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FATTY ACIDS, PART 35*

THE PREPARATION AND PROPERTIES OF THE COMPLETE SERIES OF METHYL EPOXYOCTADECANOATES

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The complete series of methyl epoxyoctadecanoates (31 isomers) has been made by epoxidation of the octadecenoates. The melting points of the acids are reported along with the chromatographic (TLC and GLC) and spectroscopic (NMR and MS) behaviour of the methyl esters.

I. Introduction

Long-chain epoxy acids have attracted interest for several reasons, including the stereochemical relationships occurring between the epoxides and those compounds from which they are made or to which they are so easily converted[1]), the natural occurrence of epoxy glycerides[2]), and the preparation of epoxidised glycerides on an industrial scale for use as stabilisers and plasticisers. Recent reports further suggest that these compound provide the basis of a method for determining the amount of *cis* and *trans* alkenoate esters in natural or in partially hydrogenated oils[3]).

We have now prepared all the methyl *cis* and *trans* epoxyoctadecanoates (31 isomers) by epoxidation of the corresponding unsaturated esters[4,5]).

II. Discussion

A. Synthesis

Each unsaturated ester was epoxidised by reaction with *m*-chloroperbenzoic acid in chloroform solution. Reaction was generally complete after 3 hr at room temperature and the product was isolated in almost quantitative yield. Those esters having unsaturation close to the ester function or to the ω-position were less reactive and the epoxides from the 2*c*, 2*t*, 3*c*, 3*t*, and

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17*e* monoene esters were obtained, sometimes in lower yield, only after prolonged reaction. Details are given in §III.

B. Melting point

Table 1 contains the melting points of all the epoxy acids and of the few solid esters. The acids were obtained from the esters by careful alkaline hydrolysis. To confirm that the epoxide function was unaffected, each acid was remethylated with diazomethane and compared (GLC, TLC, NMR spectrum) with the original ester. The *cis* and *trans* 3,4-; 4,5-; and 5,6-epoxy esters and the 17,18-epoxy ester did not furnish the epoxy acid but the reaction products have not yet been identified: the remaining esters gave the expected epoxy acids.

TABLE 1

Melting points of the epoxyoctadecanoic acids and some of their methyl esters

isomer	*cis* acids	*trans* acids
2,3	84.0–86.5°[a]	85.0–88.0[b]
3,4	–[s]	–[t]
4,5	–[j, u]	–[k, v]
5,6	–[w]	–[x]
6,7	56.5–58.0[c]	64.5–65.5[d]
7,8	46.5–48.0	54.0–55.0
8,9	55.0–56.0	52.5–54.0
9,10	56.0–57.0[e]	52.0–53.0[f]
10,11	55.0–56.0	51.0–52.5
11,12	41.5–44.0[g]	51.0–52.0[l]
12,13	52.0–53.5	51.0–53.5
13,14	46.5–48.0	53.0–55.0[m]
14,15	54.5–56.5	56.0–58.5[n]
15,16	47.0–49.0	59.5–62.0[o]
16,17	57.0–58.5[p]	80.0–82.0[q]
17,18	———— [h, r, y]	————

[a–h]Melting points previously reported: [a] 90.5°11). [b] 87.5°11); 83.5°12); 89.5–90°13). [c] 59.5–60.0°14; 58.0–59.0°15). [d] 60.0–66.5°14); 64°15). [e] 59.5–59.8°16); 58.5–59.0°17); 55.0–57.5°18). [f] 52–54°19); 55.1–55.5°20); 54.9–55.3°18). [g] 46.0–47.6°21). [h] 62.5–63.5°22).
[j–r] Melting points of methyl ester: [j] 33.0–34.0°. [k] 37.0–39.5°. [l] 29.5–30.5°. [m] 32.5–34.0°. [n] 33.0–34.0°. [o] 42.0–44.0°. [p] 37.0–38.0°. [q] 40.0–43.0°. [r] 38.0–40.0°.
[s–y] Melting points of hydrolysis products which are *not* epoxy acids: [s] 94.5–96.0°. [t] 92.0–95.0°. [u] 92.0–93.0°. [v] 110.0–112.0°. [w] 93.5–95.0°. [x] 125.0–126.5°. [y] 75.0–76.5°.

The melting points of the *cis* epoxy acids show alternation through the range 6,7 to 16,17 with the unexpected exception of the 9,10 acid which has a "high" rather than a "low" melting point. Our melting point is unlikely to be in error since it is similar to several values already reported (see footnote to table 1). Unexpectedly, the *trans* isomers do not show alternation of melting point. The values lie on a curve falling from 65° (6,7 isomer) to around 52° (10,11; 11,12; and 12,13 isomers) and then rising to 81° (16,17 isomer). Because the two series of acids do not follow a similar pattern the *cis* acids melt sometimes above and sometimes below their *trans* isomers. This observation illustrates the danger of trying to correlate stereochemistry with some physical property.

