GAS CHROMATOGRAPHY OF SOME BROMINATED METHYL OCTADECANOATES*

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The identifications of 12-bromo- and several dibromooctadecanoates by gas chromatography have been investigated. On a polyester column, any polar effects of the secondary bromine substituent are of a lower order of magnitude than the effect of weight alone. The fact that the data obtained from the bromo compounds fall very close to an extrapolated plot of molecular weight *versus* log of the retention time for saturated methyl esters implies that the principal effect of the bromine groups is a contribution to the molecular weight. The relative retention times of methyl 12-bromooctadecanoate, synthesis of which is reported here, and methyl *threo*-9,10-dibromooctadecanoate obtained from oleic acid are presented in Table I. It is obvious that with a retention time more than twenty times that of stearate, the dibromo compounds will not interfere with analyses of bromine-free saturated ac-

TABLE I

EFFECT OF BROMINE SUBSTITUENTS ON RETENTION TIME OF METHYL OCTADECANOATES

Compound	*Relative retention time*	
Methyl *threo*-9,10-dibromooctadecanoate	21*	22**
Methyl 12-bromooctadecanoate	5.7	6.1
Methyl arachidate	2.0	1.9
Methyl stearate	1	1
Methyl palmitate	0.54	0.53

* 3 ft. column 183°, flash heater 233°, detector cell 223°, argon flow 150 ml/min.
** 6 ft. column 186°, flash heater 235°, detector cell 239°, argon flow 90 ml/min.

companiments. The tentative characterization of methyl *threo*-9,10-dibromooctadecanoate as having a retention volume of 1.18 with respect to methyl stearate[1] appears in light of the data presented here to be in error.

The polyester packing was found to be insensitive to the differences between *erythro* positional isomers. Methyl *erythro*-9,10-dibromooctadecanoate from elaidic acid and the *erythro*-11,12-dibromo isomer from vaccenic acid** had the same elution time.

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** Fluka AG, Chemische Fabrik, Switzerland.

A mixture of *erythro*-11,12- and *erythro*-12,13-dibromooctadecanoates obtained from "vaccinic" acid* had the same retention time as the other *erythro* isomers without any apparent peak broadening due to the heterogeneity of the eluate.

Contrary to the indifference of the polyester stationary phase to positional isomerism of these *erythro* vicinal dibromides, a difference was observed between the two 9,10-dibromooctadecanoate diastereoisomers, Table II. The *erythro* compound

TABLE II

RETENTION TIMES OF DIASTEREOISOMERIC METHYL DIBROMOOCTADECANOATES

Compound	*Retention time*	
Methyl *erythro*-9,10-dibromooctadecanoate	48.8 min*	204 min**
	48.5	
Methyl *threo*-9,10-dibromooctadecanoate	51.0	215
	51.6	
Methyl *erythro*-11,12-dibromooctadecanoate	48.3	
Methyl *erythro*-11,12- and -12,13-dibromooctadecanoate (equal mixture)	48.3	
Methyl stearate	2.4	8.6

* 3 ft. column 183°, flash heater 233°, detector cell 223°, argon flow 150 c.c./min.
** 6 ft. column 185°, flash heater 218°, detector cell 242°, argon flow 192 c.c./min.

was eluted more rapidly from the column than the *threo* isomer, but the 5 % difference in their retention times is apparently insufficient to permit their complete separation in such columns.

In a consideration of the difference observed between diastereoisomers, a useful qualitative rule may be formulated on the basis of a postulated relationship between dipole moment and retention times of isomers on a polar column. The *threo* isomer, being less symmetrical than the *erythro*, will have a higher dipole moment. Increased dipole–dipole interaction between the solute (the fatty ester) and the solvent (the polyester liquid phase of the column) shifts the partitioning of the solute between the gas and liquid phases to favor solubility of the *threo* over the *erythro* isomer in the liquid phase and thus causes a longer retention time for the *threo* compound.

