorbsil) using 20-25 g per g of material to be separated. Elution was usually effected with petroleum ether containing increasing proportions of diethyl ether. The separation was monitored by TLC and/or GLC.

Gas liquid chromatography was carried out on a Pye series 104 chromatograph equipped with flame ionisation detector using DEGS (20%) at 185°C, SP-222-PS (10%) at 190°C, or SP 2340 (10%) at 240°C as stationary phases on chromosorb WAW (100–120 mesh). Carrier gas (nitrogen) was used at a flow rate of 60-70 ml/min. Quantitation was based on peak heights and retention distance. Retention behaviour is reported as ECL (stationary phase) using saturated esters as standards.

Ultraviolet spectra were recorded on a Unicam SP 800B spectrophotometer using hexane solutions in 1 cm quartz cells.

Infrared spectra were obtained on a Perkin Elmer 257 grating spectrophotometer usually as thin flims between sodium chloride discs. Absorption frequencies  $(cm^{-1})$  usually associated with long-chain esters are not quoted but only unusual absorptions of diagnostic value.

<sup>1</sup>H NMR spectra were recorded at 100 MHZ on a Varian HA instrument using 10– 15% solutions in carbon tetrachloride with 3% tetramethylsilane as internal standard. Chemical shift values are given in ppm downfield from tetramethylsilane ( $\delta = 0$ ). Signals commonly present in long-chain esters which are not of diagnostic significance are not quoted.

Mass spectra were obtained following direct probe insertion of samples into the source of the mass spectrometer (AEI MS 902). Source pressure was  $2.7 \times 10^{-5}$  Pa, source temperature 200°C, and the ionisation voltage 70 eV. The fragment ions associated with (CH<sub>2</sub>)<sub>n</sub>CO<sub>2</sub>CH<sub>3</sub>, C<sub>n</sub>H<sub>2n+1</sub>, C<sub>n</sub>H<sub>2n-1</sub>, and C<sub>n</sub>H<sub>2n-3</sub> are not cited.

Catalytic hydrogenation and silulation were effected as already described [1].

The starting materials required for these studies were isolated from appropriate natural sources by methods which have been discribed previously. The following esters were each obtained from the named seed oil: methyl vernolate and methyl 12,13-dihydroxyoleate from *Cephalocroton cordofanus* or *Vernonia anthelmintica* [17,21], methyl octadec-*trans*-11-en-9-ynoate and its epoxide from *Santalum album* [3], methyl crepenynate and its epoxide from *Afzelia cuanzensis* [3], methyl ricinoleate, its *trans* isomer, acetylenic analogue, and methyl 12-oxo-oleate from castor oil [1,22], and methyl 9-hydroxyoctadec-12-enoate from *Strophanthus courmontii* [23].

Epoxidation was effected with *m*-chloroperbenzoic acid using appropriate quantities of peracid and the products were purified by chromatography [24].

Methyl octadeca-trans-8, trans-10-dienoate was prepared from oleic acid [25].

## B. Palladium(II) - catalysed reaction

(i) General procedure. The ester (2.00 mmol), palladium(II) chloride (0.10 mmol), cupric chloride (dehydrated by heating at  $110^{\circ}$ C for 2 h, 2.00 mmol), and dimethylformamide (15 ml), were heated on a steam bath (90–100°C) in a two-necked flask (100 ml) and agitated by a stream of dry air (passed through silica gel) drawn through the reaction mixture. Progress of the reaction was monitored by gas liquid chromatography.

When the starting material was completely or largely consumed the reaction mixture was cooled, diluted with water (30 ml), and extracted with ether (2 × 25 ml). Combined extracts were filtered (to remove suspended palladium), washed (water), and dried (anhydrous sodium sulphate). Individual components were isolated by preparative thin layer chromatography and identified by chromatography and spectroscopy.

### 202 F.D. Gunstone and R.C. Wijesundera, Reactions of long-chain oxygenated acids

(ii) Methyl vernolate (620 mg) gave a product (450 mg) after 18 h which was separated into fractions A (180 mg), B (40 mg), and C (125 mg) of increasing polarity.

