

Notes

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Calculation of equivalent and modified equivalent chain length values for fatty esters

JAMIESON AND REID¹ have recently reported the possibility of determining equivalent chain length (*ECL*) and modified equivalent chain length (*MECL*) values for methylene-interrupted fatty esters as an aid in their tentative identification. The logarithmic form of a relationship developed by HAKEN^{2,3} for the calculation of relative retention data by the summation of separation factors was used. The relationship is shown by the equations

$$ECL_{(x+2, y+1)} = ECL_{(x, y)} + 2 + k_1 \quad (1)$$

$$MECL_{(x+2, y+1)} = MECL_{(x, y)} + 2 + k_1 \quad (2)$$

$$V_{R(x+2, y+1)} = V_{R(x, y)} \times V_{R(x+2, y)} \times V_{R(x, y+1)} \quad (3)$$

where

x = total carbon chain length,

y = number of methylene-interrupted double bonds,

$V_{R(x+2, y)}$ = Type IV separation factor⁴,

$V_{R(x, y+1)}$ = Type I separation factor⁵,

k_1 = difference in *ECL* or *MECL* values of pairs of esters used to calculate Type I separation factors.

The same workers have shown calculated *ECL* and *MECL* values for esters of the type $(x + 4, y + 2)$. The equations were not reported but the logarithmic form and that involving separation factors are shown:

$$ECL_{(x+4, y+2)} = ECL_{(x, y)} + 4 + 2k_1 \quad (4)$$

$$ECL_{(x+4, y+2)} = ECL_{(x+2, y+1)} + 2 + k_1 \quad (5)$$

$$V_{R(x+4, y+2)} = V_{R(x, y)} \times V_{R(x+2, y)} \times V_{R(x+2, y)} \times V_{R(x, y+1)} \times V_{R(x, y+1)} \quad (6)$$

$$V_{R(x+4, y+2)} = V_{R(x+2, y+1)} \times V_{R(x+2, y+1)} \times V_{R(x, y+1)} \quad (7)$$

While both of these relationships (eqns. 1 and 4) show an increase in chain length (x) and number of double bonds (y) one parameter only may be varied, *i.e.* either x or y . The summation of separation factors has been shown to be of more general application^{2,3} and the extension of the logarithmic form is shown here by conversion of the relationship for calculation of esters of the type $(x + 4, y + 1)$ ^{2,3}

$$V_{R(x+4, y+1)} = V_{R(x, y)} \times V_{R(x+2, y)} \times V_{R(x+2, y)} \times V_{R(x, y+1)} \quad (8)$$

$$ECL_{(x+4, y+1)} = ECL_{(x, y)} + 4 + k_1 \quad (9)$$

and of the type $(x+2, y+2)$

$$V_{R(x+2, y+2)} = V_{R(x, y)} \times V_{R(x+2, y)} \times V_{R(x, y+1)} \times V_{R(x, y+1)} \quad (10)$$

$$ECL_{(x+2, y+2)} = ECL_{(x, y)} + 2 + 2k_1 \quad (11)$$

Data

The retention data used are as previously reported² and have been converted to *ECL* values by the use of a calibration line.

Discussion and results

Tables I and II show relative retention and *ECL* values calculated for esters of the type $(x+2, y+1)$ and $(x+4, y+1)$, together with the differences between the calculated and observed values. The variations of *ECL* values are comparable with those shown by JAMIESON AND REID¹ and as expected there is little relative difference between calculations using either series of data. An ester which deviates from a systematic relationship is obvious irrespective of the method of data presentation.

The use of *MECL* values allows some refinement of the calculated values as plots of certain of the unsaturated homologous series nearly parallel the plot of the esters $x:1 \omega 9$. The improvements that are achieved have been shown¹ and are not repeated here.

