CHROM. 12,208

Note

Gas chromatographic separations of polyunsaturated fatty acid methyl esters on cyanoalkylpolysiloxane phases — a novel acetylenic–olefinic selectivity

G. R. JAMIESON, A. L. McMINN and ELIZ. H. REID

Chemistry Department, The Paisley College of Technology, Paisley PA1 2BE (Great Britain)
(Received June 27th, 1979)

For many years polyester-type stationary phases have been used for the gas–liquid chromatographic separation of unsaturated fatty acid methyl esters (FAME)[1,2] and tabulated retention data obtained on these phases have provided a rapid and convenient method for the tentative identification of these esters[3–5].

A disadvantage of polyester phases is their relatively poor thermal stability[6,7]. However, polar cyanoalkylpolysiloxanes, which are now readily available, have been found to have a greater thermal stability and to be suitable for FAME separations. Thus no significant variations in equivalent chain length (ECL) values were found over a period of 2 years with OV-225 and over 6 months with SILAR 5CP and SILAR 10C (ref. 8). It is claimed that any FAME separation obtained on polyester phases should be able to be carried out on the cyanoalkylpolysiloxane phases[9].

Although FAME with *cis*-unsaturation give similar separations on both polyester and the cyanoalkyl phases, the latter type of phase has been found[9–11] to give enhanced *cis–trans* selectivity, the *trans*-isomer being eluted earlier than the *cis*-isomer. In the present paper we wish to report an acetylenic–olefinic selectivity on these cyanoalkyl phases, the acetylenic FAME being eluted earlier than would be expected from data obtained on polyester phases.

The tentative identification of polyunsaturated FAME has been facilitated by the use of tables of ECL values[3,5]. These tables were generated from retention data obtained on polyester and modified polyester (*e.g.*, EGSS-X, EGSS-Y) phases and a preliminary investigation indicated that they were reasonably accurate for the cyanoalkyl phase, SILAR 5CP (ref. 12). However, it has also been reported[7] that, with cyanoalkyl phases, experimental ECL values were appreciably different from the table values in some cases and it was presumed from this that the method used to generate the tables did not make sufficient allowance for the individual selectivity of the stationary phases.

Some comparisons of experimental and table ECL values for C_{18}, C_{20} and C_{22} polyunsaturated FAME on cyanoalkylpolysiloxane phases are given in Table I. The data include values obtained in our laboratory and also some calculated from published retention data. The differences (experimental — table value) are similar to the differences found with polyester phases[3] and in our opinion the tables of ECL values can be used with retention data from both polyester and cyanoalkyl phases.

The approach to the problem of correlating retention data with polyester phase

TABLE I

COMPARISON OF ECL VALUES OF POLYUNSATURATED FAME ON CYANOALKYL POLYSILOXANE STATIONARY PHASES

Phase	No. of Results	Differences (expt. − tables) in ECL units					Ref.
		positive		negative		zero	
		No.	mean	No.	mean	No.	
OV-225	9	0	—	9	0.08	0	7, 8
SILAR 5CP	10	0	—	9	0.10	1	7, 8
SILAR 5CP	7	1	0.05	6	0.07	0	9
SILAR 5CP	5	2	0.09	3	0.03	0	2
SILAR 5CP	8	2	0.04	6	0.07	0	2
SILAR 5CP	12	4	0.05	8	0.07	0	2
SILAR 5CP	6	1	0.09	3	0.06	2	15
SILAR 7CP	12	8	0.09	4	0.05	0	2
SILAR 10C	7	3	0.11	4	0.19	0	9
SILAR 10C	3	2	0.10	0	—	1	15
SILAR 10C	6	2	0.10	4	0.10	0.	11
SP 2330	98	55	0.08	35	0.08	8	*
OV-275	37	24	0.08	12	0.08	1	*
	220	104	0.08	103	0.07	13	

* Present work.