A generalization of this kind is not meant to deny the contribution of other factors affecting the approach to thermodynamic equilibria which determine the retention times of various solutes. Rather, in this case, there is provided an opportunity to dissect dipole effects from other parameters affecting the partitioning potentialities of the system. The differential behavior of *cis* and *trans* isomers of unsaturated fatty esters on columns of this type may also be rationalized by recourse to this generalization.

The vapor phase separation of diastereoisomers in general has been little exploited, although references may be made in this regard to a report of separation by

* Nutritional Biochemicals Corp., Cleveland, Ohio. This sample was shown to be an approximately equal mixture of 11- and 12-octadecenoic acids (personal communication from Dr. ARMAND FULCO).

conventional distillation[2] and to another involving activated charcoal as the non-volatile component in a gas-phase separation[3]. Gas–liquid chromatography has been successfully employed in separating *meso* and racemic 2,3-dichlorobutane[4] and diastereoisomeric 2,3,4-trimethylhexanes[5].

To dispel any concern over the possibility of decomposition having occurred during these chromatographic studies, samples of methyl 12-bromo- and of *threo*-9,10-dibromooctadecanoate were recovered from the column and rechromatographed. No evidence of decomposition was discernible. Further evidence of the stability of these dibromides under the operating conditions employed here was obtained by debrominating (with zinc in methanol) a recovered sample of chromatographed *threo*-9,10-dibromide and identifying the product as methyl oleate on the basis of its gas-phase chromatographic behavior.

EXPERIMENTAL

The chromatographic runs were made using a Barber Coleman Model 10 Chromatograph using argon and a radium detector. The glass columns contained 20% succinic acid–ethylene glycol polymer on siliconized Johns-Manville Chromosorb, 80–100 mesh. The samples were injected as 1% acetone solutions with the exception of the samples which were to be collected, and these were injected neat. The operating conditions are given in the tables. Retention times were measured from solvent front to the maximum height of peak.

threo-9,10-Dibromooctadecanoic acid was prepared according to the method of NEVENZEL AND HOWTON[6].

erythro-11,12-Dibromooctadecanoic acid was prepared from vaccenic acid by adding the calculated amount of Br_2 in CCl_4 to a CCl_4 solution of the acid. "Vaccinic" acid was brominated in a similar manner to yield a mixture of *erythro-10,11* and *11,12-dibromooctadecanoic acid*. *erythro-9,10-Dibromooctadecanoic acid* was prepared similarly from elaidic acid. All of the acids were esterified with diazomethane prior to chromatography. A combination of gas chromatography and infrared spectrophotometry showed the vaccenic and "vaccinic" acids to be at least 75% *trans*.

12-Bromooctadecanoic acid. Since there is no published report of this compound, its preparation will be given in detail. A sealed Pyrex tube containing 6.0 g (0.02 mole) of 12-hydroxyoctadecanoic acid (Eastman) and 25 ml of 25% HBr in acetic acid (w/w) was heated at 100° for 16 h. The dark brown oil remaining after removal of the solvent and excess HBr was taken up in 30–60° petroleum ether, washed and dried over $MgSO_4$. Two crystallizations from 30–60° petroleum ether at —20° gave 5.3 g of colorless crystalline material melting at 33–35°. A small quantity was crystallized 3 additional times to raise the melting point to 37.0–37.8°.

Anal.: Calcd. for $C_{18}H_{35}BrO_2$: C, 59.49; H, 9.71.

Found: C, 59.66; H, 9.67.

SUMMARY

During gas chromatography on a polyester column, the principal effect of bromine substituents on a fatty ester molecule was to increase the retention time in proportion to the increase in molecular weight. Secondary effects arose from configurational isomerism. Methyl *threo*-9,10-dibromooctadecanoate was retained longer than the *erythro* diastereoisomer. The chromatographic difference between diastereoisomers was attributed to a change in dipole moment.

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