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FATTY ACIDS

XVII*. CHROMATOGRAPHIC PROPERTIES OF ALL ISOMERIC C₁₈ FURAN ESTERS

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SUMMARY

The gas-liquid chromatographic properties of all synthetic C₁₈ furan esters was studied on polar (FFAP, DEGS and SILAR 10C) and non-polar (Apiezon L and SE-30) stationary phases. The equivalent chain length of each isomer was recorded and the possibility of the separation of these isomers is discussed. The thin-layer chromatographic behaviour of these isomeric esters on ordinary silicic acid and silver nitrate impregnated silicic acid plates showed some degree of sub-fractionation.

INTRODUCTION

Fatty acids containing a furan system have been isolated from seed² and fish oils³⁻⁵, but their function in nature remains unknown. Recently we have developed methods for the partial synthesis of certain C₁₈ furan ester isomers from methyl ricinoleate⁶ or from synthetic C₁₈ diacetylenic esters⁷. Gunstone and co-workers have also described the production of such esters from methyl linoleate⁸ and ricinoleate⁹.

We have recently synthesized all 14 possible furan-containing straight-chain acids of the C₁₈ series¹. The purpose of this exercise was to study the physical, chemical and biological properties of this new class of fatty acids.

EXPERIMENTAL AND RESULTS

Gas-liquid chromatography

The gas-liquid chromatographic (GLC) results were obtained under the conditions given in Table I on a Pye 104 or Varian 940 chromatograph equipped with a flame-ionization detector. Equivalent chain lengths (ECLs) were calculated from the distances between the solvent front and the peak of the eluted component with saturated esters (C₁₅, C₁₆, C₁₈, C₁₉, C₂₀ and C₂₂) as internal standards.

* For Part XVI, see ref. 1.

TABLE I
CONDITIONS FOR GLC
Column length, 2 m.

Stationary phase	Temperature (°C)	Carrier gas (nitrogen) flow-rate (ml/min)	Internal diameter (mm)	Number of theoretical plates
5% Apiezon L	220	120	3.1	500
10% SE-30	225	55	6.2	540
10% FFAP	235	100	6.2	1994
20% DEGS	190	80	6.2	1190
10% SILAR 10C	195	30	6.2	1100

The ECLs of all methyl C_{18} furan esters are compared in Fig. 1 and the actual values are recorded in Tables II-VI.

The methyl ester derivatives of the furan acid isomers gave a consistent retention pattern on all five stationary phases used, the highest ECLs being exhibited by the isomers containing the furan system at the C_2 position or at the terminal end of

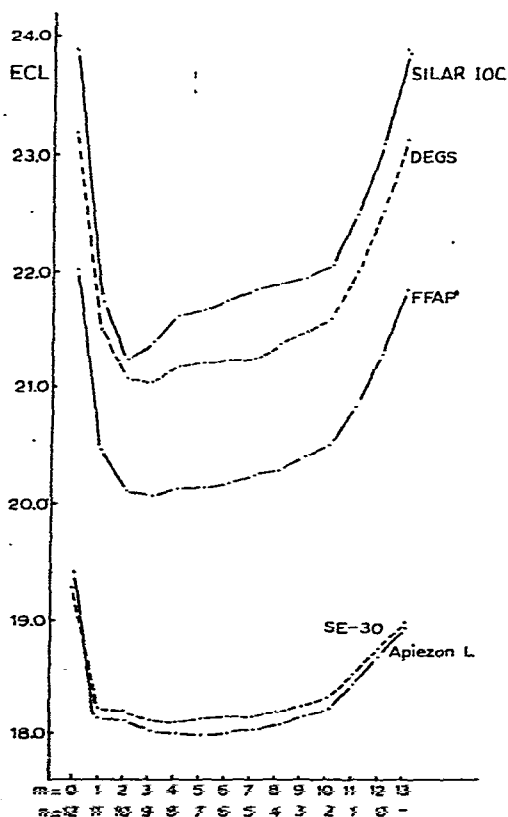
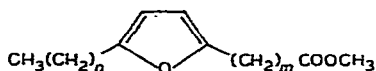


Fig. 1. Equivalent chain lengths of methyl C_{18} furan esters. For structure, see Table II.

TABLE II

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL METHYL C₁₈ FURAN ESTERS AND THEIR MIXTURES ON APIEZON L

Isomer		ECL	A1*	A2**	A3***	A4‡
<i>m</i>	<i>n</i>					
0	12	19.39				
1	11	18.12				18.06
2	10	18.09				
3	9	18.00				
4	8	17.98				
5	7	17.97				18.06
6	6	17.99				
7	5	18.02				
8	4	18.06		18.09		
9	3	18.14	18.13			
10	2	18.21				
11	1	18.43		18.43		
12	0	18.66	18.67		18.71	
13	—	18.94			18.92	

* Baseline separation.

