

CHROM. 9200

Note

Fatty acids

IX*. The thin-layer chromatographic behaviour of all of the *cis*, *cis*- and *trans*, *trans*-dimethylene-interrupted methyl octadecadienoates and methyl octadecadienoates

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Gunstone *et al.*² demonstrated the unique subfractionation behaviour of mono-ethylenic fatty esters according to the position of the double bond in the fatty ester chain by silver-ion thin-layer chromatography (TLC). This technique, since its first application to lipids³⁻⁵, has been extensively employed in the isolation of unsaturated⁶ and oxygenated⁷ fatty esters. We now report the TLC properties of the dimethylene-interrupted *cis,cis* and *trans,trans*-methyl octadecadienoates and methyl octadecadienoates on silica impregnated with silver nitrate.

EXPERIMENTAL

Silica (Merck, Darmstadt, G.F.R.; GF 254 Type 60) was impregnated with silver nitrate (20% w/w) and coated on glass plates (20 × 20 cm) to give a uniform layer of 0.3-mm thickness. The plates were activated by heating at 110° for 1 h. Diethyl ether-light petroleum (b.p. 60-80°) (7:18, v/v) was used to develop the plates. Samples (20-30 μg) dissolved in acetone (1 μl) were spotted on to the plate by means of a microsyringe. After development, the spots were made visible by spraying with a 10% ethanolic solution of phosphomolybdic acid⁸ and heated in an oven at 150-200° for ca. 10 min or until the spots became visible.

RESULTS

Methyl octadecadienoates

With the exception of the $\Delta^{2a,6a}$, $\Delta^{3a,7a}$ and $\Delta^{4a,8a}$ esters, the remainder of the methyl octadecadienoate isomers formed a shallow sinusoidal curve with a minimum at the $\Delta^{6a,10a}$ isomer and a maximum at the $\Delta^{10a,14a}$ ester (Fig. 1). The R_F values of these isomers are presented in Table I. The $\Delta^{2a,6a}$ ester exhibited similar behaviour

* For Part VIII, see ref. 1.