TABLE II

COMPARISON OF ACETYLENIC FAME ECL VALUES ON CYANOALKYLPOLYSIL-OXANE STATIONARY PHASES

Column 1: 10% SP 2330 on Chromosorb W AW, 6 ft. × 1/8 in. (Supelco, Bellefonte, Pa., U.S.A.); column 2: 15% OV-275 on Chromosorb P AW DMCS, 10 ft. × 1/8 in. (Phase Separations, Queensferry, Great Britain).

ECL Value						
18:3 n − 3	18:3 6a,9,12			20:3 8a,11,14		
Expt.	Expt.	Calc.*	Δ	Expt.	Calc.*	Δ
Column 1						
20.33	21.81	22.13	+0.32	23.71	23.94	+0.23
20.48	22.06	22.36	+0.30	24.00	24.17	+0.17
20.76	22.42	22.79	+0.37	24.38	24.59	+0.21
20.91	22.62	23.02	+0.40	24.62	24.80	+0.21
21.12	22.81	23.34	+0.53	24.81	25.13	+0.32
		mean	+0.38			+0.23
Column 2						
20.08	21.36	21.75	+0.39	23.04	23.56	+0.52
20.26	21.58	22.03	+0.45	23.33	23.83	+0.50
20.40	21.76	22.24	+0.48	23.56	24.05	+0.49
21.08	22.66	23.28	+0.62	24.66	25.07	+0.41
21.24	22.90	23.53	+0.63	24.96	25.31	+0.35
21.51	23.29	23.94	+0.65	25.11	25.72	+0.61
		mean	+0.54			+0.48

* Reference 13.

polarity was also found to be successful for long-chain acetylenic methyl esters and computer-derived equations were obtained for three olefinic-acetylenic methyl esters[13]. When these equations were used with retention data obtained on cyanoalkyl phases it was found that there were significant differences between the experimental and calculated ECL values and that these differences were greater with a phase containing a higher percentage of cyanoalkyl groups (Table II).

It may be argued that these differences are due to a fault in our universal approach to correlation of liquid phase polarity and retention data since, in most cases, two structures with different methyl end-chains are being correlated, the standard of comparison being retention of 18:3 $n - 3$. It may be more meaningful if the retention data of 18:3 6a, 9, 12 were compared with that of 18:3, 6,9,12 (18:3 $n - 6$), since there is a close structural resemblance between these two compounds, the difference being the replacement of one of the olefinic groups by an acetylenic group. The linear relationship between $ECL_{18:3\ 6a,9,12}$ and $ECL_{18:3\ n-6}$ on polyester phases (with a single point for Apiezon L included) is shown in Fig. 1. The corresponding data obtained on cyanoalkyl phases do not fall on this line. The acetylenic compounds have shorter retention times on the cyanoalkyl phase than would be expected from their retention behaviour on polyester phases. Lie Ken Jie[14] published retention data on all the position isomers of methyl undecenoate and methyl undecynoate on various types of stationary phase and when the ECL values of the compounds with unsaturation in the 6-position (i.e. in the middle of the chain) are compared (Fig. 2) then it is found that methyl undecynoate has shorter retention
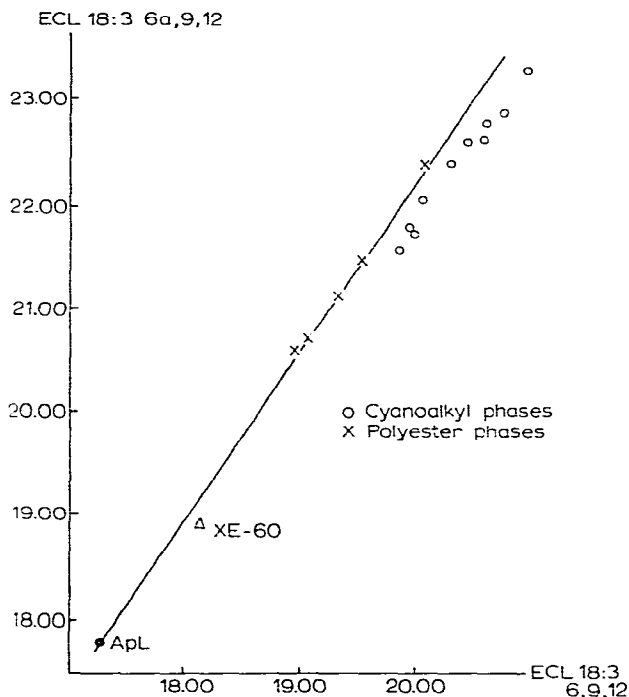

