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FATTY ACIDS

VII. THE GAS-LIQUID CHROMATOGRAPHIC PROPERTIES OF ALL DIMETHYLENE INTERRUPTED METHYL *cis,cis*-OCTADECADIENOATES

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SUMMARY

The gas-liquid chromatographic behaviour of all the dimethylene interrupted methyl *cis,cis*-octadecadienoates was studied on polar (Carbowax 20M, FFAP, DEGA, DEGS and Silar 10C*), semi-polar (XE-60) and non-polar (SE-30, OV-101 and Apiezon L) stationary phases. The equivalent chain length of each isomer is recorded: the possibility of separation and the retention pattern of these isomers are discussed.

INTRODUCTION

Only a few isomers of the dimethylene interrupted methyl *cis,cis*-octadecadienoates have been isolated from natural sources. Methyl *cis,cis*-5,9- and methyl *cis,cis*-11,15-octadecadienoates were present in trace amounts in seed oils²⁻⁵ and animal fats^{6,7}, respectively. Recently Murawski *et al.*⁸ isolated two of these isomers ($\Delta^{8c,12c}$ and $\Delta^{9c,13c}$) from human milk and these two compounds were also identified in partially hydrogenated seed oils⁹⁻¹¹. Of the twelve possible isomers only four ($\Delta^{6c,10c}$, $\Delta^{7c,11c}$, $\Delta^{8c,12c}$ and $\Delta^{11c,15c}$) were previously synthesised¹²⁻¹⁴.

Jamieson and Reid¹⁵ studied the chromatographic properties of the $\Delta^{5c,9c}$ isomer on EGSS-X stationary phase using newly packed and aged columns. Gunstone *et al.*¹² measured the equivalent chain length (ECL) values of $\Delta^{6c,10c}$ and $\Delta^{8c,12c}$ isomers on Apiezon L (APL), XE-60 and DEGS phases. In this paper, we report the ECL values of all the twelve dimethylene interrupted methyl *cis,cis*-octadecadienoates on five polar, one semi-polar and three non-polar stationary phases.

All the dimethylene interrupted methyl *cis,cis*-octadecadienoates were prepared by partial hydrogenation of the corresponding synthetic octadecadienoates¹⁶.

* Recently renamed¹ as Apolar 10C.

EXPERIMENTAL

Partial hydrogenation

A mixture of methyl octadecadiynoates¹⁶ (0.8 g), Lindlar catalyst (0.1 g), quinoline (0.2 g) and ethyl acetate (70 ml) was shaken in an atmosphere of hydrogen. The rate of hydrogen uptake decreased markedly after the theoretical amount (124 ml) was absorbed (10 min). The catalyst was filtered off and the filtrate washed successively with dilute hydrochloric acid and water. Gas-liquid chromatographic (GLC) analysis of the product showed 98–99% conversion into the *cis,cis* isomers.

The same procedure was applied to the preparation of $\Delta^{13c,17e}$ (0.28 g) isomer using isoquinoline (38 mg)¹⁷ in place of quinoline. Hydrogenation was stopped after 6% excess (49 ml) of the theoretical amount of hydrogen (46.6 ml) was absorbed. GLC analysis of the product indicated the presence of the *cis,cis*-diolefinic isomer (70%) and *cis*-monoolefinic ester (30%). Separation and purification of the esters were achieved using preparative silver ion thin-layer chromatography.

Oxidative cleavage of the methyl *cis,cis*-octadecadienoates gave the corresponding mono and/or dicarboxylic acid moieties only. Infrared analysis showed no absorption at 965 cm⁻¹ indicating the absence of *trans* isomer.

Gas-liquid chromatography

The GLC results were obtained under the conditions given in Table I, on a Pye 104 or Varian 940 gas chromatograph equipped with a flame ionisation detector.

TABLE I
CONDITIONS FOR GLC
Column length, 2 m.