Fraction A (10,13-furan) had ECL of 21.2 (DEGS), ultraviolet absorption at 222 nm ( $\epsilon_{max}$  9500), infrared absorption at 3100, 1610, 1560, 1010, 950, and 775 cm<sup>-1</sup>, <sup>1</sup>H NMR signals at  $\delta$ 1.58, 2.50, and 5.70 associated with the furan system, and expected fragment ions at 308 (M,8), 277 (3), 251 (7), 165 (13), 151 (100), 95 (64), 81 (23), 74 (31) and 69 (28).

Fraction B showed three major GLC peaks of ECL (DEGS) 21.6 (20%), 24.9 (43%), and 25.8 (37%) which were unchanged after attempted silylation. It ran as a single spot on TLC between the furan (fraction A) and the starting epoxy ester. The infrared spectrum showed weak bands at 3420 and 970 cm<sup>-1</sup> apart from the usual absorptions. GC-MS showed that the peak of ECL 21.6 produced fragments ions of m/e310 (M,8), 279 (M - 31,8), 267 (M - 43,4), 254 (?,7), 239 (a,100), 221 (a - 18,5), 207 (a - 32,32), 189 (a - 50,6), 171 (?,7), 155 (?,8), 153 (b,9), 151 (?,16), 147 (?,10), 139 (?,3), 121 (?,3), and 74 (10).

Fraction C (ECL 28.0) could be silvlated (ECL 22.9 DEGS;  $M^+$  382) but was not identified.

(*iii*) Methyl cis-9,10-epoxyoctadec-12-ynoate (616 mg), after reaction for 30 min, gave a product (573 mg) which contained only polar products. Similar results were obtained when the reaction was carried out at room temperature overnight and the reaction was not investigated further.

(*iv*) Methyl trans-11,12-epoxyoctadec-9-ynoate (308 mg) reacted very quickly (a fine black precipitate of palladium powder being deposited within seconds of mixing the reactants) and reaction was therefore effected at room temperature overnight. The product showed a single peak on GLC (ECL 20.6 on SP 2300) and a purified product (175 mg) was isolated by preparative TLC. This was shown to be the 9,12-furan on the basis of infrared peaks at 3100, 1610, 1560, 1010, 950, and 775 cm<sup>-1</sup>; ultraviolet absorption at 222 nm; <sup>1</sup>H NMR signals at 1.58 (4H), 2.52 (4H), and 5.72 (2H), and MS fragment ions at 308 (M,10), 277 (4), 251 (2), 237 (10), 179 (9), 165 (100), 95 (70), 81 (23), 74 (10), 69 (15).

(v) Methyl threo-12,13-dihydroxyoctadec-cis-9-enoate (656 mg) reacted completely in 20 min. The product (620 mg) was almost entirely the 10,13-furan and pure ester was isolable by preparative TLC in 64% yield. Its spectroscopic properties resembled those already reported in section (ii).

(vi) Methyl 9-hydroxyoctadec-cis-12-enoate (624 mg) was reacted for 20 min and the product (620 mg) was examined in a number of ways.

(a) A portion of the reaction product (100 mg) submitted to catalytic hydro-

genation (10% Pd/C) gave 4 fractions on preparative TLC: A (5 mg, ECL 18.0 (DEGS), methyl stearate), B (5 mg, ECL 19.5 (DEGS), methyl 9,13-epoxystearate), C (26 mg, ECL 20.7 and 20.9 (DEGS), methyl 9,12-epoxystearate), and D (15 mg ECL, 24.6 (DEGS), methyl 9-hydroxystearate). Structures were assigned on GLC evidence and MS data. The latter are recorded for fractions B, C, and D.

Fraction B: 312 (M, 0.5), 281 (M – 31,0.2), 269 (M – 43,0.2), 241 (a,6), 223 (a – 18,7), 209 (a – 32,10), 191 (a – 50,5), 155 (b,55), 137 (b – 18,40), and 74 (80).

Fraction C: 312 (M,0.2), 281 (M - 31,0.2), 227 (*a*,27), 209 (*a* - 18,6), 195 (*a* - 32,37), 177 (*a* - 50,10), 155 (*b*,32), 137 (*b* - 18,32), and 74 (21).