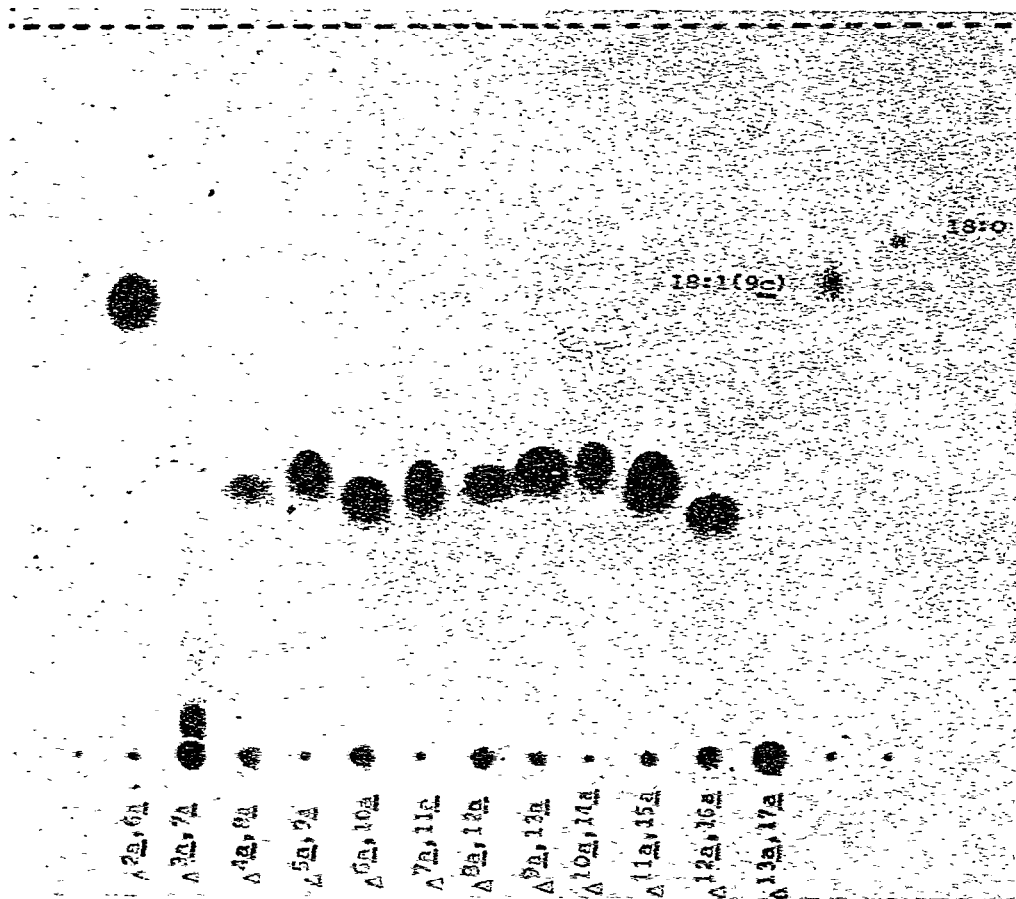


Fig. 1. TLC of methyl octadecadienoates. For details see Table I.

to a monounsaturated fatty ester and gave an R_F value identical to that observed for methyl oleate. The low extent of interaction of the unsaturated centre at the Δ^2 position with silver ions is probably due to its conjugation with the methoxycarbonyl group, where the π -electrons are delocalized. The $\Delta^{3a,7a}$ isomer decomposed during the process of development and produced a continuous streak on the plate. The $\Delta^{13a,17a}$ isomer formed a silver salt, due to the presence of a terminal triple bond, and thus remained at the origin after development.

Methyl cis,cis- and trans,trans-octadecadienoates

Both series of *cis,cis*- and *trans,trans*-isomers were run either separately (Figs. 2 and 3) or jointly in pairs of positional isomers (Fig. 4) on a single TLC plate. The R_F values of both series are recorded in Table I.

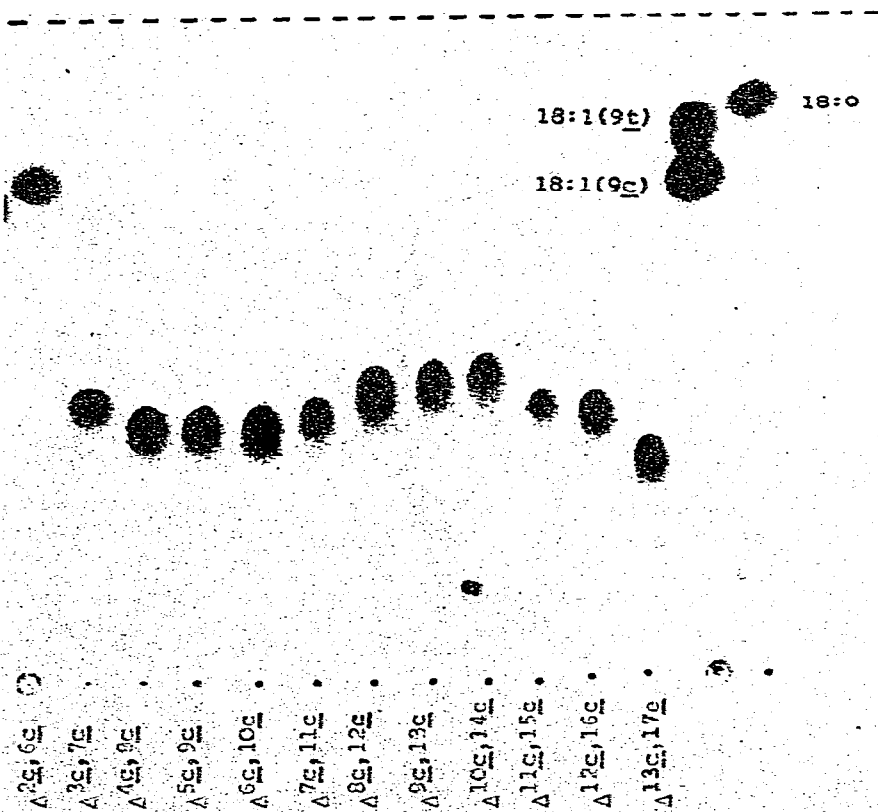
The *cis,cis*-compounds formed a distinct sinusoidal curve with a minimum at the $\Delta^{4c,8c}$, $\Delta^{5c,9c}$ and $\Delta^{6c,10c}$ isomers and a maximum at the $\Delta^{10c,14c}$ isomer. The $\Delta^{2c,6c}$ ester behaved very differently from the remaining isomers as its R_F value slightly

TABLE I

 R_F VALUES OF METHYL OCTADECADIENOATES AND OCTADECADIENOATES

18:2(*a,a*) = Methyl octadecadienoates, 18:2(*c,c*) = methyl *cis,cis*-octadecadienoates and 18:2(*t,t*) = methyl *trans,trans*-octadecadienoates.

