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Note

Thin-layer chromatography of methoxyhalogenomercuri derivatives of mono-unsaturated long-chain esters

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Fractionation of mixtures of fatty acid methyl esters according to their degree of unsaturation is commonly carried out either by argentation chromatography or by conversion of olefinic esters to methoxyacetoxymercuri adducts and chromatographic separation of these derivatives. (For a review see ref. 1.) A disadvantage in the use of methoxyacetoxymercuri adducts is that they are very polar in comparison with the parent esters; special conditions for thin-layer chromatography (TLC) are necessary involving the use of relatively polar solvent mixtures and long development times[1]. Conversion of methoxyacetoxymercuri adducts to methoxybromomercuri derivatives brings about a reduction in the polarity and a consequent improvement in the chromatographic properties[2–4]. This communication reports a study of the TLC behaviour of methoxyhalogenomercuri (chloro-, bromo- and iodo-) derivatives of methyl esters of *cis*- and *trans*-mono-unsaturated fatty acids of varying chain-length.

RESULTS AND DISCUSSION

Methoxybromomercuri adducts of methyl palmitoleate, oleate, elaidate and erucate were prepared as described previously[2]. Methoxychloromercuri and methoxyiodomercuri adducts of these esters were prepared by the same procedure, sodium bromide being substituted by sodium chloride and sodium iodide, respectively. TLC of the adducts was carried out on layers (0.5 mm) of silica gel (Merck $PF_{254+366}$); unidimensional multiple chromatography using a threefold development with hexane–diethyl ether (90:10) was found to resolve the various derivatives satisfactorily (Fig. 1). A sample of the methyl 9(10)-methoxyoctadecanoates prepared by methoxymercuration–demercuration of methyl oleate[5] was used as a chromatographic reference compound. Separated components containing mercury were located as purple-red spots by spraying with a 1% solution of S-diphenylcarbazone in ethanol[1]; all lipids were detected by spraying with dichromate–sulphuric acid reagent and charring at 150°.

The polarity of the methoxyhalogenomercuri derivatives decreased in the expected order Cl > Br > I. The chloro derivatives chromatographed less well than the others, tailing spots being characteristic. The bromo and iodo derivatives of methyl oleate and elaidate were clearly separated in this chromatographic system dem-

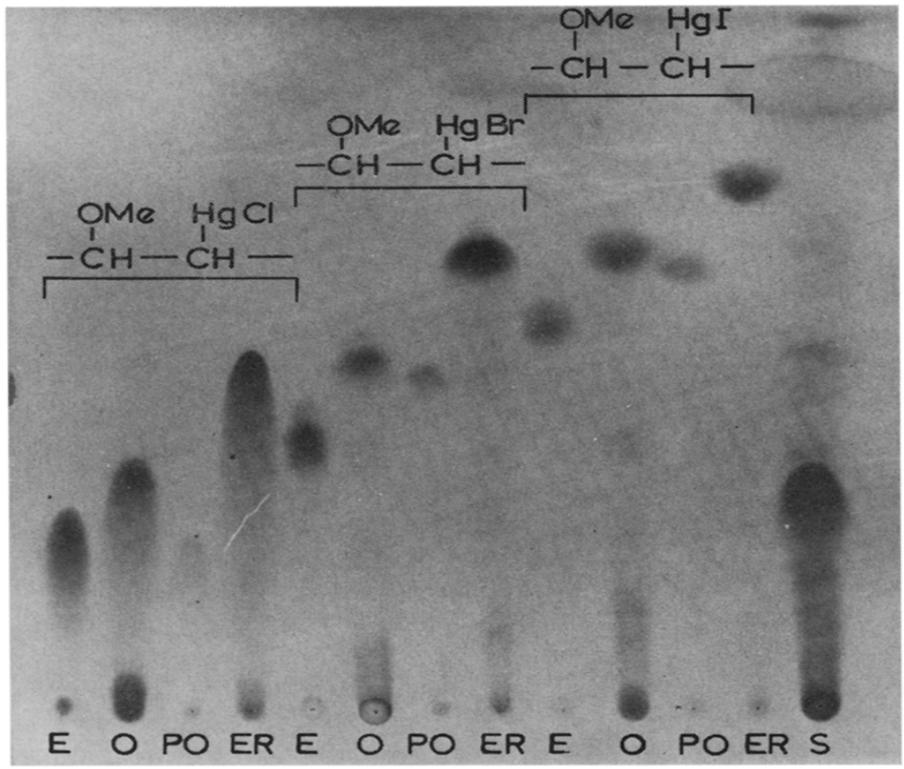

Fig. 1. TLC on a silica gel plate of methoxyhalogenomercuri adducts of methyl esters of monounsaturated long-chain fatty acids using hexane–diethyl ether (90:10, three passes). The separated components were revealed by charring at 150° after spraying with dichromate–sulphuric acid reagent. Abbreviations: (E) adducts from methyl elaidate, (O) from methyl oleate, (PO) from methyl palmitoleate, and (ER) from methyl erucate; S = methyl 9(10)-methoxyoctadecanoates (lower spot).

onstrating that *cis*- and *trans*-isomers may be resolved. In a previous study[2] methoxybromomercuri adducts of methyl oleate and elaidate were not separated in a single development with heptane–dioxan (60:40) and methoxyacetoxymercuri adducts of these esters were not resolved[1]. Argentation chromatography has been the method of choice for the resolution of *cis*- and *trans*-isomers of unsaturated fatty acid esters on thin-layer chromatograms[1]; the present study shows that the same result (Fig. 1) may be achieved by TLC of methoxybromomercuri and methoxyiodomercuri adducts. It is interesting to note that the methoxyhalogenomercuri derivative of a *trans*-unsaturated ester is more polar than that of the corresponding *cis*-ester. On argentation chromatography *trans*-unsaturated esters are less polar than their *cis*-isomers[1]. Methoxyhalogenomercuri adducts may be quantitatively converted to the original esters by treatment with mineral acid[2–4] and on demercuration with sodium borohydride should produce methoxylated esters suitable for mass spectrometric location of the double bond[5].

Methoxyhalogenomercuri adducts of methyl esters of *cis*-unsaturated long-chain acids are also resolved to some extent according to their chain-length (Fig. 1).

The separation between the derivatives of methyl palmitoleate (16 carbons) and oleate (18 carbons) is quite small and mixtures of the adducts from these two esters are not clearly resolved. The derivatives of methyl erucate (22 carbons) are clearly resolved, however, from the derivatives of methyl palmitoleate and oleate. This resolution, according to chain-length, may be of value in the fractionation of complex mixtures of unsaturated fatty acids.

In summary, the present results show that by choice of suitable methoxymercuri adducts, particularly methoxyiodomercuri derivatives, unsaturated fatty acid esters can be fractionated on TLC plates according to the number and stereochemistry of double bonds and also partially according to chain-length. Such separations have usually been carried out by argentation chromatography; chromatography of methoxyiodo- (or bromo)mercuri adducts is a technique of comparable potential for the separation of unsaturated fatty acid esters.

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