Fraction D: 187 (a,17), 158 (b+1,23), 155 (a - 32,100), and 74 (65).

$$cH_3(CH_2)_8 \begin{bmatrix} OH \\ CH \\ CH \end{bmatrix} (CH_2)_7 CO_2 CH_3$$

(b) The reaction product (25 mg) after reduction with sodium borohydride was examined by GLC before (major component not eluted) and after (ECL 22.5) silylation. The reduced product (methyl 9,12-dihydroxystearate) was unchanged after attempted catalytic hydrogenation. The bis TMS ether (two peaks (1:3) at 22.0 and 22.4 on DEGS) had ion fragments 358 (a - 31,0.2), 317 (d,2), 227 (b - 32,6), 75 (HO=SiMe<sub>2</sub>,100), 74 (12), and 73 (SiMe<sub>3</sub>,100)

$$\mathsf{CH}_3(\mathsf{CH}_2)_5 \begin{bmatrix} \mathsf{OSiMe}_3 & \mathsf{OSiMe}_3 \\ \mathsf{CH}_1(\mathsf{CH}_2)_2 \begin{bmatrix} \mathsf{CH}_1 & \mathsf{OSiMe}_3 \\ \mathsf{CH}_2(\mathsf{CH}_2)_2 \end{bmatrix} \\ \mathsf{CH}_2 & \mathsf{OSiMe}_3 \\ \mathsf{CH}_2 & \mathsf{OSiMe}_3$$

(c) TLC of the reaction product (100 mg) gave several fractions of which the largest (42 mg) appeared to be methyl 9-hydroxy-12-oxostearate. A similar fraction resulted by crystallisation of the product from petrol at  $-20^{\circ}$ C. Infrared absorption at 3340, 1710, 930, 890, and 750 cm<sup>-1</sup>; <sup>1</sup>H NMR signals at 0.84 (3H, CH<sub>3</sub>CH<sub>2</sub>), 1.2–1.6 [(CH<sub>2</sub>)<sub>n</sub>)], 2.17 (2H,  $-CH_2$ CO<sub>2</sub>Me), 2.5 (?), and 3.54 (3H,  $-COOCH_3$ ); fragment ions at 310 (M – 18,5), 243 (a,9), 211 (a – 32,15), 171 (e,5), 156 (b – 31, 15), 141 (d,6), 113 (c,29), 74 (15), and 55 (100).

(vii) Methyl ricinoleate (624 mg) gave a product (574 mg) after reaction for 10 h of which a portion (180 mg) was separated (PE30) into fractions A (19 mg), B (71 mg), C (11 mg), and D (16 mg).

Fraction A was shown to be the 9,12-furan on the basis of the following evidence and in comparison with an authentic sample. ECL 20.8, (DEGS), infrared peaks at 3100, 1610, 1560, 1010, 950, 775 cm<sup>-1</sup>, ultraviolet absorption at 222 nm, and mass spectral peaks at 308 (M,2), 277 (1), 237 (2), 165 (14), 95 (17), 81 (18), 74 (42), and 69 (35) with the base peak at 57.

Fraction B was the dihydrofuran 14: ECL 20.8 (DEGS), <sup>1</sup>H NMR signals at  $\delta 4.64$  (1H) and 5.70 (1H), and fragment ions at m/e 310 (M,2), 279 (M-31,2) 225 (a,33), 193 (a - 32,1), 153 (b,100) and 74 (50).



Catalytic hydrogenation of the dihydrofuran gave a product with two GLC peaks (ECL 20.5 and 20.8 in 3:1 ratio on DEGS). Fragment ions at 227 (*a*,3), 209 (a - 18,1), 195 (a - 32,3), 177 (a - 50,1), 165 (?,7), 161 (?,7), 155 (*b*,8), 137 (b - 18,4), 125 (?,5), 124 (?,6) and 74 (100) are consistent with the structure:

(viii) Methyl ricinelaidate (312 mg) had completely reacted after 20 min but preliminary investigation showed mainly polar products and these were not examined further.

(ix) Methyl 12-hydroxyoctadec-9-ynoate (122 mg) gave a product (102 mg) after 20 min which was separated by preparative TLC (PE30) into fractions A (37 mg) and B (24 mg).

