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Chromatography of isomeric methylene interrupted methyl *cis,cis*-octadecadienoates

I. Argentation thin layer chromatography

Argentation chromatography (recently reviewed¹) on thin layers or columns has become one of the more valuable separation techniques available to lipid chemists. Though a wide variety of applications in the lipid field have been described, comparatively few reports of studies with model compounds are available and the full potential of the method has not been determined. Two reports of the chromatographic behaviour of isomeric methyl octadecenoates on thin layers of silica gel impregnated with silver nitrate have recently appeared^{2,3}. The isomeric methylene-interrupted methyl *cis,cis*-octadecadienoates⁴ (*i.e.*, methyl *cis,cis*-2,5-octadecadienoate to methyl *cis*-14,17-octadecadienoate) have now been examined in a similar manner.

Experimental

Silica Gel G (Merck) layers (0.25 mm) containing silver nitrate (10%) were activated by heating at 110° for 2 h. Plates were developed in unlined tanks with hexane-diethyl ether (9:1) as solvent system and visualised by charring with sulphuric acid (10%) at 150°.

Results and discussion

As might be expected, the migration pattern of the isomers conforms to a sinusoidal curve (Fig. 1). The 2,5-isomer has a remarkably high R_F value in comparison to other members of the series. The 3,6- to 6,9-isomers can be separated but the

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remainder conform to a gentle curve with a slight but real drop at the 12,15-isomer. A similar pattern has been found with mono-enoic esters^{2,3} though the curve is more marked and better separations can be achieved.

A similarly high R_F value has been obtained for methyl *cis*-2-octadecenoate² contrary to the predictions of MORRIS *et al.*³ However, some other factor must be operating in this case as even on untreated silica plates, this isomer migrates ahead of methyl stearate^{5,6}. This also pertains to methyl *cis*, *cis*-2,5-octadecadienoate.

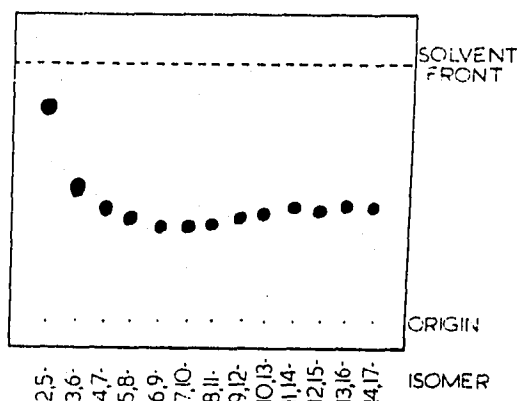


Fig. 1. Argentation thin layer chromatogram of the complete series of methylene-interrupted methyl *cis*, *cis*-octadecadienoates.

GUNSTONE *et al.*² have explained the differences in migration rates of the isomeric mono-enes on the basis of a dual interaction between the polar ester groups with the silica and the double bonds with silver ion. The extent of this would depend on the conformation of each molecule which would vary with the position of the double bond. To account for the distinctive behaviour of *cis*-2 isomers, however, some other factor must operate and a solvent effect may have to be taken into account. Methyl *cis*, *cis*-2,5-octadecadienoate has unusually high critical solution temperatures⁴ in comparison to other members of the series and this may reflect differences in other solution properties. Any explanation must be speculative, however, until more detailed physical measurements on the series are made.

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