Isomer	R_F values				
	Fig. 1; 18:2(<i>a,a</i>)	Fig. 2; 18:2(<i>c,c</i>)	Fig. 3; 18:2(<i>t,t</i>)	Fig. 4 18:2(<i>t,t</i>) 18:2(<i>c,c</i>)	
$\Delta^{2,6}$	0.63	0.76	0.78	0.74	0.74
$\Delta^{3,7}$	—	0.42	0.64	0.65	0.45
$\Delta^{4,8}$	0.37	0.40	0.63	0.65	0.41
$\Delta^{5,9}$	0.39	0.40	0.64	0.66	0.42
$\Delta^{6,10}$	0.36	0.40	0.64	0.66	0.45
$\Delta^{7,11}$	0.38	0.41	0.66	0.67	0.46
$\Delta^{8,12}$	0.38	0.45	0.68	0.70	0.48
$\Delta^{9,13}$	0.39	0.47	0.69	0.71	0.51
$\Delta^{10,14}$	0.41	0.48	0.67	0.73	0.53
$\Delta^{11,15}$	0.39	0.42	0.63	0.71	0.50
$\Delta^{12,15}$	0.33	0.42	0.62	0.70	0.48
$\Delta^{13,17}$	0.00	0.35*	0.40**	0.54**	0.43*
Methyl stearate	0.70	0.87	0.88		0.84
Methyl oleate	0.63	0.75	—		0.78
Methyl elaidate	—	0.83	0.84		0.80

* $\Delta^{13c,17c}$ Isomer.** $\Delta^{13t,17t}$ Isomer.Fig. 2. TLC of methyl *cis,cis*-octadecadienoates. For details see Table I.

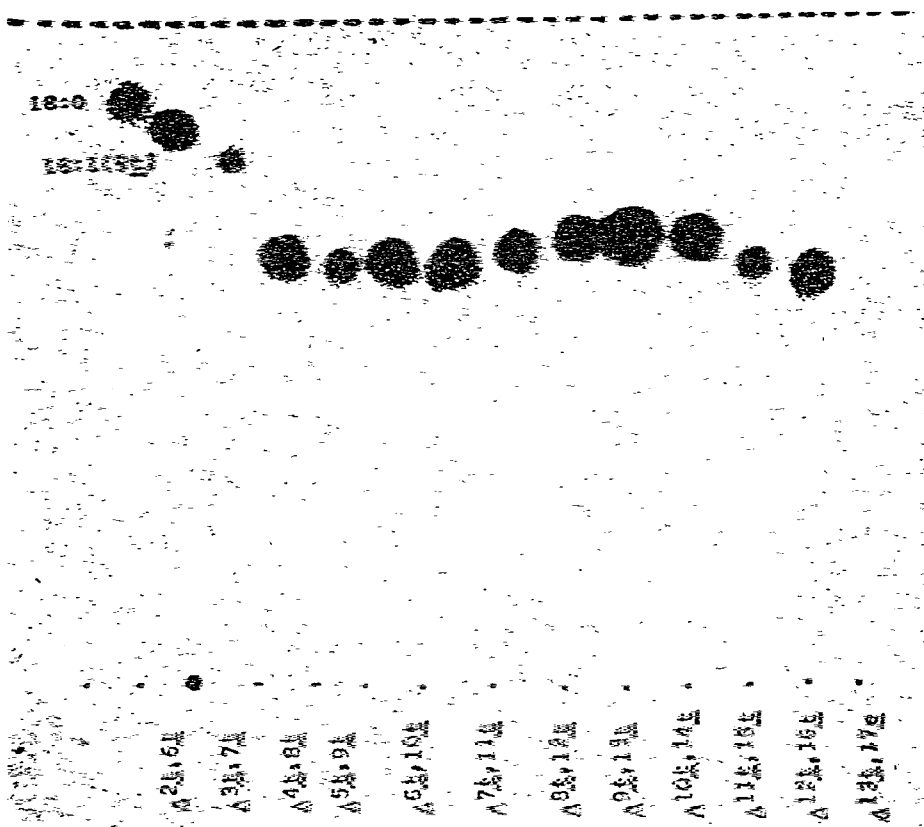


Fig. 3. TLC of methyl *trans,trans*-octadecadienoates. For details see Table I.