** Twin-peak separation.

*** Shoulder separation.

‡ No separation.

TABLE III

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL METHYL C₁₈ FURAN ESTERS AND THEIR MIXTURES ON SE-30

Structure as in Table II.

Isomer		ECL	B1*	B2**	B3***	B4‡
<i>m</i>	<i>n</i>					
0	12	19.26				
1	11	18.22				
2	10	18.20				
3	9	18.10				
4	8	18.08				18.18
5	7	18.12				
6	6	18.13				
7	5	18.14		18.12		
8	4	18.18	18.16			
9	3	18.24				18.18
10	2	18.31				
11	1	18.52		18.53		
12	0	18.73	18.73		18.72	
13	—	18.97			18.97	

* Baseline separation.

** Twin-peak separation.

*** Shoulder separation.

‡ No separation.

TABLE IV

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL METHYL C₁₈ FURAN ESTERS AND THEIR MIXTURES ON FFAP

Structure as in Table II.

Isomer	ECL	C1*	C2*	C3**	C4***
<i>m</i>	<i>n</i>				
0	12	22.00			
1	11	20.46		20.41	
2	10	20.11			
3	9	20.06	20.07		20.13
4	8	20.12			
5	7	20.12			
6	6	20.16			
7	5	20.23		20.24	20.13
8	4	20.28			
9	3	20.39	20.38		
10	2	20.51	20.40		
11	1	20.82	20.82		
12	0	21.38			
13	—	21.83			

* Twin-peak separation.

** Shoulder separation.

*** No separation.

TABLE V

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL METHYL C₁₈ FURAN ESTERS AND THEIR MIXTURES ON DEGS

Structure as in Table II.

Isomer	ECL	D1*	D2**	D3***	D4‡
<i>m</i>	<i>n</i>				
0	12	23.17			
1	11	21.49			
2	10	21.06		21.03	
3	9	21.02	21.02		
4	8	21.16			
5	7	21.19			
6	6	21.21			21.32
7	5	21.23		21.16	
8	4	21.35	21.35		21.32
9	3	21.45	21.45		
10	2	21.57			
11	1	21.97	21.97		
12	0	22.50			
13	—	23.08			

* Baseline separation.

** Twin-peak separation.

*** Shoulder separation.

‡ No separation.

TABLE VI

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL METHYL C₁₈ FURAN ESTERS AND THEIR MIXTURES ON SILAR 10C

Structure as in Table II.

Isomer		ECL	E1*	E2*	E3**	E4***
<i>m</i>	<i>n</i>					
0	12	23.87				
1	11	21.72	21.66			
2	10	21.23	21.23			
3	9	21.35			21.34	
4	8	21.59			21.57	
5	7	21.63		21.57		21.65
6	6	21.72				
7	5	21.82				21.65
8	4	21.87				
9	3	21.93		21.93		
10	2	22.03				
11	1	22.45				
12	0	23.05				
13	—	23.84				

* Twin-peak separation.

** Shoulder separation.

*** No separation.

the C₁₈ chain. The behaviour of the furan esters on the non-polar stationary phases (*viz.*, Apiezon L and SE-30) was similar, as their ECLs were found to be almost identical (Fig. 1). On the polar stationary phases, FFAP was the least polar and SILAR 10C the most polar, while DEGS had an intermediate position. The lowest ECLs were exhibited by methyl 5,8-epoxyoctadeca-5,7-dienoate on FFAP and DEGS, while methyl 4,7-epoxyoctadeca-4,6-dienoate gave the lowest ECL on SILAR 10C.

In general, the ECLs of these isomers increased gradually as the furan system was located further from the ester group, and this trend was best demonstrated on the polar stationary phases. On the non-polar stationary phases, the ECLs continued to increase significantly when the furan system was four carbon atoms away from the terminal end of the C₁₈ chain. This trend was also observed in the tetrahydrofuran derivatives of the C₁₈ esters¹⁰.

Mixtures of these isomers were also examined (Table II–VI) and the results are summarized in Table VII. The degree of separation is described as baseline, twin peak and shoulder. On the polar stationary phases, the efficiency of separation of the isomers was best on DEGS, while on the non-polar stationary phases both Apiezon L and SE-30 gave almost identical performances. The ECLs were highly reproducible on all stationary phases and no sign of decomposition of any isomer was observed, as demonstrated by examination of the mixtures or individual member of these isomers.