Compound A (9,12-furan) had ECL 20.7 (DEGS), a single spot on TLC, ultraviolet absorption at 222 nm, infrared bands at 3100, 1610, 1560, 1010, 950, and 775 cm<sup>-1</sup>, and fragment ions at 308 (M,6), 277 (3), 251 (1), 237 (8), 179 (7), 165 (100), 95 (72), 81 (22), 74 (10), and 69 (21).

Fraction B (ECL 17.7 (12%), 20.9 (67%), and 23.3 (21%) on DEGS) absorbed at 3460 and  $1710-1750 \text{ cm}^{-1}$  in the infrared. On catalytic hydrogenation (Pd/C) it

gave methyl 9,12-epoxystearate: ECL 20.4 (double peak) on DEGS and fragment ions at 227 (a,12), 209 (a – 18,7), 195 (a – 32,12), 177 (a – 50,7), 155 (b,42), 137 (b – 18,25) and 74 (62) with a base peak at 55.

(x) Methyl 12-oxo-oleate. After 20 min all the ester (104 mg) had reacted but the product contained only polar materials.

#### C. Epoxide rearrangements

(i) Methyl cis-9,10-,cis-12,13-diepoxystearate. A mixture of ester (326 mg), iodopropane (850 mg), and sodium iodide (750 mg) in dimethylsulphoxide (15 ml) was heated in a steam bath (approx. 90°C) for 90 min. The product (316 mg) was separated (PE30) into fractions A (97 mg), B (41 mg, not examined), and C(94 mg).

A was a mixture of the 9,12- and 10,13-furanoid esters. It had ECL 20.8 (SP 2300), infrared absorption at 3100, 1610, 1560, 1010, and 775 cm<sup>-1</sup>, ultraviolet absorption at 222 nm, and fragment ions at m/e, 308 (M,11), 297 (4), 251 (6), 237 (6), 165 (61), 151 (65), 95 (100), 81 (33), 74 (7), and 69 (21).

Fraction C (ECL 30.1 (85%), and 30.9 (15%) on SP 2300) is a mixture of dioxostearates: infrared absorption at 1710 and 1740 cm<sup>-1</sup>, <sup>1</sup>H NMR signals at  $\delta$  1.5 (-CH<sub>2</sub>CH<sub>2</sub>CO-), 2.22 (-CH<sub>2</sub>COOCH<sub>3</sub> and -CH<sub>2</sub>CO-), 2.54 (-COCH<sub>2</sub>CO-), and ion fragments at 326 (M,1), 295 (6), and at *m/e* values indicating oxo functions at one of C-9 or C-10 and one of C-12 and C-13 such as 270 (2) 256 (2), 223 (10), 209 (6), 199 (5), 185 (9), 184 (7), 170 (8), 169 (10), 155 (18), 141 (26), 127 (20), 115 (16), and 99 (40).

(*ii*) Diepoxides of methyl linolenate. The mixture of diepoxides (648 mg), after reaction (3 h) with iodopropane/sodium iodide/dimethylsulphoxide, gave a product (630 mg) which was separated (PE30) into fractions A (70 mg), B (81 mg), and C (73 mg).

Fraction A was a mixture of furanoid esters: ultraviolet absorption at 222 nm, infrared absorption at 3100, 3000, 1610, 1560, 1010, 950 and 775 cm<sup>-1</sup>, <sup>1</sup>H NMR

 $\pi$ 

165 (8) from the 13,16-furan  $\Delta$  9,237 (7) and 163 (7) from the 9,12-furan  $\Delta$  15, and 149 (17) from the 10,13-furan  $\Delta$  15.