Stationary phase	Temperature (°C)	Carrier gas (nitrogen) flow-rate (ml/min)	Internal diameter (mm)
5% APL	215	90	6.2
1.5% OV-101	185	50	3.1
3% SE-30	190	50	3.1
20% XE-60	195	90	6.2
10% Carbowax 20M	195	50	3.1
10% FFAP	200	50	3.1
10% DEGA	195	75	6.2
20% DEGS	170	50	3.1
10% Silar 10C	170	50	6.2

ECL values

ECL values were calculated from distances between the solvent front and the peak of the eluted components with saturated methyl esters (C₁₅, C₁₆, C₁₈, C₁₉ and C₂₀) as internal standards.

The ECL values of all the dimethylene interrupted methyl *cis,cis*-octadecadienoates are compared in Fig. 1 and the actual values are recorded in Tables II–X.

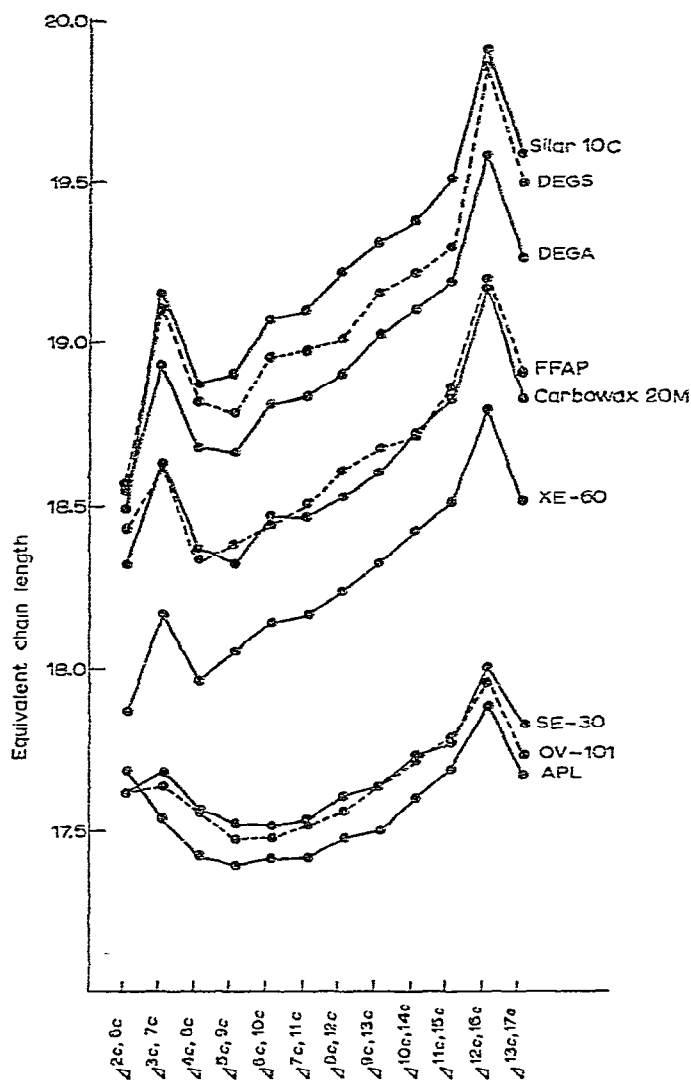


Fig. 1. Equivalent chain lengths of *cis,cis*-diolefinic C₁₈ methyl esters.

RESULTS

On the three non-polar stationary phases (APL, SE-30 and OV-101) the methyl *cis,cis*-octadecadienoates gave ECL values below 18.00 with the lowest values recorded on APL ranging from 17.39 to 17.88. SE-30 and OV-101 gave almost identical retention behaviour with ECL values ranging from 17.47 to 17.95 and 17.51 to 17.99, respectively. On these three non-polar phases, the $\Delta^{5c,9c}$, $\Delta^{6c,10c}$ and $\Delta^{7c,11c}$ isomers gave the lowest ECL values, while $\Delta^{12c,16c}$ exhibited the highest value. The $\Delta^{2c,6c}$ isomer had a higher ECL value on APL than $\Delta^{5c,7c}$ but not on OV-101 and SE-30.

