

CHROM. 9940

Note

Fatty acids

XV*. Thin-layer chromatographic behaviour of acetylenic fatty esters on silicic acid

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(Received January 18th, 1977)

The separation of polyethylenic fatty esters according to their degree of unsaturation is readily achieved by column or thin-layer chromatography (TLC) using silver nitrate-impregnated silicic acid as the adsorbent². We have recently reported the behaviour of the entire series of *cis,cis*- and *trans,trans*-dimethylene-interrupted methyl octadecadienoates and their corresponding diacetylenic esters when using silver-ion TLC³. Earlier we drew attention to the labile character of acetylenic esters during the mercury(II) acetate adduct formation method in the chromatographic separation of unsaturated from saturated fatty esters⁴. In our latest attempts to distinguish acetylenic from ethylenic esters, we observed a distinct and facile separation between ethylenic and acetylenic fatty esters when using ordinary silicic acid TLC.

This paper demonstrates the ease of separation of mono- and diacetylenic fatty esters from ethylenic and/or saturated fatty esters by silicic acid TLC, which has often been regarded as a method that is not applicable to the separation of unsaturated systems owing to impregnation of the adsorbent with silver nitrate.

EXPERIMENTAL

Silicic acid (GF₂₅₄ Type 60, Merck Darmstadt G.F.R.) was coated on glass plates (20 × 20 cm) to give a uniform layer of thickness 0.3 mm. The plates were activated by heating them at 120° for 1½ h. Methyl stearate, oleate and linoleate were obtained from commercial suppliers; the remainder of the unsaturated fatty esters used were synthesized as reported earlier^{3,5}. Samples (20–30 µg) dissolved in acetone (1 µl) were spotted on to the plate by means of a micro-syringe. Light petroleum (b.p. 60–80°)–diethyl ether (23:3) was used to develop the plates. After development, the spots were made visible by spraying with a 10% ethanolic solution of molybdophosphoric acid and heated in an oven at 150–200° for *ca.* 10 min or until the spots became visible.

* Part XIV: ref. 1.

RESULTS AND DISCUSSION

Ethylenic fatty esters, whether mono- or polyethylenic, cannot be separated from their corresponding saturated derivatives by ordinary silicic acid TLC, as the ethylenic bond does not contribute any substantial degree of adsorptivity. Nevertheless, methyl oleate shows a marginal difference in R_F value from methyl stearate (Fig. 2). However, on silver-ion TLC the π -electrons of the ethylenic bond of unsaturated fatty esters are readily complexed with silver ions, enabling separation to be achieved according to the number of double bonds present in the molecule. Acetylenic esters, on the other hand, are not significantly more polar than their corresponding *cis*-ethylenic esters when chromatographed on silver nitrate-impregnated silicic acid³.

When the entire series of dimethylene-interrupted methyl octadecadiynoate isomers⁵ was re-chromatographed on ordinary silicic acid TLC (Fig. 1), sub-fractionation of methyl 2,6- and 3,7-octadecadiynoate from the remaining isomers was