C. TLC behaviour

On thin-layer chromatography the isomeric methyl epoxyoctadecanoates have R_f values which fall on two sinusoidal curves like the series of isomeric hydroxyoctadecanoates[6]) and of *cis* and *trans* octadecenoates[7]). As is seen from fig. 1 the two 2,3-epoxy esters do not separate from each other but the remaining *cis* and *trans* isomers fall on two curves with the trans isomer always having the higher R_f value.

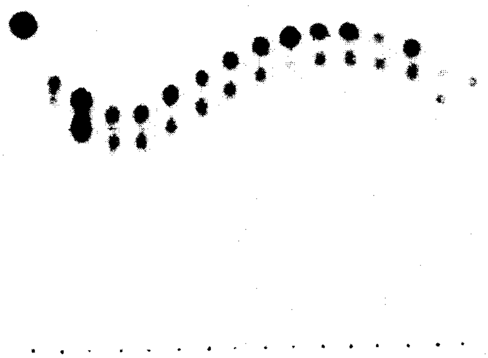


Fig. 1. TLC of methyl 2,3 to 17,18-epoxyoctadecanoates from left to right. The *trans* isomer has the higher R_f value in each case except for the two 2,3-epoxy esters which are not separated. Adsorbant: silica gel; solvent: PE2O.

D. GLC behaviour

The GLC behaviour of the *cis* and *trans* epoxy esters is summarised in table 2. It is to be expected that the values obtained on the ApL column will be fairly reproducible but that those on the DEGS column will show more variation.

Emken[3]) has reported that the *cis* epoxides from the $\Delta 6$, $\Delta 9$, and $\Delta 12$ octadecenoates are eluted later than, and well separated from, the corresponding *trans* isomers whether the *cis trans* pairs are present singly or together.

TABLE 2

ECL of the methyl epoxyoctadecanoates on packed ApL and DEGS columns

isomer	ApL		DEGS	
	cis	*trans*	*cis*	*trans*
2,3	19.08	19.37	23.08	23.45
3,4	[a]	[a]	23.55[b]	23.04[b]
4,5	19.13	19.16	[a]	23.12
5,6	19.27	[c]	23.74[b]	23.48[b]
6,7	19.26	19.17	23.93	23.65
7,8	19.26	19.19	24.08	23.61
8,9	19.26	19.19	24.00	23.79
9.10	19.32	19.19	23.92	23.81
10,11	19.30	19.20	24.17	23.85
11,12	19.24	19.18	24.19	23.78
12.13	19.35	19.23	24.17	23.82
13,14	19.37	19.23	24.24	23.89
14,15	19.41	19.26	24.32	23.76
15,16	19.50[b]	19.27[b]	24.48	23.93
16,17	19.57	19.36	24.87	24.11
17,18	— 19.87 —		— 25.49 —	

[a] Complete decomposition during GLC.

[b] Partial decomposition during GLC, ECL of major peak is given.

[c] Partial decomposition during GLC, but no major peak.

He finds less satisfactory separations, however, when the *cis* and *trans* 15,16-epoxides are also present. Our ECL data show this to be expected and indicate what other mixtures would be difficult to separate.

On ApL columns most of the *trans* octadecenoates have a higher ECL than their *cis* isomers. This is reversed with the epoxyoctadecanoates and the *cis* isomer has the higher ECL in most, but not all, cases.

Although most of the epoxy esters give a single peak on GLC we found that some gave more complex results indicating partial or complete decomposition. This was more apparent on the DEGS column and with those esters having the epoxide near to the ester function.

E. NMR spectroscopy

A detailed account of the NMR spectra of these esters will be given when we have completed the study of their 220 MHz spectra. The results summarised in table 3 are taken from our 100 MHz spectra. For most isomers the epoxide protons give a signal around 7.3 τ (*cis* epoxides) or 7.55 τ (*trans* epoxides), though these values change slightly when the epoxide group is near to the ester or ω-methyl group. Our values are slightly higher than those previously reported by Aplin and Coles[8]) (7.12 and 7.34 τ for *cis* and *trans* epoxides respectively). The epoxide group exerts a weak deshielding influence which is apparent in the τ values for the $\mathrm{C\underline{H}_3}$ signal and the $\mathrm{C\underline{H}_2COOMe}$ signal when the epoxides approaches these groups.