TABLE II

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₅ METHYL ESTERS ON APL

Isomer	ECL	A1*	A2**	A3**	A4***	A5‡
$\Delta^{2c,6c}$	17.69	—	17.69	—	—	—
$\Delta^{3c,7c}$	17.54	—	—	17.54	—	—
$\Delta^{4c,8c}$	17.42	—	—	—	—	—
$\Delta^{5c,9c}$	17.39	—	—	17.39	17.41	—
$\Delta^{6c,10c}$	17.41	17.41	—	—	—	—
$\Delta^{7c,11c}$	17.41	—	—	—	—	17.43
$\Delta^{8c,12c}$	17.47	—	17.46	—	—	17.43
$\Delta^{9c,13c}$	17.49	—	—	—	17.46	—
$\Delta^{10c,14c}$	17.59	—	—	—	—	—
$\Delta^{11c,15c}$	17.68	17.67	—	—	—	—
$\Delta^{12c,16c}$	17.88	—	—	—	—	—
$\Delta^{13c,17c}$	17.66	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

‡ No separation.

TABLE III

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₅ METHYL ESTERS ON OV-101

Isomer	ECL	B1*	B2**	B3**	B4***	B5‡
$\Delta^{2c,6c}$	17.62	—	—	—	—	—
$\Delta^{3c,7c}$	17.64	—	—	—	—	—
$\Delta^{4c,8c}$	17.55	—	—	—	—	—
$\Delta^{5c,9c}$	17.47	17.47	—	—	—	—
$\Delta^{6c,10c}$	17.47	—	—	—	—	17.53
$\Delta^{7c,11c}$	17.51	—	—	17.51	—	—
$\Delta^{8c,12c}$	17.55	—	17.56	—	17.61	—
$\Delta^{9c,13c}$	17.63	—	—	—	—	17.53
$\Delta^{10c,14c}$	17.71	—	—	—	—	—
$\Delta^{11c,15c}$	17.78	—	—	17.77	17.76	—
$\Delta^{12c,16c}$	17.95	17.95	17.95	—	—	—
$\Delta^{13c,17c}$	17.72	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

‡ No separation.

On the semi-polar XE-60 phase, the ECL values were in the range 17.87 to 18.79 with $\Delta^{2c,6c}$ and $\Delta^{12c,16c}$ isomers exhibiting the lowest and highest values, respectively. There was a significant and gradual increase in the ECL value for each isomer as the double bonds "moved away" from the carboxyl group in the system; and in the cases of $\Delta^{3c,7c}$ and $\Delta^{12c,16c}$ isomers characteristically high ECL values were recorded.

On the polar phases, the isomers exhibited a similar retention ECL pattern

TABLE IV

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₈ METHYL ESTERS ON SE-30

Isomer	ECL	C1*	C2**	C3**	C4**	C5***
$\Delta^{2c,6c}$	17.62	—	—	—	—	—
$\Delta^{3c,7c}$	17.68	—	—	—	17.65	—
$\Delta^{4c,8c}$	17.56	—	—	17.55	—	—
$\Delta^{5c,9c}$	17.52	—	—	—	17.52	17.52
$\Delta^{6c,10c}$	17.51	—	—	—	—	—
$\Delta^{7c,11c}$	17.52	—	—	—	—	—
$\Delta^{8c,12c}$	17.60	17.60	—	—	—	—
$\Delta^{9c,13c}$	17.63	—	17.64	—	—	17.62
$\Delta^{10c,14c}$	17.72	—	—	—	—	—
$\Delta^{11c,15c}$	17.76	—	—	17.77	—	—
$\Delta^{12c,16c}$	17.99	17.99	18.00	—	—	—
$\Delta^{13c,17c}$	17.82	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

