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FATTY ACIDS

III*. FURTHER STUDY OF THE GAS–LIQUID CHROMATOGRAPHIC PROPERTIES OF ALL OF THE METHYL UNDECYNOATES AND METHYL *cis*-UNDECENOATES

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SUMMARY

The gas–liquid chromatographic properties of both series of C_{11} unsaturated fatty esters were further studied on non-polar (OV-101 and SE-30), semi-polar (XE-60) and polar (FFAP and Carbowax 20M) stationary phases. The equivalent chain length of each isomer is recorded and the efficiency of the stationary phases in separating these isomers is discussed.

INTRODUCTION

The gas–liquid chromatographic (GLC) behaviour of the methyl undecynoates and *cis*-undecenoates were studied earlier[1] on Apiezon L (APL), diethylene glycol succinate polyester (DEGS) and Silar 10C** stationary phases. The properties of the more recently developed polysiloxane stationary phases were discussed and the retention behaviour of homologous compounds on these phases was reported by Haken[2,3]. Gunstone and co-workers[4,5] studied the properties of the entire series of *cis*- and *trans*-methyl octadecenoates on APL, DEGS and XE-60. With the increasing importance and availability of polysiloxane stationary phases, the C_{11} unsaturated fatty esters were chromatographed on OV-101 (liquid methyl silicone), SE-30 (methyl silicone gum rubber), XE-60 (nitrile silicone gum) and also on two other polar stationary phases (FFAP and Carbowax 20M).

GAS–LIQUID CHROMATOGRAPHY

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

* Part II: *J. Chromatogr.*, 109 (1975) 81.
** Recently re-named[6] as APOLAR 10C.

TABLE I

CONDITIONS FOR GLC

Column length, 2 m.

Stationary phase	*Temperature (°C)*	*Carrier gas (nitrogen) flow-rate (ml/min)*	*Internal diameter (mm)*
1.5% OV-101	150	45	3.1
10% FFAP	160	45	3.1
20% XE-60	190	80	6.3
3% SE-30	130	60	6.3
10% Carbowax 20M	155	60	3.1

The equivalent chain length (ECL) values were calculated from distances between the solvent front and the peak of the other eluted components. Saturated methyl esters were used as internal standards: C_{10} and C_{12}, (and C_{10} only in some instances on XE-60) for both series of esters.

The ECLs of all acetylenic and *cis*-ethylenic C_{11} esters on OV-101, SE-30, XE-60, FFAP and Carbowax 20M are compared in Figs. 1 and 2 and actual values are recorded in Tables II–VI.

Methyl undecynoates

The behaviours of these isomers on the non-polar OV-101 and SE-30 phases were almost identical and ECL values ranged from 11.16 to 11.62 and from 11.15