F. Mass spectrometry

Among the methyl epoxyoctadecanoates the mass spectra of only the *cis* and *trans* 9,10 isomers have been reported[8,9] and we have taken the opportunity to examine the spectra of all 31 isomers. These have been measured at 16 and 70 eV, but the former are more informative and our discussion is confined to these. We have extended the two major fragmentation pathways proposed by Aplin and Coles[8] (**1** and **2** in the scheme below) to four (**1**–**4**). Each ion represents two fragments depending on which side of the epoxide group fission occurs, fragments still containing the $\mathrm{COOCH_3}$ group can lose a further 32 mass units, and both fragments (**1**) can lose 18 mass units. This gives a total of fifteen possible species which together account for 20–40% of the total ion current in most cases. This total is somewhat less for the 2,3-epoxy esters and also when the epoxide group lies at or beyond the 12,13 position. In general, there is very little difference between the spectra of a pair of *cis* and *trans* isomers.

TABLE 3

Principal features in the 100 MHz spectra of the isomeric methyl epoxyoctadecanoates [chemical shifts are expressed in ppm downfield from internal TMS ($\tau = 10$)]

isomer	$\mathrm{C\underline{H}_3}-$	$\overset{\mathrm{O}}{-\mathrm{C\underline{H}C\underline{H}}-}$	$-\mathrm{C\underline{H}_2COOMe}$
cis isomers:			
2,3	9.12	6.70, 7.01	–
3,4	9.13	6.84, 7.15	7.40, 7.64
4,5	9.13	7.25	7.61
5,6	9.12	7.29	7.69
6,7–13,14	9.07–9.12	7.30–7.32	7.75–7.80
14,15	9.03	7.32	7.80
15,16	8.99	7.33	7.80
16,17	8.79	7.17, 7.31	7.80
17,18	–	7.28, 7.47, 7.74	7.80
trans isomers:			
2,3	9.12	7.01	–
3,4	9.12	7.14, 7.44	7.42, 7.70
4,5	9.13	7.46	7.66
5,6–13,14	9.09–9.12	7.51–7.55	7.72–7.79
14,15	9.06	7.54	7.80
15,16	9.05	7.55	7.80
16,17	8.83	7.46, 7.48	7.80

TABLE 4

Mass spectra (16 eV) of the isomeric methyl epoxyoctadecanoates.
The ten dominant peaks in each spectrum are given along with their intensities relative to the base peak (= 100). Those marked with an asterisk correspond to fragments resulting from one or other of the 15 fragmentation routes discussed in the text.

2,3-epoxy:	
cis	82(43), 83*(63), 90(100), 95(88), 97(79), 100(43), 111(51), 116(68), 117(79), 253*(45)
trans	57*(68), 71(58), 82(53), 83*(90), 90(95), 95(55), 97(100), 111(63), 116(74), 117(74)
3,4-epoxy:	
cis	57(26), 83*(26), 84(44), 87*(100), 97*(29), 98(33), 115*(71), 116(46), 130(31), 283(60)
trans	68(47), 82(68), 83*(50), 87*(47), 96(44), 97*(38), 103*(100) 105(38), 116(41), 130(32), 143(32)
4,5-epoxy:	
cis	82(19), 85*(34), 101*(64), 112(19), 117*(100), 130(79), 143(26), 144(30), 156(23)
trans	68(16), 82(22), 83*(20), 85*(52), 100(28), 101*(68), 117*(100), 130(28), 143(19)
5,6-epoxy:	
cis	82(19), 96(17), 98(19), 99*(81), 112(17), 114(23), 115*(62), 131*(100), 144(40), 211*(37)
trans	68(13), 82(18), 83(23), 98(25), 99*(100), 114(31), 115*(58), 131*(53), 149(14), 211*(18)
6,7-epoxy:	
cis	68(16), 82(17), 83(16), 97*(21), 112(29), 113*(100), 129*(37), 144(13), 145*(33), 197*(27)
trans	82(15), 97*(13), 112(33), 113*(100), 128(13), 129*(44), 144(21), 145*(54), 197*(51), 238(16)
7,8-epoxy:	
cis	74(35), 82(36), 96(36), 98(33), 111*(32), 127*(100), 142(38), 143*(38), 157*(36), 183*(32)
trans	74(32), 82(30), 83(24), 98(21), 111*(26), 126(19), 127*(100), 142(23), 143*(34), 183*(24)
8,9-epoxy:	
cis	74(40), 82(38), 83(38), 87(53), 96(33), 125*(26), 139*(49), 141*(100), 157*(33), 169*(28)
trans	74(50), 82(38), 83(44), 87(56), 96(30), 125*(26), 139*(38), 141*(100), 157*(38), 169*(31), 185(26)
9,10-epoxy:	
cis	74(46), 82(29), 87(23), 96(26), 97(28), 127*(32), 139*(18), 153*(28), 155*(100), 171*(20)
trans	56(33), 68(35), 69(33), 74(92), 82(43), 83(35), 87(50), 96(45), 97(42), 155*(100)
10,11-epoxy:	
cis	74(44), 81(36), 108(56), 110(50), 127*(36), 134(63), 141*(100), 150(38), 169(94), 185*(50), 213*(53)
trans	74(80), 87(47), 108(67), 110(40), 111(31), 134(32), 141*(53), 150(29), 169(100), 185*(35)