TABLE V

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₈ METHYL ESTERS ON XE-60

Isomer	ECL	D1*	D2**	D3***	D4 [†]
$\Delta^{2c,6c}$	17.87	17.89	—	—	—
$\Delta^{3c,7c}$	18.17	—	18.17	—	—
$\Delta^{4c,8c}$	17.96	—	17.97	—	—
$\Delta^{5c,9c}$	18.05	—	—	—	18.09
$\Delta^{6c,10c}$	18.14	—	—	—	18.09
$\Delta^{7c,11c}$	18.16	—	—	18.24	—
$\Delta^{8c,12c}$	18.23	18.23	—	—	—
$\Delta^{9c,13c}$	18.32	—	—	18.33	—
$\Delta^{10c,14c}$	18.42	—	—	—	—
$\Delta^{11c,15c}$	18.50	—	—	—	—
$\Delta^{12c,16c}$	18.79	—	—	—	—
$\Delta^{13c,17c}$	18.50	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

[†] No separation.

as on the XE-60, but with higher ECL values. The highest ECL values were obtained on Silar 10C phase ranging from 18.49 to 19.89. The DEGS phase was more polar than the DEGA phase and the ECL values ranged from 18.55 to 19.84 and from 18.56 to 19.57, respectively. Carbowax 20M and FFAP showed nearly identical retention behaviour with ECL values ranging from 18.32 to 19.16 and from 18.33 to 19.18, respectively.

No sign of decomposition of the $\Delta^{2c,6c}$ and $\Delta^{3c,7c}$ isomers on the polar phases

TABLE VI

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₃ METHYL ESTERS ON CARBOWAX 20M

Isomer	ECL	E1*	E2**	E3**	E4***	E5‡
$\Delta^{2c,6c}$	18.32	—	—	—	18.46	—
$\Delta^{3c,7c}$	18.63	—	—	—	18.63	—
$\Delta^{4c,8c}$	18.37	—	—	—	—	—
$\Delta^{5c,9c}$	18.32	—	18.35	—	—	18.42
$\Delta^{6c,10c}$	18.46	—	—	18.46	—	—
$\Delta^{7c,11c}$	18.46	18.46	—	—	—	—
$\Delta^{8c,12c}$	18.52	—	—	—	—	18.42
$\Delta^{9c,13c}$	18.59	—	—	—	—	—
$\Delta^{10c,14c}$	18.72	—	18.70	—	—	—
$\Delta^{11c,15c}$	18.82	—	—	18.81	—	—
$\Delta^{12c,16c}$	19.16	19.16	—	—	—	—
$\Delta^{13c,17c}$	18.82	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

‡ No separation.

TABLE VII

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₃ METHYL ESTERS ON FFAP

Isomer	ECL	F1*	F2**	F3***	F4‡
$\Delta^{2c,6c}$	18.43	—	18.43	—	—
$\Delta^{3c,7c}$	18.62	—	—	—	18.46
$\Delta^{4c,8c}$	18.33	—	—	—	—
$\Delta^{5c,9c}$	18.38	18.38	—	—	—
$\Delta^{6c,10c}$	18.44	—	—	—	18.46
$\Delta^{7c,11c}$	18.50	—	—	—	—
$\Delta^{8c,12c}$	18.60	—	—	18.60	—
$\Delta^{9c,13c}$	18.67	—	—	—	—
$\Delta^{10c,14c}$	18.71	—	—	—	—
$\Delta^{11c,15c}$	18.85	—	18.83	18.84	—
$\Delta^{12c,16c}$	19.18	19.19	—	—	—
$\Delta^{13c,17c}$	18.90	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

‡ No separation.

was observed as previously reported¹⁶ in the case of the corresponding diacetylenic esters.

Mixtures of these isomers were also examined (Tables II–X) and the results are summarised in Table XI. The degree of separation is described as base-line, twin peak and shoulder. On the non-polar stationary phases the efficiency of separation of the isomers on APL and OV-101 was almost identical, but better than on SE-30. Among the polar phases studied, Silar 10C and DEGA were superior in separating