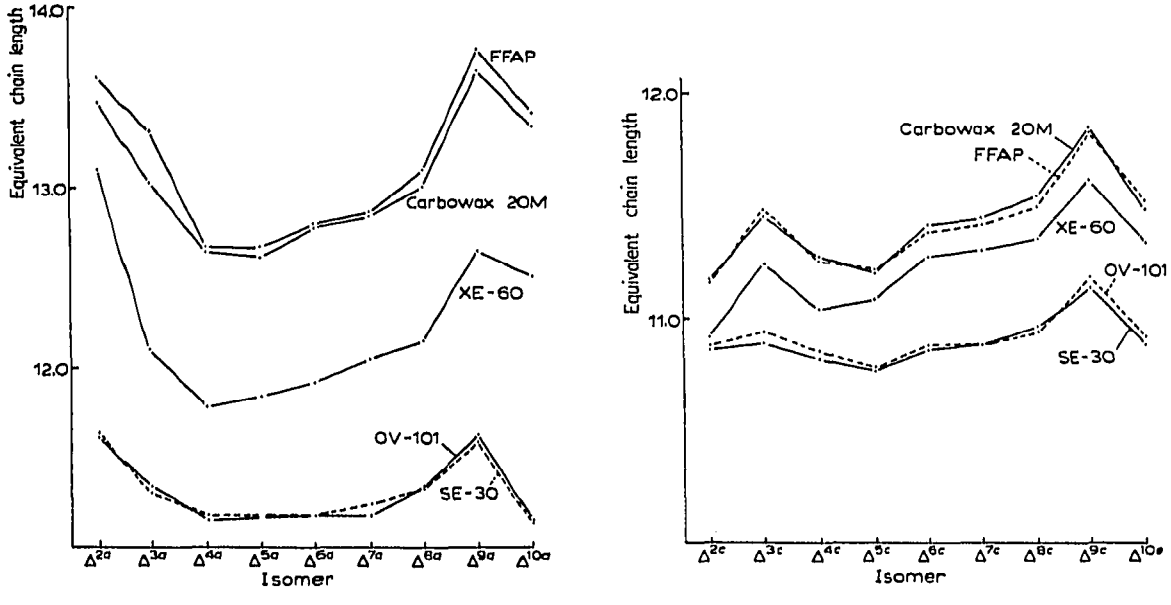

Fig. 1. Equivalent chain lengths of acetylenic C_{11} esters on different stationary phases.

Fig. 2. Equivalent chain lengths of *cis*-ethylenic C_{11} esters on different stationary phases.

TABLE II

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF UNSATURATED C_{11} METHYL ESTERS ON OV-101

Isomer	*ECL*	*A1**	*A2***	*A3***	*A4***	*A5§*	*Isomer*	*ECL*	*B1***	*B2***	*B3****	*B4§*	*B5§*
Δ^{2a}	11.62	—	—	11.63	—	—	Δ^{2c}	10.88	—	—	—	10.92	—
Δ^{3a}	11.34	—	—	11.34	—	—	Δ^{3c}	10.94	—	—	—	10.92	10.90
Δ^{4a}	11.16	—	—	—	—	—	Δ^{4c}	10.85	—	—	—	—	—
Δ^{5a}	11.17	—	—	—	—	—	Δ^{5c}	10.78	—	—	—	—	—
Δ^{6a}	11.18	—	—	—	—	—	Δ^{6c}	10.88	—	10.86	—	—	10.90
Δ^{7a}	11.18	—	—	—	—	11.30	Δ^{7c}	10.87	—	—	—	—	—
Δ^{8a}	11.34	—	11.35	—	11.35	11.30	Δ^{8c}	10.94	—	—	11.01	—	—
Δ^{9a}	11.63	11.65	11.63	—	—	—	Δ^{9c}	11.18	11.17	11.15	11.12	—	—
Δ^{10a}	11.16	11.16	—	—	11.15	—	Δ^{10c}	10.92	10.95	—	—	—	—

* Baseline separation.
** Twin peak separation.
*** Shoulder separation.
§ No separation.

TABLE III

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF UNSATURATED C_{11} METHYL ESTERS ON SE-30

Isomer	*ECL*	*C1**	*C2***	*C3***	*C4****	*C5§*	*C6§*	*Isomer*	*ECL*	*D1***	*D2***	*D3****	*D4§*	*D5§*
Δ^{2a}	11.63	—	—	11.60	—	—	—	Δ^{2c}	10.86	—	—	—	10.90	10.89
Δ^{3a}	11.31	—	—	11.31	11.31	—	—	Δ^{3c}	10.89	—	—	—	10.90	—
Δ^{4a}	11.18	—	11.12	—	11.18	—	—	Δ^{4c}	10.82	—	—	10.80	—	—
Δ^{5a}	11.18	—	—	—	—	11.15	—	Δ^{5c}	10.77	—	—	—	—	—
Δ^{6a}	11.18	11.15	—	—	—	—	—	Δ^{6c}	10.86	—	10.85	—	—	—
Δ^{7a}	11.24	—	—	—	—	—	11.28	Δ^{7c}	10.88	—	—	—	—	10.89
Δ^{8a}	11.33	—	11.32	—	—	—	11.28	Δ^{8c}	10.96	—	—	10.93	—	—
Δ^{9a}	11.59	11.59	—	—	—	—	—	Δ^{9c}	11.13	11.11	11.12	—	—	—
Δ^{10a}	11.15	—	—	—	—	11.15	—	Δ^{10c}	10.88	10.89	—	—	—	—

* Baseline separation.
** Twin peak separation.
*** Shoulder separation.
§ No separation.