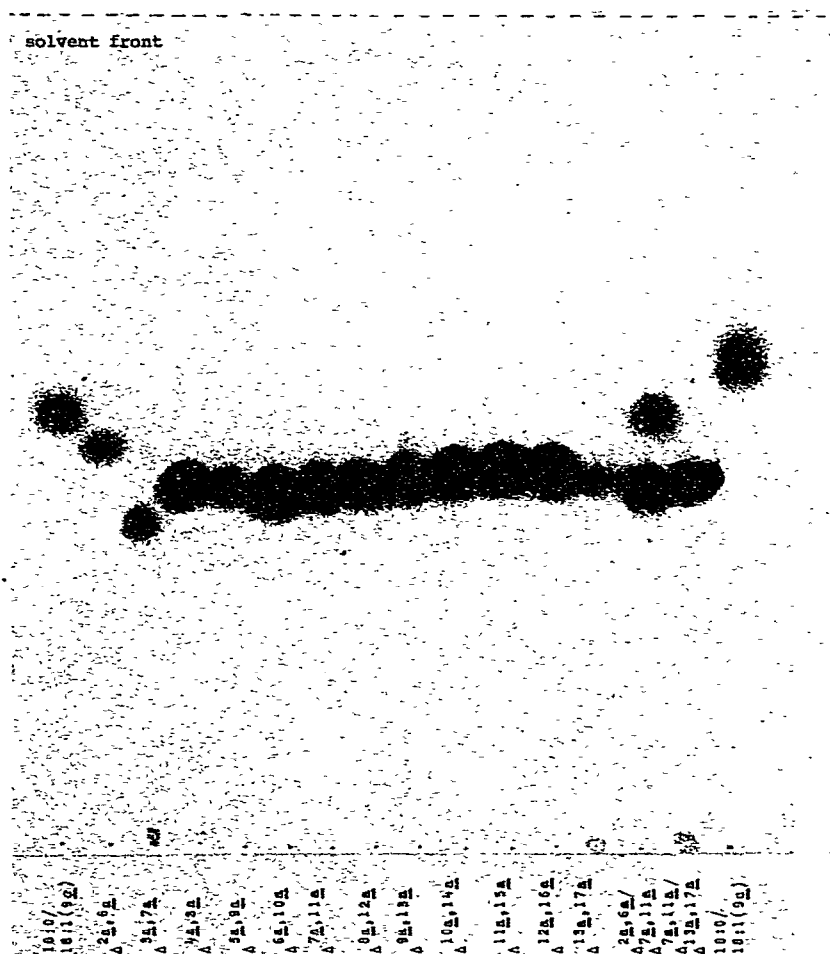


Fig. 1. TLC of methyl octadecadiynoates on silicic acid.

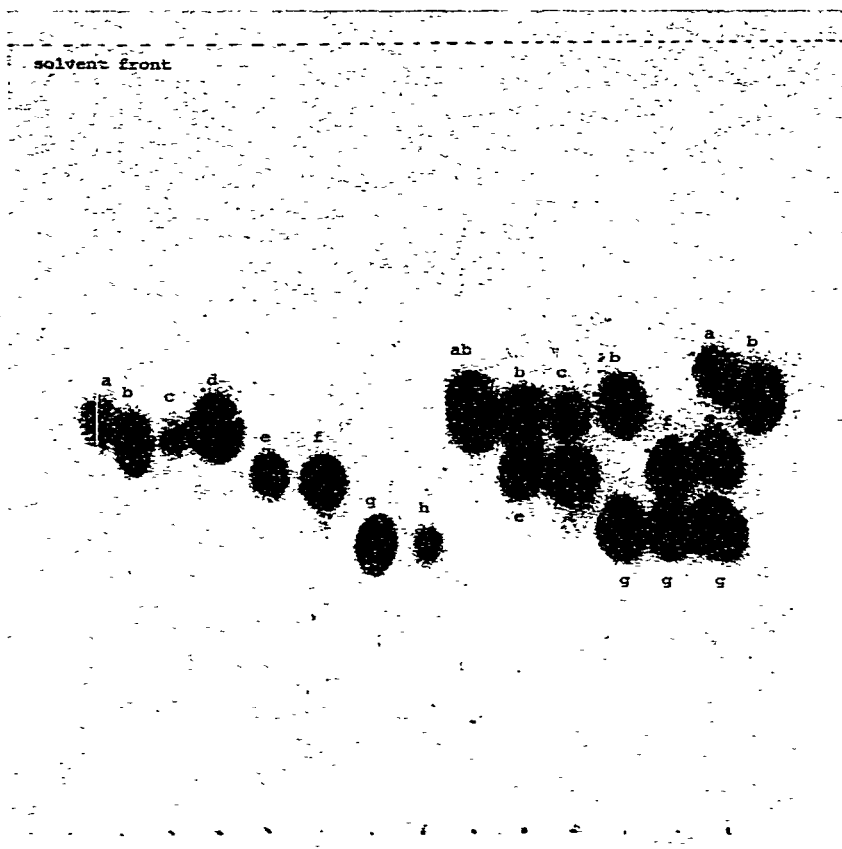


Fig. 2. TLC of saturated and unsaturated C_{18} -fatty esters on silicic acid. a = Methyl stearate; b = methyl oleate; c = methyl linoleate; d = methyl 5-*cis*-9-*cis*-octadeca-dienoate; e = methyl 5-octadec-ynoate; f = methyl octadec-*cis*-10-en-5-ynoate; g = methyl 7,11-octadeca-diynoate; h = methyl 9,14-octadeca-diynoate.