Table 1 (contd.)

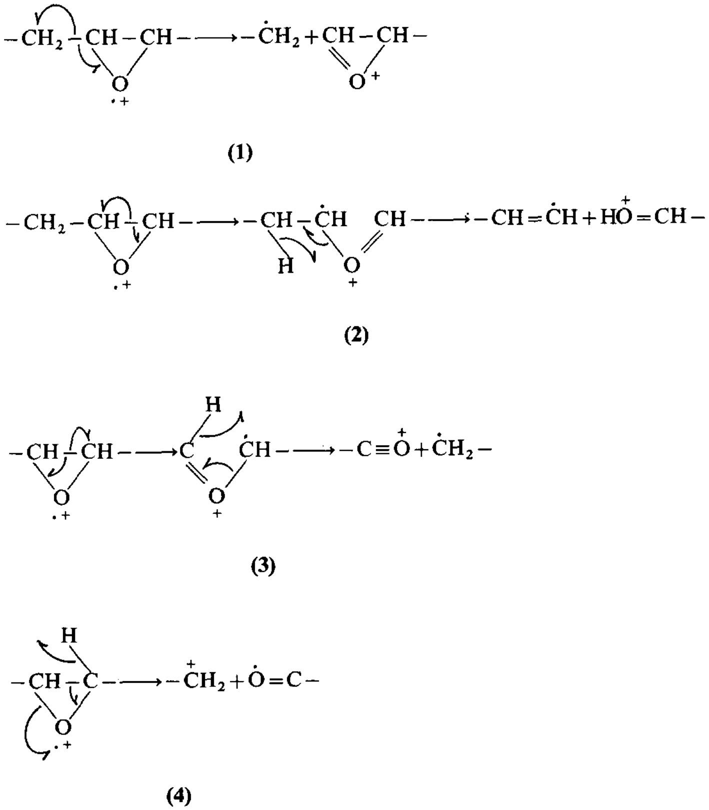
11,12-epoxy:	
cis	74(100), 81(40), 87(43), 96(53), 127*(77), 148(49), 155(57), 183*(83), 199*(55), 210(57)
trans	74(28), 87(14), 96(17), 127*(22), 148(14), 149(100), 183*(22) 199*(16), 205(25), 223(42)
12,13-epoxy:	
cis	55(85), 67(83), 74(94), 79(62), 81*(76), 82(57), 95*(60), 113*(64), 143(100), 169(57)
trans	74(51), 82(24), 87(31), 96(23), 98(23), 113*(23), 143(33), 149(100), 223*(21)
13,14-epoxy:	
cis	55(70), 67(64), 74(100), 79(44), 81*(49), 82(56), 87*(44), 96(52), 141(46), 143(70)
trans	74(100), 82(26), 87*(69), 96(26), 98(21), 99*(24), 127(24), 143(41), 227*(29), 255*(24)
14,15-epoxy:	
cis	55(75), 67*(61), 74(100), 81(78), 82(58), 87(49), 95(56), 96(63), 143(74), 269*(50)
trans	74(100), 75(26), 82(43), 87(54), 96(48), 98(28), 125(26), 143(52), 241*(24), 269*(35)
15,16-epoxy:	
cis	74(100), 81(51), 82(61), 87(63), 95(46), 96(74), 97(39), 98(51), 139(41), 143(54)
trans	74(100), 82(65), 87(56), 96(72), 98(44), 139(47), 143(60), 149(51), 223*(58)
16,17-epoxy:	
cis	74(100), 75(25), 82(57), 83(24), 85(61), 87(70), 96(57), 97(25), 98(33), 143(29)
trans	70(25), 73(30), 74(100), 75(36), 82(52), 85(36), 87(52), 96(56), 98(40), 143(39)
17,18-epoxy:	
	71(46), 74(81), 82(91), 84(39), 87(39), 95(39), 97(39), 98(74), 110(37)

III. Experimental

A. Synthesis

The appropriate methyl octadecenoate (200 mg) reacted with *m*-chloroperbenzoic acid (160 mg) in chloroform (20 ml) at room temperature for 3–4 hr. The epoxy ester, recovered by ether extraction in almost quantitative yield, was purified by preparative TLC using silica (1 mm) and ether/petroleum (20:80) as developing solvent. The following octadecenoates required more peracid and/or longer reaction times: 2*c* and 2*t* (600 mg of peracid, 12 days reaction), 3*c* (150 mg of peracid, 24 hr reaction), 3*t* and 17*e* (160 mg of peracid, 48 hr reaction).