TABLE IV

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF UNSATURATED C_{11} METHYL ESTERS ON XE-60

Isomer	*ECL*	*E1**	*E2**	*E3***	*E4***	*E5****	*E6****	*Isomer*	*ECL*	*F1***	*F2***	*F3***	*F4***	*F5§*
Δ^{2a}	13.10	—	13.10	—	—	—	—	Δ^{2c}	10.92	10.92	10.90	—	—	—
Δ^{3a}	12.10	—	12.09	12.09	—	—	12.06	Δ^{3c}	11.24	11.25	—	—	—	11.28
Δ^{4a}	11.78	—	—	11.78	11.78	—	—	Δ^{4c}	11.06	—	—	—	—	—
Δ^{5a}	11.84	—	—	—	—	—	—	Δ^{5c}	11.08	—	—	—	11.08	—
Δ^{6a}	11.92	—	—	—	11.86	—	11.89	Δ^{6c}	11.27	—	—	—	—	—
Δ^{7a}	12.05	12.04	—	—	—	—	—	Δ^{7c}	11.30	—	11.27	—	—	—
Δ^{8a}	12.15	—	—	—	12.11	—	—	Δ^{8c}	11.35	—	—	—	11.33	—
Δ^{9a}	12.65	—	—	—	—	12.62	—	Δ^{9c}	11.61	—	—	11.60	—	—
Δ^{10a}	12.51	12.49	—	—	—	12.49	—	Δ^{10c}	11.33	—	—	11.34	—	11.28

* Baseline separation.
** Twin peak separation.
*** Shoulder separation.
§ No separation.

TABLE V

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF UNSATURATED C_{11} METHYL ESTERS ON FFAP

Isomer	*ECL*	*G1**	*G2**	*G3***	*G4***	*G5§*	*G6§*	*Isomer*	*ECL*	*H1**	*H2***	*H3****	*H4§*	*H5§*
Δ^{2a}	13.61	—	—	13.59	—	—	—	Δ^{2c}	11.16	—	—	—	11.20	—
Δ^{3a}	13.31	13.26	13.31	13.31	—	—	—	Δ^{3c}	11.48	—	—	11.45	—	11.43
Δ^{4a}	12.67	—	12.71	—	—	—	—	Δ^{4c}	11.25	—	—	11.25	—	—
Δ^{5a}	12.67	—	—	—	—	—	12.69	Δ^{5c}	11.21	—	—	—	11.20	—
Δ^{6a}	12.80	12.77	—	—	—	—	12.69	Δ^{6c}	11.38	11.43	—	—	—	11.43
Δ^{7a}	12.86	—	—	—	—	12.87	—	Δ^{7c}	11.41	—	—	—	—	—
Δ^{8a}	13.10	—	—	—	13.08	12.87	—	Δ^{8c}	11.49	—	11.51	—	—	—
Δ^{9a}	13.77	13.77	—	—	13.69	—	—	Δ^{9c}	11.82	11.80	11.82	—	—	—
Δ^{10a}	13.42	—	—	—	13.40	—	—	Δ^{10c}	11.52	—	—	—	—	—

* Baseline separation.
** Twin peak separation.
*** Shoulder separation.
§ No separation.

to 11.63, respectively. The Δ^{2a} and Δ^{9a} isomers exhibited the highest ECL values, while Δ^{4a}–Δ^{7a} isomers gave the lowest and nearly identical ECL values.

On the semi-polar XE-60 phase, the ECL values were in the range 11.78–13.10. Unlike its behaviour on polar phases such as DEGS, Silar-10C, FFAP and Carbowax 20M, the Δ^{2a} isomer gave the highest ECL value (13.10) instead of the Δ^{9a} isomer.

These isomers gave ECL values ranging from 12.67 to 13.77 on FFAP and from 12.62 to 13.65 on Carbowax 20M. On both polar phases the Δ^{9a} isomer had the highest ECL value, while the Δ^{4a} isomer had the lowest.

When the chromatographic behaviour of mixtures of these isomers was examined on non-polar, semi-polar and polar stationary phases (Tables II–VI), it was possible to describe the degree of separation as baseline, twin peak or shoulder. The results are summarized in Table VII. The efficiency of separation on OV-101 and SE-30 was slightly better than on APL. XE-60, FFAP and Carbowax 20M performed more efficiently in separating these isomers than on DEGS, but less than on Silar 10C.