TABLE VIII

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₈ METHYL ESTERS ON DEGA

Isomer	ECL	G1*	G2**	G3**	G4***	G5 [§]
$\Delta^{2c,6c}$	18.56	—	18.55	—	—	—
$\Delta^{3c,7c}$	18.93	—	—	18.94	—	—
$\Delta^{4c,8c}$	18.68	—	—	—	—	18.69
$\Delta^{5c,9c}$	18.66	18.66	—	18.65	—	—
$\Delta^{6c,10c}$	18.81	—	—	—	—	—
$\Delta^{7c,11c}$	18.83	—	—	—	18.83	18.69
$\Delta^{8c,12c}$	18.90	—	18.90	—	—	—
$\Delta^{9c,13c}$	19.01	—	—	—	18.95	—
$\Delta^{10c,14c}$	19.09	—	—	—	—	—
$\Delta^{11c,15c}$	19.18	19.18	—	—	—	—
$\Delta^{12c,16c}$	19.57	—	—	—	—	—
$\Delta^{13c,17c}$	19.25	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

§ No separation.

TABLE IX

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₅ METHYL ESTERS ON DEGS

Isomer	ECL	H1*	H2**	H3**	H4***	H5 [§]
$\Delta^{2c,6c}$	18.55	19.75	—	—	—	—
$\Delta^{3c,7c}$	19.10	—	—	—	—	18.92
$\Delta^{4c,8c}$	18.82	—	—	18.84	—	18.92
$\Delta^{5c,9c}$	18.78	—	18.78	—	—	—
$\Delta^{6c,10c}$	18.95	—	—	—	—	—
$\Delta^{7c,11c}$	18.97	—	—	—	18.98	—
$\Delta^{8c,12c}$	19.00	—	—	—	—	—
$\Delta^{9c,13c}$	19.14	—	—	—	—	—
$\Delta^{10c,14c}$	19.20	19.20	—	19.19	—	—
$\Delta^{11c,15c}$	19.28	—	19.28	—	19.28	—
$\Delta^{12c,16c}$	19.84	—	—	—	—	—
$\Delta^{13c,17c}$	19.49	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

§ No separation.

these isomers. As demonstrated by the examination of the mixtures of these isomers, the ECL values are highly reproducible on all stationary phases studied.

DISCUSSION

On the semi-polar and polar stationary phases the retention pattern (Fig. 1) of all the isomers studied shows a general increase in the ECL value from $\Delta^{2c,6c}$ to $\Delta^{13c,17c}$ with characteristic high retention values for the $\Delta^{3c,7c}$ and $\Delta^{12c,16c}$ isomers.

TABLE X

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF *cis,cis*-DIOLEFINIC C₁₈ METHYL ESTERS ON SILAR 10C

Isomer	ECL	I1*	I2*	I3**	I4***	I5 [§]
$\Delta^{2c,6c}$	18.49	—	—	—	—	—
$\Delta^{3c,7c}$	19.15	—	—	—	—	—
$\Delta^{4c,8c}$	18.87	—	18.86	—	—	—
$\Delta^{5c,9c}$	18.90	—	—	—	—	—
$\Delta^{6c,10c}$	19.06	19.06	—	—	—	—
$\Delta^{7c,11c}$	19.09	—	—	19.08	19.10	19.18
$\Delta^{8c,12c}$	19.21	—	—	—	—	19.18
$\Delta^{9c,13c}$	19.30	—	19.30	—	19.23	—
$\Delta^{10c,14c}$	19.36	—	—	19.37	—	—
$\Delta^{11c,15c}$	19.50	19.50	—	—	—	—
$\Delta^{12c,16c}$	19.89	—	—	—	—	—
$\Delta^{13c,17c}$	19.57	—	—	—	—	—

* Baseline separation.

** Twin peak separation.

*** Shoulder separation.

§ No separation.