From the equations developed it is apparent that calculations involving all of the separation factors are feasible; the relationships, however, depend on the concept of non-interacting substituents as described by CLAYTON⁶. While isolated double bonds and methylene-interrupted double bonds near the centre of the fatty chain

TABLE I

CALCULATION OF RETENTION DATA OF ESTERS OF THE TYPE $(x+2, y+1)$ FROM THAT OF ESTERS OF THE TYPE (x, y)

Ester (x, y)	<i>V_R</i> <i>ECL</i>		Ester $(x+2, y+1)$						
			<i>V_R</i>			<i>ECL</i>			
			<i>Det.</i>	<i>Calc.</i>	<i>Diff.</i>	<i>Det.</i>	<i>Calc.</i>	<i>Diff.</i>	
16:3 ω 3	0.95	17.84	18:4 ω 3	1.97	1.92	-0.05	20.28	20.25	-0.03
18:3 ω 3	1.72	19.82	20:4 ω 3	3.51	3.47	-0.04	22.36	22.23	-0.13
20:4 ω 3	3.51	22.36	22:5 ω 3	7.00	7.02	-0.02	24.46	24.71	+0.25
20:5 ω 3	3.85	22.50	22:6 ω 3	7.75	7.70	-0.05	24.77	24.81	+0.04
16:2 ω 6	0.745	17.02	18:3 ω 6	1.54	1.50	-0.04	19.45	19.43	-0.02
18:2 ω 6	1.34	18.97	20:3 ω 6	2.76	2.69	-0.07	21.41	21.38	-0.04
18:3 ω 6	1.54	19.45	20:4 ω 6	3.04	3.09	+0.05	21.76	21.86	+0.10
20:3 ω 6	2.76	21.41	22:4 ω 6	5.50	5.52	+0.02	23.68	23.82	+0.13
20:4 ω 6	3.04	21.74	22:5 ω 6	6.09	6.09	0	24.00	24.13	+0.13
16:1 ω 7	0.634	16.47	18:2 ω 7	1.33	1.29	-0.04	18.95	18.88	-0.07
16:1 ω 9	0.625	16.42	18:2 ω 9	1.29	1.26	-0.03	18.85	18.83	-0.02
18:1 ω 9	1.12	18.38	20:2 ω 9	2.32	2.25	-0.07	20.82	20.79	-0.03
18:2 ω 9	1.29	18.85	20:3 ω 9	2.52	2.57	+0.05	21.11	21.26	+0.15

TABLE II

CALCULATION OF RETENTION DATA OF ESTERS OF THE TYPE ($x + 4, y + 1$) FROM THAT OF ESTERS OF THE TYPE (x, y)

Ester (x, y)	V_R ECL		Ester ($x + 4, y + 1$)						
			V_R			ECL			
				Det.	Calc.	Diff.	Det.	Calc.	Diff.
16:3 ω 3	0.950	17.84	20:4 ω 3	3.51	3.41	-0.10	22.36	22.25	-0.11
16:4 ω 3	1.08	18.28	20:5 ω 3	3.85	3.89	+0.02	22.50	22.49	-0.01
18:3 ω 3	1.72	19.82	22:4 ω 3	6.40	6.31	-0.09	24.14	24.23	-0.09
18:4 ω 3	1.97	20.28	22:5 ω 3	7.00	7.09	+0.09	24.46	24.69	+0.23
16:2 ω 6	0.745	17.02	20:3 ω 6	2.76	2.69	-0.07	21.41	21.46	+0.05
16:3 ω 6	0.86	17.38	20:4 ω 6	3.04	3.10	+0.06	21.74	21.79	+0.05
18:2 ω 6	1.34	18.97	22:3 ω 6	5.00	4.85	-0.15	23.38	23.38	0.00
18:3 ω 6	1.54	19.45	22:4 ω 6	5.50	5.54	+0.04	23.68	23.86	+0.18
16:1 ω 9	0.625	16.42	20:2 ω 9	2.32	2.26	-0.06	20.84	20.83	-0.01
18:1 ω 9	1.12	18.38	22:2 ω 9	4.20	4.12	-0.08	22.83	22.71	-0.12

approximate this condition, it has been shown^{7,8} that near either chain extremity significant interactions occur. Thus while mathematical procedures are a valuable aid in the tentative identification of fatty esters, such procedures should be restricted to esters where retention behaviour has been independently reported. The limitations of simple systematic relationships based on a study of the retention behaviour of several complete homologous series of substituted saturated, monoenoic, dienoic and acetylenic esters have been previously reported⁹.

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