TABLE VI

EQUIVALENT CHAIN LENGTHS OF INDIVIDUAL AND MIXTURES OF UNSATURATED C_{11} METHYL ESTERS ON CARBOWAX 20M

Isomer	*ECL*	*I1**	*I2**	*I3***	*I4§*	*I5§*	*Isomer*	*ECL*	*J1***	*J2***	*J3***	*J4§*	*J5§*	*J6§*
Δ^{2a}	13.47	—	13.49	—	—	—	Δ^{2c}	11.17	11.18	—	—	—	11.32	—
Δ^{3a}	13.03	—	13.04	—	—	—	Δ^{3c}	11.45	11.45	—	—	—	—	—
Δ^{4a}	12.64	—	12.65	—	12.69	—	Δ^{4c}	11.27	—	11.24	—	—	—	—
Δ^{5a}	12.62	12.63	—	—	—	—	Δ^{5c}	11.20	—	—	—	—	—	11.25
Δ^{6a}	12.78	—	—	—	12.69	12.75	Δ^{6c}	11.41	—	—	11.40	11.40	11.32	—
Δ^{7a}	12.84	—	—	—	—	12.75	Δ^{7c}	11.44	—	—	—	—	—	11.25
Δ^{8a}	13.01	13.01	—	13.01	—	—	Δ^{8c}	11.54	—	11.47	—	—	—	—
Δ^{9a}	13.65	—	—	13.65	—	—	Δ^{9c}	11.84	—	—	11.80	—	—	—
Δ^{10a}	13.34	—	—	13.35	—	—	Δ^{10c}	11.48	—	—	—	11.40	—	—

* Baseline separation.
** Twin peak separation.
§ No separation.

TABLE VII

SEPARATION OF MIXTURES OF METHYL UNDECYNOATES

Degree of separation	*Difference in ECL values**				
	OV-101	*SE-30*	*XE-60*	*FFAP*	*Carbowax 20M*
Baseline	0.47 (A1)	0.41 (C1)	⩾0.46 (E1–2)	⩾0.51 (G1–2)	⩾0.39 (I1–2)
Twin peak	⩾0.18 (A2–4)	⩾0.15 (C2–3)	⩾0.14 (E3–4)	⩾0.30 (G3–4)	⩾0.31 (I3)
Shoulder	—	⩾0.13 (C4)	0.08 (E5–6)	—	—
No separation	0.16 (A5)	⩽0.09 (C5–6)	—	⩽0.24 (G5–6)	⩽0.14 (I4–5)

* A1 etc. are sample numbers.

Methyl cis-undecenoates

With the exception of the Δ^{9c} isomer, all other ethylenic isomers gave ECL values below 11.00 on OV-101 and SE-30. The ECL values of these isomers were slightly higher (0.1–0.5 FCL*) on OV-101 than on SE-30 in most instances. There was little difference in the retention times among these isomers, although it is possible to recognize that the Δ^{5c} isomer had the lowest ECL value in the series on both non-polar phases.

On the semi-polar XE-60 phase, the ECL values of these isomers were all greater than 11.00, except for the Δ^{2c} isomer (10.92). The ECL values ranged from 11.16 to 11.84 on the polar FFAP and Carbowax 20M phases. In both polar and semi-polar phases, all three sets of ECL values gave almost parallel plots. Relatively high values were obtained for the Δ^{3c} and Δ^{9c} isomers.

TABLE VIII

SEPARATION OF MIXTURES OF METHYL *cis*-UNDECENOATES

Degree of separation	*Difference in ECL values**				
	OV-101	*SE-30*	*XE-60*	*FFAP*	*Carbowax 20M*
Baseline	—	—	—	0.44 (H1)	—
Twin peak	⩾0.26 (B1–2)	⩾0.25 (D1–2)	⩾0.27 (F1–4)	0.33 (H2)	⩾0.27 (J1–3)
Shoulder	⩾0.24 (B3)	0.14 (D3)	—	0.23 (H3)	—
No separation	0.06 (B4–5)	⩽0.03 (D4–5)	0.09 (F5)	⩽0.10 (H4–5)	⩽0.24 (J4–6)

* B1 etc. are sample numbers.

The behaviour of mixtures of these isomers on non-polar, semi-polar and polar stationary phases is shown in Table VIII. The separation efficiency of OV-101 and SE-30 is comparable to that of APL. In all three polar phases studied, the separation efficiency of each phase is better than that of DEGS, and comparable to that of Silar 10C.

CONCLUSION

FFAP, Carbowax 20M and XE-60 are more efficient than DEGS in this sepa-

* FCL = fractional chain length.

ration, while OV-101 and SE-30 are comparable to APL in the separation of isomeric unsaturated fatty esters. On all phases, the ECL was very reproducible, as demonstrated by the examination of mixtures of these isomers.

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