observed. The sinusoidal pattern previously observed during the silver-ion TLC of the same series of diacetylenic esters was barely recognizable. The methyl 2,6-octadecadiynoate isomer could be completely separated from the 7,11-isomer, as the acetylenic bond at the C_2 - C_3 position contributed no additional adsorptivity.

When individual and mixtures of various unsaturated fatty esters were chromatographed, the degree of separation was as shown in Fig. 2. Methyl stearate, oleate and linoleate and methyl 5-*cis*-9-*cis*-octadecadienoate gave almost identical R_F values. Methyl 5-octadecynoate and methyl octadec-*cis*-10-en-5-ynoate gave similar R_F values, while methyl 7,11- and 9,14-octadecadiynoate behaved alike. When mixtures of these isomers were examined, the separation of saturated (including mono- and diethylenic esters) and mono- and diacetylenic esters from each other was clearly feasible. The R_F values of these isomers are presented in Table I.

The significant adsorptivity of the acetylenic bond on silicic acid is probably due to two factors: (a) the electron-rich nature and (b) the unique one-dimensional

TABLE I

 R_F VALUES OF UNSATURATED C_{18} -ESTERS

18:0 = Methyl octadecanoate; 18:1(c) = methyl *cis*-octadecenoate; 18:2(c,c) = methyl *cis,cis*-octadecadienoate; 18:1(a) = methyl octadecynoate; 18:2(a,a) = methyl octadecadiynoate; 18:2(a,c) = methyl octadecenynoate. The numbers included in parentheses indicate the positions of the unsaturation centres. Solvent: light petroleum (b.p. 60–80°)–diethyl ether (23:3). Adsorbent: silicic acid, 0.3 mm thickness.

Isomer	R_F value (Fig. 1)	Isomer	R_F value (Fig. 2)
<i>Individual</i>		<i>Individual</i>	
18:0	0.51	18:0	0.51
18:2(2a,6a)	0.46	18:1(9c)	0.48
18:2(3a,7a)	0.37	18:2(9c,12c)	0.48
18:2(4a,8a)	0.43	18:2(5c,9c)	0.49
18:2(5a,9a)	0.43	18:1(5a)	0.43
18:2(6a,10a)	0.41	18:2(5a,10c)	0.43
18:2(7a,11a)	0.42	18:2(7a,11a)	0.34
18:2(8a,12a)	0.42	18:2(9a,14a)	0.34
18:2(9a,13a)	0.43		
18:2(10a,14a)	0.44	<i>Mixtures</i>	
18:2(11a,15a)	0.45	18:0	0.51
18:2(12a,16a)	0.45	18:1(9c)	0.51
18:2(13a,17a)	0.44	18:1(9c)	0.51
		18:1(5a)	0.42
<i>Mixtures</i>		18:2(9c,12c)	0.51
18:2(2a,6a)	0.52	18:2(5a,10c)	0.42
18:2(7a,11a)	0.43	18:1(9c)	0.51
18:2(7a,11a)	0.43	18:2(7a,11a)	0.36
18:2(13a,17a)	0.43	18:2(5a,10c)	0.42
18:0	0.59	18:2(7a,11a)	0.36
18:1(9c)	0.59	18:0	0.54
		18:1(5a)	0.43
		18:2(7a,11a)	0.36

shape of the triple bond. Unlike the ethylenic system, a triple bond has no steric problem when the π -electrons interact with the adsorbent. Hence, the more acetylenic bonds present in the chain, the more polar such a compound will behave on silicic acid, provided that no conjugation of the triple bond has taken place.

ACKNOWLEDGEMENT

The authors thank the Committee on Higher Degrees and Research Grants of Hong Kong University for financial support.

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