Though a single spot on TLC, gas chromatography (DEGS) of fraction B showed three incompletely resolved peaks of ECL 26.2 (18%), 26.7 (39%), and 26.9 (43%). Infrared absorption at 3440, 3100, 1720, 1610, 1560, 1010, 950 and 775 cm<sup>-1</sup>, <sup>1</sup>H NMR signals at  $\delta$  0.86 and 1.10 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>- and CH<sub>3</sub>CH<sub>2</sub>CO), 2.16-2.90

$$(-CH_2CO- and \int_{0}^{H_2})$$
, and 5.76  $\begin{pmatrix} H_2 \\ H_2 \end{pmatrix}$  together with the mass

spectrum suggested the presence of 9- and 10-oxo 12,15-furans and 15- and 16-oxo 10,13-furans. Ion fragments were detected at m/e 322 (M,9), 291 (4), 95 (38), 81 (27), 74 (18), and 69 (19) together with ions at 261 (1), 123 (100), 199 (3) for the 10-oxo-12,15-furan, 261 (1), 123 (100) and 185 (4) for the 9-oxo-12,15-furan, 251 (5), 219 (1), 165 (29) and 71 (23) for the 15-oxo-10,13-furan and 251 (5), 219 (1), 165 (29) and 57 (45) for the 16-oxo-10,13-furan.

Fraction C was probably a mixture of dioxo-octadecenoates. It showed infrared absorption at 3480, 3000, 1729, 1680 and 1580 cm<sup>-1</sup>, <sup>1</sup>H NMR signals at  $\delta$  0.8–1.14 (CH<sub>3</sub>), 2.14–2.56 (-CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and -CH<sub>2</sub>CO-), 5.2–5.4 (-CH=CH-), and ion fragments indicating a molecular weight of 324 and two oxo-groups at positions 9 or 10, 12 or 13, or 15 or 16.

(*iii*) Methyl vernolate (620 mg) gave a product (618 mg) after reaction for 3 h at 90°C. A portion (500 mg) was separated into fractions A (175 mg), B (180 mg), C (57 mg), and D (60) and fractions A and B were examined in detail.

Fraction A proved to be the 9,12-furan only. It had ECL of 21.2 (SP 222 PS), ultraviolet absorption at 222 nm, infrared absorption bands at 3100, 1610, 1560, 1010, 950, and 775 cm<sup>-1</sup>, and the <sup>1</sup>H NMR signals normally associated with the furan system. The mass spectrum showed the expected fragments at 308 (M,11), 277 (5), 237 (13), 179 (19), 165 (100), 95 (85), 81 (45), 74 (13), and 69 (25).

Fraction B showed a broad GLC peak (ECL 24.8 on SP 222 PS), strong carbonyl absorption in the infrared at 1720 and 1740 cm<sup>-1</sup>, and <sup>1</sup>H NMR signals at  $\delta$  2.14-2.40 (-CH<sub>2</sub>CH=CH- and -CH<sub>2</sub>CO-), 3.03 (-COCH<sub>2</sub>CH=CH-), 5.36 and 5.46 (-CO(CH<sub>2</sub>)<sub>n</sub>CH=CH, n = 1 or 2). The two unsaturated oxo esters showed ion fragments at 310 (M,12), 279 (M - 31,21), 207 (a - 32,11), 153 (d,14), 113 (c,100), 99 (b,100), and 74 (25):

Catalytic hydrogenation (palladium charcoal) of B gave the 12- and 13-oxostear-

ates. Of particular interest was the fragment ion  $(CH_3(CH_2)_nCO)^+$  at 99 (73, n=4) and 113 (24, n=5).

(iv) Methyl 12-oxo-oleate (60 mg) gave a product (57 mg) which proved to be the 9,12-furan (11 mg) on the basis of its GLC and TLC behaviour linked with infrared and mass spectrometric investigation.

### D. Endoperoxide formation and dehydration

(i) Sensitised photo-oxidation. Oxygen was bubbled through a methanolic solution of methyl octadeca-*trans*-8, *trans*-10-dienoate (139 mg) containing methylene blue, kept at room temperature by a cold finger, and irradiated with tungsten lamps  $(2 \times 150 \text{ W})$ . The product was separated into fractions A (17 mg), B (86 mg), and C (14 mg, polar material).

Fraction A still contained unreacted diene, furnishing more of B on further reaction.

Fraction B was endoperoxide with ECL 21.2 (on SP 222 PS), infrared absorption at 3020, 1695, 880, 790, 720, <sup>1</sup>H NMR signals at  $\delta$  4.32 and 5.80, and fragment



ions at 308 (M - 18,1), 294 (1), 223 (13), 179 (29), 95 (71), 81 (70), 69 (71), expected of the 8,11-furan formed by dehydration under the conditions of the mass spectrometer.

