

Gas chromatographic behaviour of normal aliphatic ester isomers

Throughout the gas chromatographic identification of volatile tropical fruit flavours in this laboratory the prediction of retention times from known data has become a necessity. With fruit flavours one is faced with such a wide array of possible chemical compounds that the synthesis of these to provide retention data is impracticable.

Much use has been made of plots of logarithm of retention time *versus* number of carbon atoms for an homologous series¹ but this relationship is of restricted application. As esters comprise an important fraction of known tropical fruit flavours^{2,3} an examination of isomeric esters was initiated. This revealed regular relationships between retention times and boiling points of normal aliphatic esters containing a constant number of carbon atoms, e.g. methyl *n*-caproate, ethyl *n*-valerate, *n*-propyl *n*-butyrate etc. for a group containing seven carbon atoms. These relationships have proved useful in predicting retention times unobtainable by other means.

Experimental

Apparatus

A Perkin Elmer Model 154D Vapor Fractometer fitted with a thermistor bead detector and a 2 m × 1/4 in. o.d. stainless steel column packed with dinonyl phthalate on kieselguhr was used. The instrument was operated at a column temperature of 168° and a flow rate of 46 ml of helium/min.

Reference compounds

Normal aliphatic esters containing from four to nine carbon atoms were prepared by the usual synthetic procedures. Fractional distillation was carried out where the product was grossly impure. These esters will fall into six constant number of carbon atoms groups similar to that previously illustrated and hereafter are referred to as "ester groups".

Results

For each ester group retention times under the conditions previously described were obtained and the logarithm plotted against the boiling point. In each case a straight line was obtained with only two instances of a marked deviation (Fig. 1E and F). Here it is believed accurate determination of the boiling points would reveal closer agreement.

Discussion

Mathematical extension

By the following simple mathematical extension the usefulness of the above relationship can be expanded:

From Fig. 1:

$$\frac{\log R_T}{\text{b.p.}} = k \text{ (a constant)}$$

Suppose the plots shown in Fig. 2 were made for each ester group (a_1, a_2 etc. and b_1, b_2 etc. are equal to the boiling points and $\log R_T$ values respectively).

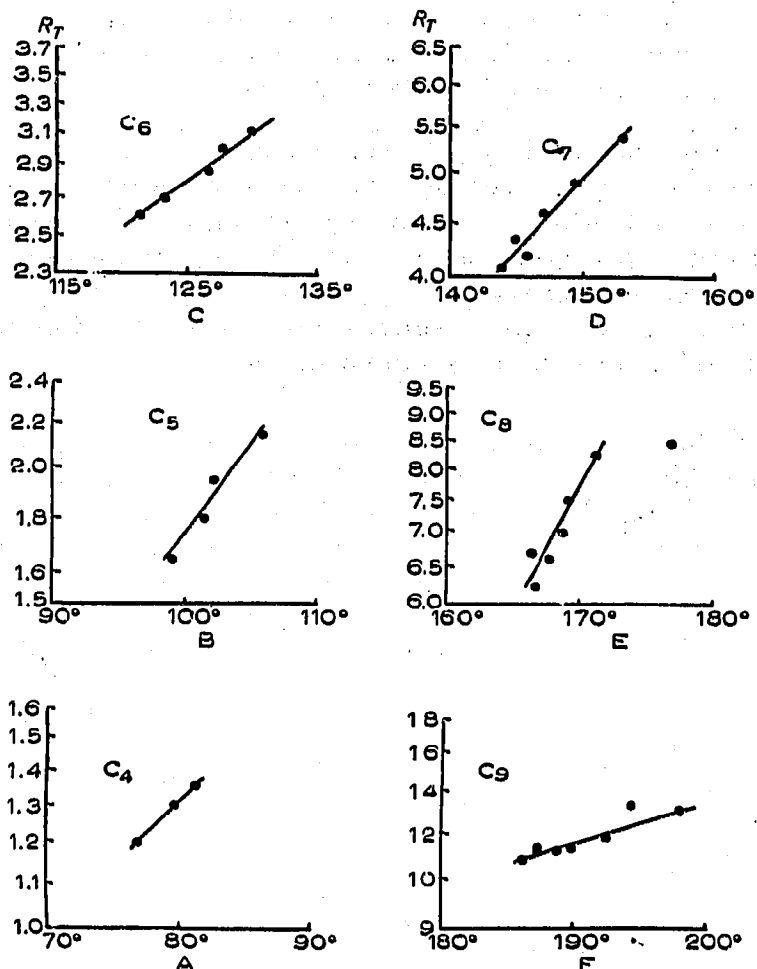


Fig. 1. Plots of logarithm of retention time (in min) *versus* boiling point (°C) for each ester group.

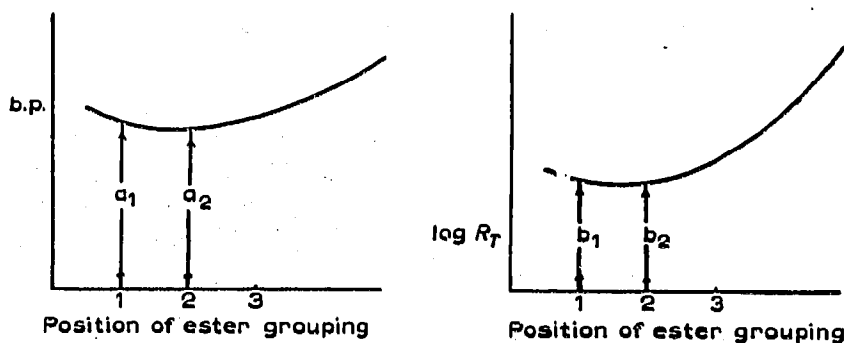


Fig. 2. Hypothetical plots of boiling point and logarithm of retention time *versus* position of the ester grouping.