Fig. 1. Relationship between ECL values of 18:3 6, 9, 12 and 18:3 6a, 9, 12 on various stationary phases.
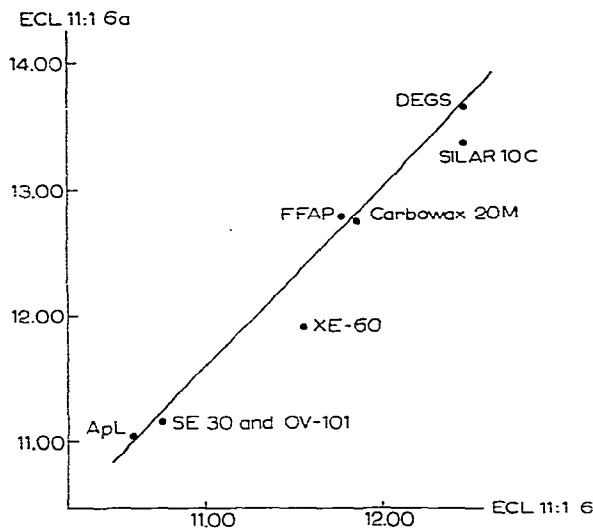
Fig. 2. Relationship between ECL values of methyl undec-6-enoate (11:1 6) and methyl undec-6-ynoate (11:1 6a) on various stationary phases.

times on the cyanoalkyl phases XE-60 and SILAR 10C than would be expected from its retention on the other phases.

REFERENCES

1 H. H. Hofstetter, N. Sen and R. T. Holman, *J. Amer. Oil. Chem. Soc.*, 42 (1965) 537.
2 R. G. Ackman, *Prog. Chem. Fats Other Lipids*, 12 (1972) 167.
3 G. R. Jamieson and E. H. Reid, *J. Chromatogr.*, 42 (1969) 304.
4 G. R. Jamieson, in F. D. Gunstone (Editor), *Topics In Lipid Chemistry*, Vol. 1, Logos Press, London, 1970, p. 167.
5 G. R. Jamieson, *J. Chromatogr. Sci.*, 13 (1975) 491.
6 O. W. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
7 R. V. Golovnya, V. P. Uralets and T. E. Kuzmenko, *Zh. Anal. Khim.*, 32 (1977) 340.
8 R. V. Golovnya, V. P. Uralets and T. E. Kuzmenko, *J. Chromatogr.*, 121 (1976) 118.
9 R. S. Henly, S. Ramachandran and S. L. MacKinley, *Gas-Chrom. Newsl.*, (Applied Science), 17 (1976) 1.
10 D. M. Ottenstein, D. A. Bartley and W. R. Supina, *J. Chromatogr.*, 119 (1976) 401.
11 H. Heckers, K. Dittmar, F. W. Melcher and H. O. Kalinowski, *J. Chromatogr.*, 135 (1977) 93.
12 R. G. Ackman (private communication) reported in G. R. Jamieson, *J. Chromatogr. Sci.*, 13 (1975) 493.
13 G. R. Jamieson and E. H. Reid, *J. Chromatogr.*, 128 (1976) 193.
14 M. S. F. Lie Ken Jie, *J. Chromatogr.*, 111 (1975) 189.
15 J. J. Myher, L. Marai and A. Kuksis, *Anal. Biochem.*, 62 (1974) 188.