Thin-layer chromatography

Thin-layer plates were prepared as described earlier¹¹. Both normal silicic acid and silver nitrate-impregnated silicic acid plates were used. Methyl oleate, linoleate,

TABLE VII
SEPARATION OF MIXTURES OF METHYL C₁₈ FURAN ESTERS

Stationary phase	Baseline separation	Degree of separation (difference in ECL)		
		Twin peak	Shoulder	No separation
Apiezon L	0.52 (A1)	0.37 (A2)	0.28 (A3)	0.15 (A4)
SE-30	0.55 (B1)	0.38 (B2)	0.24 (B3)	0.16 (B4)
FFAP	—	≥0.31 (C1-2)	0.23 (C3)	0.17 (C4)
DEGS	0.52 (D1)	0.33 (D2)	0.17 (D3)	0.14 (D4)
SILAR 10C	—	≥0.30 (E1-2)	0.24 (E3)	0.19 (E4)

TABLE VIII
R_F VALUES OF METHYL C₁₈ FURAN ESTERS
Structure as in Table II.

Isomer		R _F values	
<i>m</i>	<i>n</i>	Ordinary silicic acid plate (Fig. 2)	Silver nitrate-impregnated silicic acid plate (Fig. 4)
0	12	0.46	0.66
1	11	0.43	0.60
2	10	0.46	0.65
3	9	0.46	0.65
4	8	0.45	0.63
5	7	0.47	0.63
6	6	0.47	0.63
7	5	0.48	0.63
8	4	0.49	0.64
9	3	0.50	0.64
10	2	0.50	0.64
11	1	0.50	0.65
12	0	0.48	0.64
13	—	0.48	0.64
Methyl oleate		0.58	—
Methyl octadec-8-ynoate		0.50	0.49
Methyl octadeca-5,9-diynoate		0.43	—

octadec-8-ynoate and octadeca-5,9-diynoate were used as reference standards. The R_F values of these isomers (with a single development) are presented in Table VIII.

Figs. 2-5 illustrate the chromatograms obtained on ordinary and silver nitrate-impregnated silicic acid plates after single and double development.

Ordinary TLC plates. Development of the plate (Fig. 2) with light petroleum (b.p. 60-80°)-diethyl ether (220:30) gave a clear separation of methyl oleate, octadec-8-ynoate and octadeca-5,9-diynoate; the mobility of the furan esters corresponded with that of the monoacetylenic isomer. A shallow sinusoidal curve with a minimum at the methyl 5,8-epoxyoctadeca-5,7-dienoate isomer and a plateau at the last five isomers with the furan system near the ω-end of the chain were obtained. The methyl 3,6-epoxyoctadeca-3,5-dienoate gave a significantly lower R_F value when compared

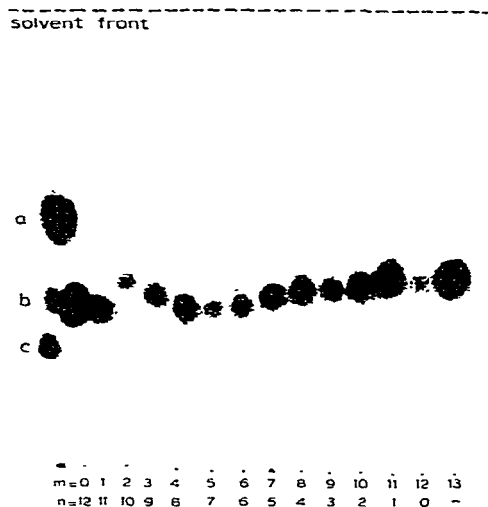
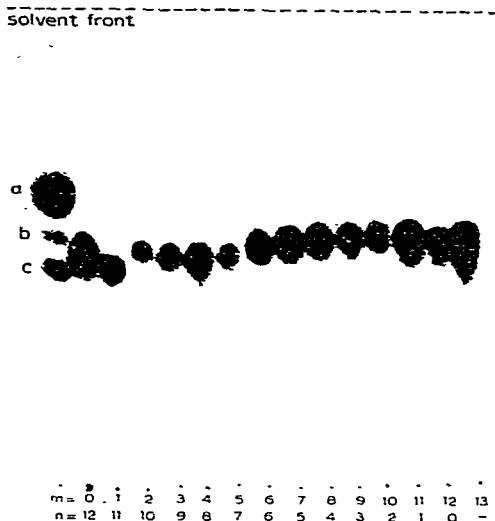


Fig. 2. TLC of C_{18} furan esters on silicic acid plates; solvent system, light petroleum (b.p. 60–80°)–diethyl ether (220:30). a = Methyl oleate; b = methyl octadec-8-ynoate; c = methyl octadeca-5,9-diynoate. For structure, see Table II.

Fig. 3. TLC of C_{18} furan esters on silicic acid plates; double development with light petroleum (b.p. 60–80°)–diethyl ether (90:10). a, b and c as in Fig. 2. For structure, see Table II.