Now:

$$\frac{a_1}{b_1} = \frac{a_2}{b_2} \dots \frac{a_n}{b_n} = k$$

Thus the curves in Fig. 2 must have the same shape.

This means the curves produced by a particular ester group will be geometrically superimposable. This can be done by taking one graphic difference in boiling points as being equivalent to the corresponding graphic difference in R_T values and altering the other values correspondingly.

Fig. 3 shows boiling point plots superimposed on retention time plots for each ester group. Substantial agreement is shown in each case.

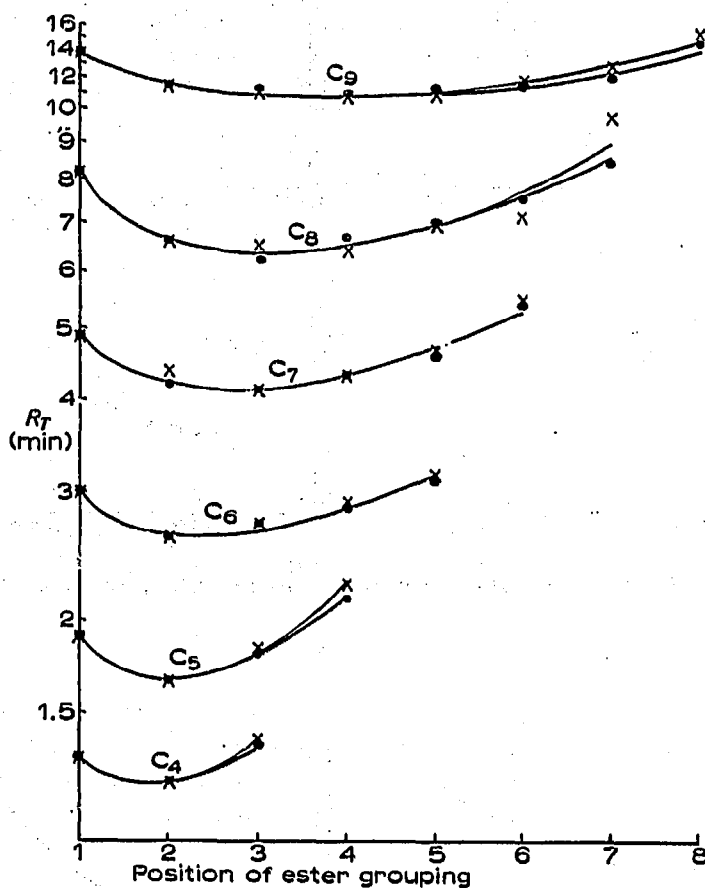


Fig. 3. Plots of boiling point *versus* position of the ester grouping (as number of C atoms in the alcohol portion of the ester), superimposed upon similar retention time plots. (x) retention times; (●) superimposed boiling points.

Application

There are two methods of application:

(i) if the retention times and precise boiling points of two esters in a group are known, a plot corresponding to those shown in Fig. 1 can be made. Thus knowledge of the boiling points of other members will enable direct reading off of the retention times.

(ii) with this method, knowledge of all the boiling points is not required but enough must be known to construct the curve for boiling points analogous to that shown in Fig. 2. Two retention times must also be known to enable the construction of the remainder of the retention time curve by geometric superimposition of the boiling point curve. From this construction retention times may be read directly for any member of the group.

The two methods depend upon precise measurement of retention times and an accurate knowledge of boiling points. In some cases where the boiling points are very close the retention times of a number of compounds may be indistinguishable.

Conclusions

Gas chromatographic examination of normal aliphatic ester isomers has revealed two relationships useful in the prediction of retention times. It is believed that these relationships can be extended not only to other similar series of esters but to any series of compounds which maintains a basic structure about which or within which a group of constant size is shifted in a regular fashion.

Food Preservation Research Laboratory,
Department of Agriculture and Stock,
Brisbane, Q^{ld.} (Australia)

D. W. CONNELL

¹ G. J. PIEROTTI, C. H. DEAL, E. L. DERR AND P. E. PORTER, *J. Am. Chem. Soc.*, 78 (1956) 2989.

² A. J. HAAGEN-SMITH, J. G. KIRCHNER, A. N. PRATER AND C. L. DEASY, *J. Am. Chem. Soc.*, 67 (1946) 1646.

³ P. ISSENBERG AND E. L. WICK, *J. Agr. Food Chem.*, 11 (1963) 2.

Received August 19th, 1963

J. Chromatog., 14 (1964) 104-107

R_F values of some catecholamines, precursors and metabolites

In an effort to find a two-dimensional paper chromatographic system suitable for the radioautography of catecholamine metabolites of tyrosine and related compounds, the R_F (s) of various commercially obtained standards were determined in a number of solvent systems. All experiments were done with Whatman No. 1 paper and with diazotized sulfanilic acid and/or ninhydrin as the detecting reagents. Descending chromatography was used except where otherwise specified. The data are tabulated in Tables I and II. The preferred bidimensional system was methanol-butanol-benzene-water (4:3:2:1), run with the grain of the paper in the long direction, followed by *n*-butanol saturated with 1 *N* hydrochloric acid, a combination which gave reasonable resolution and excellently formed spots.

Certain of these solvents were also tried in solvent reversals such as used by WEISS AND ROSSI¹. The results are given in Table III, along with the corresponding values

J. Chromatog., 14 (1964) 107-111