The ester (20 mg) was refluxed with methanolic potassium hydroxide (1 *M*, 20 ml) for 30 min. The solution was neutralised (phenolphthalein) with hydrochloric acid (4 *M*), diluted with water, and extracted immediately with ether. The solid acid was crystallised from petroleum (b.p. 40–60°). Melting points were determined on a Kofler hot-stage and are uncorrected.



Reaction scheme.

B. Chromatographic and spectroscopic procedures

The epoxy esters were separated using a thin layer (0.25 mm) of silica gel G. The layers were activated for 1 hr at 120° and after development with petroleum (b.p. 40–60°) and ether (80:20 by volume) the spots were detected by spraying with an ethanolic solution of phosphomolybdic acid (10%) followed by heating at 120° for 15 min.

Gas-liquid chromatography was carried out with a Pye series 104 chromatograph fitted with a flame ionisation detector. Separation was achieved with stainless steel columns (150 cm × 5 mm i.d.) packed with diethyleneglycol succinate (10% on HMDS Chromosorb W, 80–100 mesh) or with Apiezon L (3% on AW-DCMS Chromosorb G, 80–100 mesh). Retention behaviour is expressed as equivalent chain lengths (ECL)[10]).

NMR spectra were recorded at 100 MHz on a Varian HA100 instrument using 10% solutions in carbon tetrachloride with tetramethylsilane as internal standard.

Mass spectra were run on an AEI MS902 spectrometer using a direct insertion probe at 16 eV with a source pressure of 10^{-6} torr and a temperature of 200°.

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References

1) D. Swern, J. Am. Chem. Soc. **70** (1948) 1235
2) F. R. Earle, J. Am. Oil Chem. Soc. **47** (1970) 510
3) E. A. Emken, Lipids **6** (1971) 686
4) F. D. Gunstone and I. A. Ismail, Chem. Phys. Lipids **1** (1967) 209
5) J. A. Barve and F. D. Gunstone, Chem. Phys. Lipids **7** (1971) 311
6) L. J. Morris and D. M. Wharry, J. Chromatog. **20** (1965) 27; L. J. Morris, D. M. Wharry and E. W. Hammond, J. Chromatog. **33** (1968) 471
7) F. D. Gunstone, I. A. Ismail and M. Lie Ken Jie, Chem. Phys. Lipids **1** (1967) 376
8) R. T. Aplin and L. Coles, Chem. Comm. (1967) 858
9) R. Ryhage and E. Stenhagen, Arkiv Kemi **15** (1960) 545
10) T. K. Miwa, M. L. Mikolajczak, F. R. Earle and I. A. Wolff, Anal. Chem. **32** (1960) 1739
11) G. S. Myers, J. Am. Chem. Soc. **74** (1952) 1390
12) P. A. Artamonov, Zhur. obschei Khim. **28** (1958) 1355
13) E. N. Zvonkova, K. I. Éiler, V. I. Tselin, B. I. Mitsner and N. A. Preobrazhenkii, Zhur. org. Khim. **2** (1966) 2184
14) M. O. Farooq and S. M. Osman, Fette, Seifen, Anstrichmittel **61** (1959) 636
15) I. L. Kuranova, Y. D. Shenin and G. V. Pigulevskii, Zhur. obschei Khim. 33 (1963) 2996
16) D. Swern, T. W. Findley and J. T. Scanlan, J. Am. Chem. Soc. **66** (1944) 1925
17) Y. Suhara, Tokyo Kôgyô Shikensho Hokoku **53** (1958) 217
18) N. P. Bulatskii, Zhur. org. Khim. **2** (1966) 2260
19) E. Vioque, L. J. Morris and R. T. Holman, J. Am. Oil Chem. Soc. **38** (1961) 489
20) I. L. Kuranova and Y. D. Shenin, Zhur. priklad. Khim. **35** (1962) 1155
21) K. Hofmann and S. M. Sax, J. Biol. Chem. **205** (1953) 55
22) A. Jennen and F. Everaerts, Compt. Rend. **251** (1960) 91