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CORRELATION OF STRUCTURAL PARAMETERS AND RETENTION DATA OF UNSATURATED FATTY ACID ESTERS

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The linear relationship between log retention time and chain length developed by James and Martin (1) has been shown to hold with many types of compounds. We have recently extended this approach to compounds having two structural parameters (2), the compounds originally investigated being the α-alkyl acrylate esters which can be represented by the formula $CH_2 = CR - COOR^1$. Their retention times can be represented by a set of contour lines with R and R^1 as the axes; alternatively a nomographic representation is equally satisfactory.

We have since examined the data of Ackman (3) (4) concerning the methyl esters of the methylene interrupted unsaturated fatty acids which require three parameters to describe their structure and have found that a good correlation may be obtained for the retention times of these compounds.

These data represent a four dimensional system in which the relative retention time is a function of the three structural parameters. While a three dimensional system may be represented graphically as a set of contour lines, a four dimensional system would require a family of surfaces if normal graphical techniques are used. For such a system a nomographic representation is of particular value since suitable classes of functional relationships may be represented in two dimensions.

In Figure 1 the data in Table 1 are represented as a function of R, R^1 and R^3 as defined below,

$$CH_3\ OOC\ \underbrace{(CH_2)_m\ CH}_{R^1} = \underbrace{CH\ -\ ....\ -\ CH}_{R^2} = \underbrace{CH\ -\ (CH_2)_n\ -\ CH_3}_{R^3}$$

where the total fatty acid carbon (R) = $R^1 + R^2 + R^3$

and the number of double bonds present (N) = $1 + \frac{R^2}{3}$

FIG. 1

Relation between relative retention time and structural parameters for methyl esters of methylene-interrupted unsaturated fatty acids.

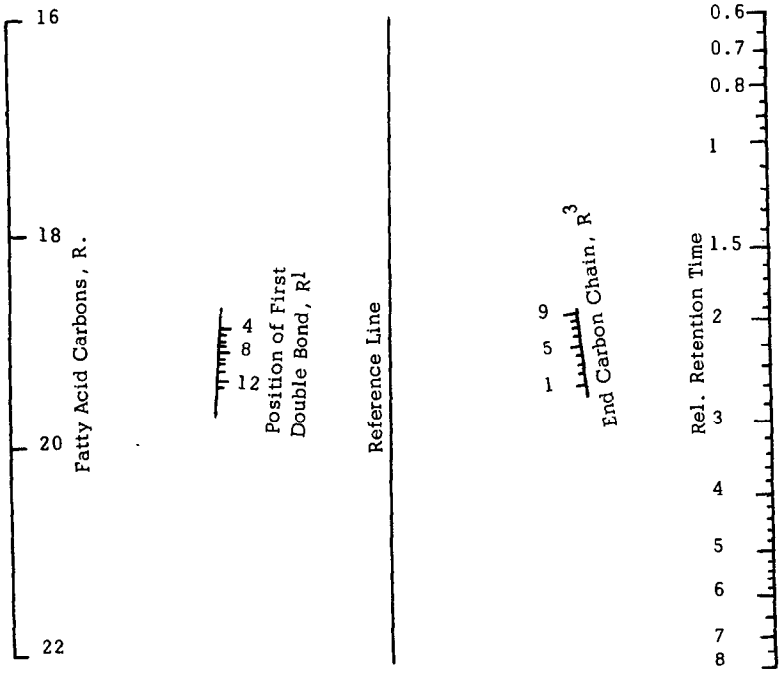

TABLE 1

FATTY ESTER STRUCTURE AND RETENTION DATA

	Fatty Acid (a)	End Carbon Chain (a)	Ret. Data (b)(c)	R^1	R^2	R^3	N
18:1	9	9	1.12	9	0	9	1
20:1	11	9	2.02	11	0	9	1
22:1	13	9	3.68	13	0	9	1
16:2	6, 9	7	0.740	6	3	7	2
18:2	8, 11	7	1.33	8	3	7	2
16:2	9, 12	4	0.810	9	3	4	2
18:2	11, 14	4	1.45	11	3	4	2
16:3	7, 10, 13	3	0.950	7	6	3	3
18:3	9, 12, 15	3	1.72	9	6	3	3
18:4	6, 9, 12, 15	3	1.97	6	9	3	4
20:4	8, 11, 14, 17	3	3.51	8	9	3	4
18:2	6, 9	9	1.29	6	3	9	2
20:2	8, 11	9	2.32	8	3	9	2
18:2	9, 12	6	1.34	9	3	6	2
20:2	11, 14	6	2.45	11	3	6	2
22:2	13, 16	6	4.38	13	3	6	2
18:3	6, 9, 12	6	1.54	6	6	6	3
20:3	8, 11, 14	6	2.76	8	6	6	3
20:4	5, 8, 11, 14	6	3.04	5	9	6	4
22:4	7, 10, 13, 16	6	5.50	7	9	6	4
20:5	5, 8, 11, 14, 17	3	3.85	5	12	3	5
22:5	7, 10, 13, 16, 19	3	7.00	7	12	3	5
16:1	7	9	0.625	7	0	9	1
16:1	9	7	0.634	9	0	7	1
16:2	7, 10	6	0.745	7	3	6	2
16:3	4, 7, 10	6	0.86	4	6	6	3
16:3	6, 9, 12	4	0.904	6	6	4	3
16:4	4, 7, 10, 13	3	1.08	4	9	3	4
16:4	6, 9, 12, 15	1	1.11	6	9	1	4
18:2	10, 13	5	1.37	10	3	5	2
22:5	4, 7, 10, 13, 16	6	6.09	4	12	6	5
22:6	4, 7, 10, 13, 16, 19	3	7.75	4	15	3	6

(a) Notation after Ackman (4)

(b) Data of Ackman (4)

(c) Relative to Stearic Acid

The data in Table 1 were taken from Ackmans later paper (4) and contain his data for the class concerned with the exception of two compounds of doubtful structure.

The nomograph in Figure 1 was drawn directly from these data using a procedure similar to that described by Winn (5). From this nomograph the retention times of the esters can be read with a probable error of about $\pm$ 1.5% which appears to be most satisfactory in view of the range of structures involved.

The nomograph vividly illustrates the validity of Ackman's hypotheses concerning the straight line plots of his data and in addition confirms his statement that a decrease in R^3 leads to increased retention time. In addition, the nomograph may permit the identification of an unknown from its relative retention time and limited structural information.

Our preliminary examination of compounds with two and three structural parameters suggests that nomographs should find considerable application as a means of correlating retention data with structural parameters.

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