exceeded that of methyl oleate (Table I). The *trans,trans*-isomers gave a very shallow sinusoidal curve with a recognisable maximum at the $\Delta^{9,13}$ isomer. Like the corresponding *cis,cis*-isomer, the $\Delta^{2,6}$ compound gave a high R_F value. The R_F values of both series are recorded in Table I.

When pairs of the same positional isomers of the *cis,cis*- and *trans,trans*-isomers were spotted on to the same TLC plate (Fig. 4), the separation of the *trans,trans*- from the *cis,cis*-isomers was well defined except for the $\Delta^{2,6}$ esters. On the whole the *trans,trans*-compounds were less polar than their corresponding *cis,cis*-isomers.

ACKNOWLEDGEMENT

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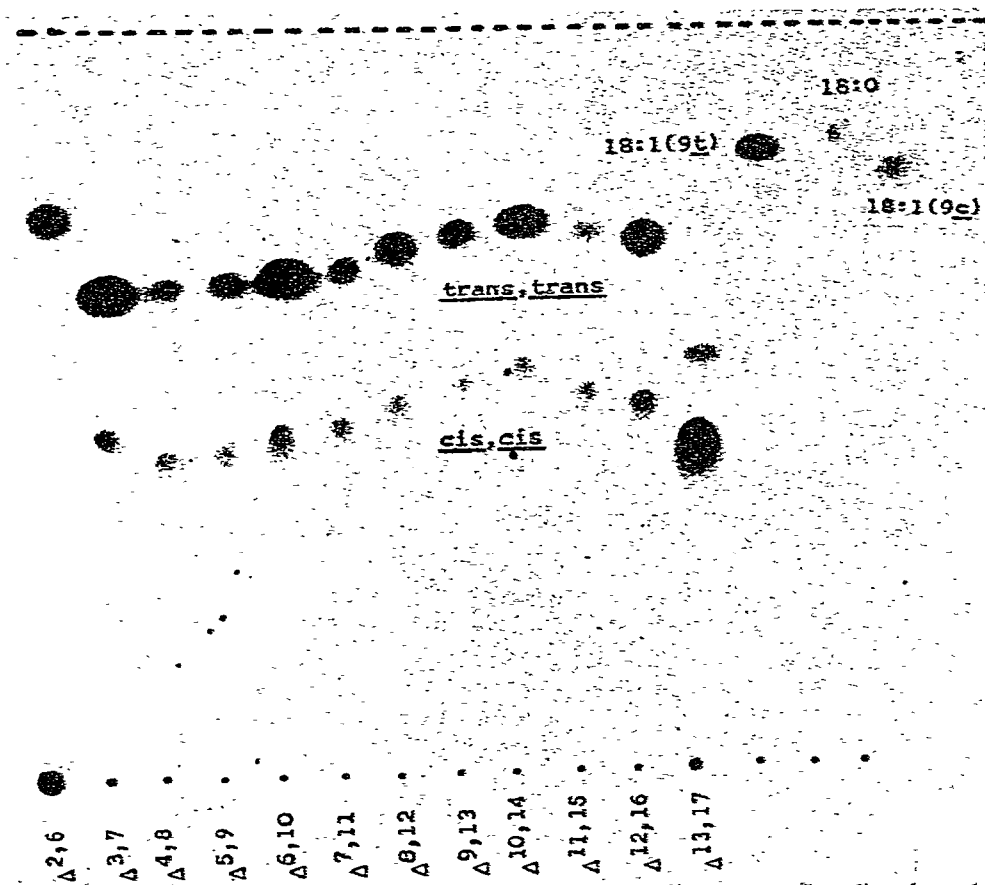


Fig. 4. TLC of methyl *cis,cis*- and *trans,trans*-octadecadienoates. For details see Table I.

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