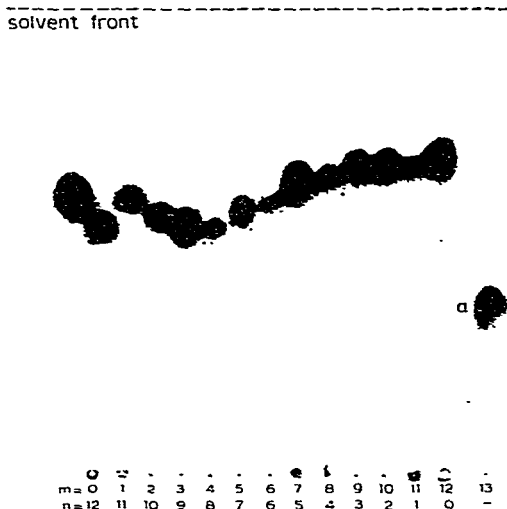
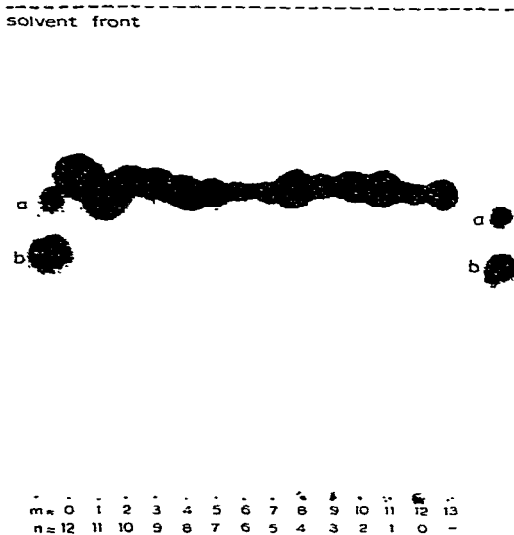


Fig. 4. TLC of C_{18} furan esters on silver nitrate-impregnated silicic acid plates; solvent system, light petroleum (b.p. 60–80°)–diethyl ether (130:20). a and b as in Fig. 2. For structure, see Table II.

Fig. 5. TLC of C_{18} furan esters on silver-impregnated silicic acid plates; double development with light petroleum (b.p. 60–80°)–diethyl ether (240:10). a = Methyl octadec-8-ynoate. For structure, see Table II.

with its two "neighbouring" isomers (*viz.*, the 2,5-epoxy-2,4-diene and 4,7-epoxy-4,6-diene isomers). On double development with light petroleum (b.p. 60–80°)–diethyl ether (90:10), the sinusoidal curve became a more prominent feature (Fig. 3).

Silver nitrate-impregnated TLC plates. The furan isomers behaved in a similar manner to methyl oleate in mobility on single development with light petroleum (b.p. 60–80°)–diethyl ether (230:20). Sub-fractionation was noted only with methyl 3,6-epoxyoctadeca-3,5-dienoate. Methyl octadec-8-ynoate was clearly separated from methyl oleate (Fig. 4).

When the plate was developed twice with light petroleum (b.p. 60–80°)–diethyl ether (240:10), the furan esters migrated further than methyl oleate (Fig. 5). The sinusoidal curve became pronounced and methyl 3,6-epoxyoctadeca-3,5-dienoate continued to be located out of position on this curve. The isomers with the furan system at the ω -end gave higher R_F values than the remaining isomers of the series.

REFERENCES

- 1 M. S. F. Lie Ken Jie and C. H. Lam, *J. Chem. Soc.*, submitted for publication.
- 2 L. J. Morris, M. O. Marshall and W. Kelly, *Tetrahedron Lett.*, (1966) 4249.
- 3 R. L. Glass, T. P. Krick and A. E. Eckhardt, *Lipids*, 9 (1974) 1004.
- 4 R. L. Glass, T. P. Krick, D. M. Sand, C. H. Rahn and H. Schlenk, *Lipids*, 10 (1975) 695.
- 5 F. D. Gunstone and R. C. Wijesundera, *Chem. Commun.*, (1976) 630.
- 6 M. S. F. Lie Ken Jie and C. H. Lam, *Chem. Phys. Lipids*, in press.
- 7 M. S. F. Lie Ken Jie and C. H. Lam, *Chem. Phys. Lipids*, in press.
- 8 G. G. Abbot and F. D. Gunstone, *Chem. Phys. Lipids*, 7 (1971) 290.
- 9 G. G. Abbot, F. D. Gunstone and S. D. Hoyes, *Chem. Phys. Lipids*, 4 (1970) 351.
- 10 M. S. F. Lie Ken Jie and C. H. Lam, *J. Chromatogr.*, 129 (1976) 181.
- 11 M. S. F. Lie Ken Jie and C. H. Lam, *J. Chromatogr.*, 124 (1976) 147.