TABLE XI

SEPARATION OF MIXTURES OF METHYL *cis,cis*-OCTADECADIENOATES

Stationary phase	Degree of separation (difference in ECL)			
	Baseline separation	Twin peak separation	Shoulder separation	No separation
APL	0.27 (A1)	≥0.15 (A2-3)	0.10 (A4)	0.06 (A5)
OV-101	0.48 (B1)	≥0.27 (B2-3)	0.23 (B4)	0.16 (B5)
SE-30	0.39 (C1)	≥0.16 (C2-4)	0.11 (C5)	—
XE-60	0.36 (D1)	0.21 (D2)	0.16 (D3)	0.09 (D4)
Carbowax 20M	0.70 (E1)	≥0.36 (E2-3)	0.31 (E4)	0.20 (E5)
FFAP	0.80 (F1)	0.42 (F2)	0.25 (F3)	0.18 (F4)
DEGA	0.52 (G1)	≥0.27 (G2-3)	0.18 (G4)	0.15 (G5)
DEGS	0.65 (H1)	≥0.38 (H2-3)	0.31 (H4)	0.28 (H5)
Silar 10C	≥0.43 (I1-2)	0.25 (I3)	0.19 (I4)	0.12 (I5)

On the non-polar stationary phases, $\Delta^{2c,6c}$ gave almost identical ECL values as $\Delta^{3c,7c}$ except on APL phase where $\Delta^{2c,6c}$ exhibited a significantly higher value. A similar ECL pattern was reported on the methylene interrupted methyl *cis,cis*-octadecadienoates¹⁸, methyl *cis*-octadecenoates¹⁹ and methyl *cis*-undecenoates^{20,21} series.

Haken and co-workers²²⁻²⁵ studied the retention behaviour of series of aliphatic saturated and branched chain esters on various stationary phases and attributed the influence of the polarity of the stationary phase on the retention increment of the homologous series of aliphatic esters to the boiling point, polarisability, steric effect and the molecular shape of the esters; they also pointed out the change in retention index of the unsaturated ester especially where conjugation occurred²⁶.

We believe that the polarisability and the degree of exposure of the unsaturated

centres of the fatty esters studied to the polar functional groups of the semi-polar and polar stationary phases are the two major operating factors to influence the retention time. On the non-polar stationary phases the boiling point of the compound may be a dominating factor in addition to minor contributions from the two other aforementioned factors.

On the semi-polar and polar phases (except FFAP) the $\Delta^{2c,6c}$ isomer furnished the lowest ECL value of the series. This low ECL value of the $\Delta^{2c,6c}$ isomer is probably due to the delocalisation of the π -electrons of the C_2 - C_3 double bond, as this unsaturated centre is in a conjugative position to the $-\text{COOMe}$ group, thus "reducing" the number of polar centres in the molecule. On the non-polar stationary phases, the conjugation effect may increase the boiling point instead, resulting in $\Delta^{2c,6c}$ to show a higher ECL value than expected.

The ECL values of the $\Delta^{3c,7c}$ isomer are significantly higher than $\Delta^{4c,8c}$ on all stationary phases studied. This characteristic behaviour is apparent in all instances where the unsaturated centre is located at the Δ^3 position. It can, therefore, be assumed that the increase in ECL value of the $\Delta^{3c,7c}$ isomer is most likely due to the acidic nature of the methylene group situated between the $-\text{COOCH}_3$ group and the unsaturated centre at C_3 - C_4 . This active methylene seems to add to the polarity of the molecule.

In the remaining isomers, the unsaturated centres move gradually away from the $-\text{COOCH}_3$ end and the ECL values increase steadily, presumably due to a better degree of exposure of the unsaturated centres to the polar groups of the polar stationary phase. On the non-polar phases the increase is less significant as the unsaturated centres move towards the ω -end of the chain. In these instances it is probable that the slight increase in the ECL values is due to the difference in boiling point of the isomers.

On all phases the $\Delta^{12c,16c}$ isomer gave the highest ECL values. This characteristic behaviour of all $\Delta^{\omega-1}$ isomers is most likely due to the strong positive inductive effect exercised by the terminal methyl group on the double bond, which becomes more readily polarisable and allows thereby a stronger interaction with the stationary phase.

The $\Delta^{13c,17c}$ isomer exhibits a high ECL value mainly due to its unhindered exposure of the double bond at the end of the chain.

Further work is necessary to correlate the molecular shapes of the stationary phase and that of the compound being chromatographed; also, the energies involved during the partition process should be taken into account in order to obtain a clearer picture of the retention behaviour.

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