(ii) Dehydration. A sample of fraction B (75 mg) in THF (3 ml) was stirred at room temperature (5 h) following the addition, all at once, of a solution of hydrated iron (II) sulphate (127 mg) in water (3.5 ml). THF was removed under reduced pressure, water added, and the solution acidified to facilitate removal of ferric sulphate. Extraction gave a product (62 mg) separated into fractions A (34 mg) and B (13 mg) of which the latter was unreacted endoperoxide.

Fraction A (8,11-furan) had ECL 21.1 (SP 222 PS) absorbed at 222 nm in the ultraviolet, at 3100, 1610, 1560, 1010, 960, and 775 cm<sup>-1</sup> in the infrared, and showed expected fragmentation at 308 (M,28), 277 (10), 223 (20), 179 (100), 95 (100), 81 (40), and 69 (19).

### Acknowledgements

RCW holds a Commonwealth Scholarship and acknowledges leave of absence form the Ceylon Institute of Scientific and Industrial Research, Colombo.

# References

- 1 G.G. Abbot, F.D. Gunstone and S.D. Hoyes, Chem. Phys. Lipids, 4 (1970) 351.
- 2 G.G. Abbot and F.D. Gunstone, Chem. Phys. Lipids, 7 (1971) 279.
- 3 G.G. Abbot and F.D. Gunstone, Chem. Phys. Lipids, 7 (1971) 290.
- 4 G.G. Abbot and F.D. Gunstone, Chem. Phys. Lipids, 7 (1971) 303.
- 5 F.D. Gunstone and R.P. Inglis, Chem. Phys. Lipids, 10 (1973) 89.
- 6 F.D. Gunstone and R.P. Inglis, Chem. Phys. Lipids, 10 (1973) 105.
- 7 F.D. Gunstone and B.S. Perera, Chem. Phys. Lipids, 11 (1973) 43.
- 8 F.D. Gunstone and H.R. Schuler, Chem. Phys. Lipids, 15 (1975) 174.
- 9 R.L. Glass, T.P. Krick and A.E. Eckhardt, Lipids, 9 (1974) 1004.
- 10 R.L. Glass, T.P. Krick, D.M. Sand, C.H. Rahn and H. Schlenk, Lipids, 10 (1975) 695.
- 11 R.L. Glass, T.P. Krick, D.L. Olson and R.L. Thorson, Lipids, 12 (1977) 828.
- 12 F.D. Gunstone, R.C. Wijesundera, R.M. Love and D. Ross, Chem. Commun., (1976) 630.
- 13 F.D. Gunstone, R.C. Wijesundera and C.M. Scrimgeour, J. Sci. Food Agric., 29 (1978) 539.
- 14 M.S.F. Lie Ken Jie and C.H. Lam, Chem. Phys. Lipids, 20 (1977) 1.
- 15 E.N. Frankel, W.K. Rohwedder, W.E. Neff and D. Weisleder, J. Org. Chem., 40 (1975) 3247.
- 16 J.E. Baldwin, Chem. Commun., (1976) 734.
- 17 H.B.S. Conacher and F.D. Gunstone, Chem. Phys. Lipids, 3 (1969) 203.
- 18 D. Bethell, G.W. Kenner and P.J. Powers, Chem. Commun., (1968) 227.
- 19 J.A. Turner and W. Herz, J. Org. Chem., 42 (1977) 1900.
- 20 D. Cobern, J.S. Hobbs, R.A. Lucas and D.J. Mackenzie, J. Chem. Soc. C, (1966) 1897.
- 21 F.D. Gunstone, J. Chem. Soc. (1954) 1611; K.E. Bharucha and F.D. Gunstone, J. Chem. Soc. (1956) 1611.
- 22 J. Nichols and E. Schipper, J. Am. Chem. Soc., 80 (1958) 5705.
- 23 F.D. Gunstone and A.I. Said, Phys. Lipids, 7 (1971) 121.
- 24 F.D. Gunstone and F.R. Jacobsberg, Chem. Phys. Lipids, 9 (1972) 27.
- 25 S.C. Gupta and F.A. Kummerow, J. Am. Oil Chem. Soc., 37 (1960) 32.