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Note

Use of retention time plots as a means of identifying isomeric methyl ketononanoates

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In connection with studies aimed at the photochemical "remote oxidation" of oleic acid^{1,2}, we were faced with the problem of identifying various ketononanoic acids. The most suitable method would be a gas chromatographic procedure applied to the methyl esters of these isomeric keto acids. However, this approach would require the availability of standard keto acids in order to be able to compare retention times with those of the unknown compounds. The difficulty with this method is that most of these compounds are not commercially available. In this study, six ketononanoic acids were synthesized and it is demonstrated that a linear relationship exists between the logarithm of retention time ($\log t_R$) and the position of the keto group. It is therefore possible to use the retention time data of a few representative methyl ketononanoates for the identification of other isomers. Even though the application of such plots is widely used for homologous series of organic compounds, to our knowledge this work constitutes the first example of the application of retention time plots for the identification of positional isomers of keto acid esters with the same number of carbon atoms.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 5710 gas chromatograph equipped with a flame ionization detector and 5 ft. \times 1.8 in. O.D. stainless-steel columns was used. The packings employed were 10% Carbowax 20M terminated with terephthalic acid, 10% Carbowax 20M and 3% OV-225 on 100-120-mesh Gas-Chrom Q supports. The columns were conditioned at 200°C prior to use. Analyses were performed isothermally at 150°C. The injector block and detector temperatures were 200 and 250°C, respectively. The gas flow-rates were nitrogen at 30 ml/min, hydrogen at 30 ml/min and air at 300 ml/min.

Materials

3-Ketononanoic acid was prepared by γ -alkylation of methyl acetoacetate³. This acid is not stable at ordinary temperatures and slowly decomposes to 2-octanone. 4-Ketononanoic acid (m.p. 69°C) was prepared from 2-hexylidenesuccinic acid by the method of Takeda *et al.*⁴. 5-Keto- and 8-ketononanoic acids (m.p. 44 and

40°C, respectively) were prepared by ozonolysis and oxidative work-up of 1-butylcyclopentene and 1-methylcyclooctene, respectively¹. 6-Keto- and 7-ketononanoic acids (m.p. 43 and 42°C, respectively) were prepared by alkaline cleavage of butyrylcyclopentanone and propionylcyclohexanone, respectively⁵. All keto acids were characterized by comparing their physical constants with literature values³⁻⁶ and from additional IR, NMR and mass spectroscopic data¹. The acids were converted into their methyl esters using dimethylformamide dimethyl acetal.

RESULTS AND DISCUSSION

Numerous trials were made to determine the optimum conditions for the gas chromatographic separation of the synthetic ketononanoic acid methyl esters. It was found that excellent resolutions were obtained using 10% Carbowax 20M terminated with terephthalic acid. Carbowax 20M gave poorly resolved peaks and OV-225 gave reasonable separations. The retention times of the isomeric methyl ketononanoates increased with increasing distance of the keto group from the carbomethoxy group. This observation led us to speculate whether a linear retention time plot would be obtained by plotting $\log t_R$ against the position of the keto carbonyl group. Table I shows the $\log t_R$ values obtained for the various keto esters.

A plot of $\log t_R$ against the position of the keto group is shown in Fig. 1; all the points lie on a straight line. It became evident that such a linear plot could be used for the identification of unknown keto esters, and also that only a representative number of standards would be needed to obtain the linear plot.

An unknown mixture of ketononanoic acids was esterified and subjected to the same chromatographic analysis. The $\log t_R$ values for the components of the unknown mixture closely matched those of the standard keto esters. It was therefore possible to identify them from either the retention time plot or Table I.

The use of retention time plots dates as far back as 1952, when James and Martin⁷ showed the existence of a linear relationship between $\log t_R$ and the number of carbon atoms for normal and iso fatty acids. Since then, a number of workers have shown that similar relationships are observed for several other homologous series of organic compounds, such as aldehydes, ketones, alcohols and esters⁸⁻¹³. Indeed, it is generally well known that retention times can be correlated with physical properties such as vapour pressure, boiling point and number of carbon atoms¹⁴.

TABLE I

LOG t_R VALUES OF STANDARD METHYL KETONONANOATES AND COMPONENTS OF THE UNKNOWN MIXTURE

<i>Standard keto ester</i>	<i>Log t_R</i>	<i>Log t_R of unknown component</i>
Methyl 2-ketononanoate	2.35	2.35
Methyl 3-ketononanoate	2.42	2.41
Methyl 4-ketononanoate	2.48	2.47
Methyl 5-ketononanoate	2.55	2.53
Methyl 6-ketononanoate	2.61	2.61
Methyl 7-ketononanoate	2.68	2.69
Methyl 8-ketononanoate	2.74	2.75

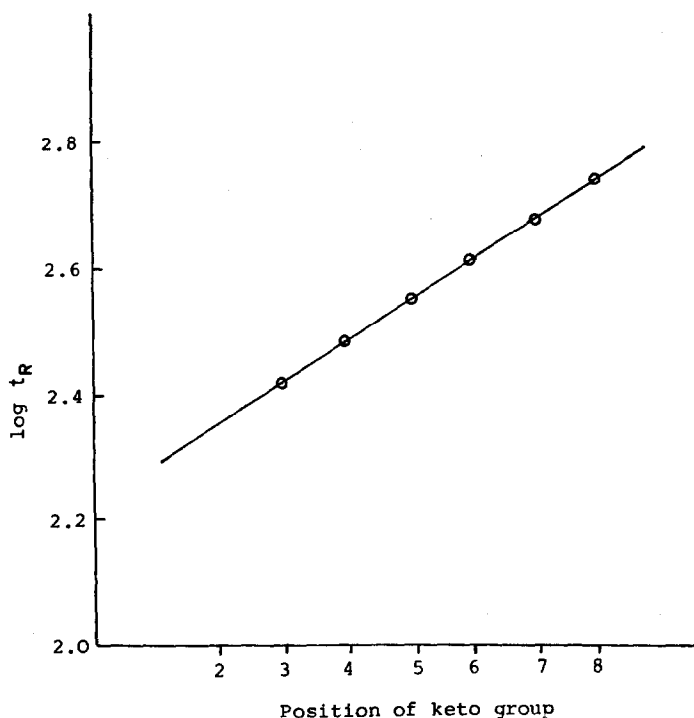


Fig. 1. Plot of $\log t_R$ vs. position of keto group.

Even so, most of the instances in the literature where retention time plots have been used deal with homologous series of organic compounds having a particular functional group.

The most popular use of retention time plots is in fatty acid analysis^{15,16}, where such plots are reliably used for accurately identifying saturated fatty acids and for detecting the presence of unsaturated derivatives. With compounds such as fatty acids one is dealing with compounds with different carbon contents (C_{12} , C_{14} , C_{16} , etc.) and one can easily rationalize the longer retention times for the compounds with their higher molecular weight. With the ketononanoic acids investigated here, all the compounds have the same molecular weight and the only difference in the series is the position of the keto group. The nature of the inter- and intramolecular forces that are responsible for the increased retention times with increasing distances of the keto group from the carbomethoxy moiety is unclear. The gas chromatographic behaviour of the keto esters is, however, simple and reproducible and makes the method described here a very attractive and reliable method of identification.

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