Gas Chromatographic Equivalent Chain Lengths of Isomeric Methyl Octadecenoates and Octadecynoates[1]

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Abstract

Equivalent chain lengths (ECL) have been determined for methyl *cis*-5-, 6-, 8-, 9-, 10-, 11-, 12-, 15-; *trans*-2-, 3-, 5-, 6-, 8-, 9-, 10-, 11-, 12-, 15-; and 17-octadecenoates and for methyl 5-, 6-, 8-, 9-, 10-, 11-, 12- and 15-octadecynoates on diethylene glycol succinate, polyphenyl ether and 100% β-cyanoethylmethylsiloxane capillary columns. Although the levels of ECL values differed, the patterns were similar for the different substrates. For methyl octadecenoates, except for 2-isomers, ECL generally increased with distance of double bond from the ester group but changed little from the 6 to the 10 position. Differences were smaller among isomeric *trans* esters than among *cis*. In methyl octadecynoates there was a greater and more regular increase of ECL occurred as the triple bond moved away from the ester group.

Introduction

In comparing retention values of fatty methyl esters in gas chromatography the use of equivalent chain length (ECL) proposed by Miwa et al. (1) and by Woodford and van Gent (2), under the name "carbon number," has been widely accepted. Although many data have been reported for various column substrates and different experimental conditions, with few exceptions those for methyl octadecenoates have been limited to the more common isomers. The only comprehensive study of which we are aware is that of Gunstone et al. (3). Except for this study by Gunstone and that by Hofstetter et al. (4), few data are available for methyl octadecynoates other than stearolates.

Some time ago at the Northern Laboratory we were given crude samples from the synthesis of octadecenoic acids with double bond position from 5 to 12 (5). From these samples *cis* and *trans* monoenoic methyl esters and the corresponding acetylenic methyl esters were separated and used, along with other isomers available here, for the chromatograms discussed in this paper. Almost all our data are for substrates different from those used by Gunstone et al. (3); our data correspond to theirs only in the values for *cis* esters on diethylene glycol succinate (DEGS).

Experimental Procedures

Methyl Esters

The crude mixtures of synthetic fatty acids were esterified with methanol and boron trifluoride catalyst. The esters were passed through a partially vulcanized rubber column with 88% acetone as solvent (6). Since acetylenic esters are eluted on this column at approximately the same time as linoleate would be, acetylenic, monoenoic and stearic fractions were isolated. The monoenoic esters were passed through a silver resin column (7) to separate *cis* and *trans* isomers. Ozonization (8) showed double bonds predominately in the expected positions, except for the 7-octadecenoates. They contained a large amount of the 9-isomer and ECL values for the 7-isomers are omitted.

Methyl *cis*-15-octadecenoate was isolated by silver resin chromatography (9). A portion was isomerized by a nitrous acid procedure modeled after that of Litchfield et al. (10), and the *trans* ester was isolated on the silver resin column.

Additional esters were obtained as concentrates and mixtures from other workers at this Laboratory.

Gas Chromatography

All chromatograms were run on 0.01-in. I.D. stainless steel capillary columns in a Barber Coleman Model 20 Chromatograph with a radium D argon ionization detector. Columns were coated by passing a solution of the coating material through the column under pressure and conditioning as described by Litchfield et al. (11).

Three different 200 ft DEGS columns were used, all coated with a 10% solution of DEGS and 0.3% Arquad 2HT-75 (12). These columns were operated at 165 C and 45 psi and had a flow rate of 2.05 ml/min. For stearate, retention times varied from 32 to 48 min, and values of 1900 to 3900 theoretical plates were calculated.

Two 200 ft cyanoethylsilicone columns were used, each coated with 13% General Electric experimental nitrile silicone 238-149-99 in acetone. These columns were operated at 200 C and 20 psi. They had an argon flow rate of 0.50 ml/min, and stearate was retained from 20 to 25 min. Values of 4500 to 7700 theoretical plates were calculated for stearate.

The polyphenyl ether column was 150 ft long and coated with a 10% solution of six-ring polyphenyl ether and 0.39% Arquad 2HT-75 in chloroform. The column was operated at 190 C and 40 psi. It had an argon flow rate of 2.66 ml/min, and stearate was retained about 45 min. A value of about 18,000 theoretical plates was calculated for stearate.

Saturated esters of shorter and longer retention times were run with each unsaturated ester, and ECL values were calculated from the retention distances measured from a petroleum ether peak as the starting point.

Results and Discussion

Our best values for the various methyl esters on the three kinds of capillary columns are summarized in Table I. Standard deviations computed from repeated runs under the same conditions are included in the table. Although several investigators have reported ECL values for the more common methyl octadecenoates, especially oleate and elaidate, few have been previously published for a series of isomeric esters; our results generally agree with them. With DEGS our values for *cis* esters are slightly lower than those of Gunstone et al. (3). Hofstetter et al. (4) gave values for *cis*-6-, 9- and 12-isomers

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TABLE I

ECL[a] of Isomeric Methyl Octadecenoates and Octadecynoates on DEGS, 100% Cyanoethyl Silicone and Polyphenyl Ether Capillary Columns

Isomer	DEGS[b]			Cyanoethyl silicone[c]			Polyphenyl ether[d]		
	c	t	a	c	t	a	c	t	a
2	....	19.50	....	....	19.84	....	....	19.68	....
3	....	18.69	....	....	....	....	....	18.30	....
5	18.28	18.29	19.85	18.30	18.11	19.58	17.93	18.08	18.88
6	18.38	18.33	19.94	18.40	18.17	19.60	17.99	18.10	18.96
8	18.38	18.30	19.93	18.44	18.19	19.74	17.98	18.10	18.99
9	18.39	18.33	19.98	18.44	18.20	19.78	18.01	18.10	19.03
10	18.44	18.34	20.03	18.44	18.22	19.86	18.02	18.14	19.09
11	18.49	18.36	20.10	18.51	18.22	19.91	18.08	18.16	19.14
12	18.54	18.41	20.20	18.60	18.27	20.02	18.13	18.19	19.19
15	18.80	18.60	20.65	18.76	18.37	....	18.30	18.26	19.42
17	18.83						18.32		....

[a] ECL, equivalent chain lengths; DEGS, diethylene glycol succinate; c, *cis*, t, *trans*, a, acetylenic.
[b] Standard deviation *cis,trans*, 0.019; Standard deviation acetylenic, 0.048.
[c] Standard deviation, 0.012.
[d] Standard deviation, 0.031.

slightly higher than either ours or Gunstone's; also, Hofstetter's values for *trans* isomers are higher than ours. These differences are apparently temperature effects. Our chromatograms were run at 165 C, Gunstone's at 190 C and Hofstetter's at 226 C. We have run chromatograms at 155 and 175 C on *cis*-9-, 12- and 15- and *trans*-9- and 12-octadecenoates and found an average increase of 0.0032 ECL units per degree. A comparison of our *cis* monoene and 17-monoene values with those of Gunstone, omitting the 15-monoene which has a greater difference, gives an increase of 0.0031 ECL units per degree; and a comparison of our *cis*-6-, 9- and 12-monoenes, *trans*-6-, 8-, 9-, 10-, 11-, and 12-monoenes and 17-monoene with Hofstetter's values gives 0.0032 ECL units per degree. There may also be differences between different columns. One of our DEGS columns replaced in the instrument after previously satisfactory use and another freshly prepared column gave ECL values about 0.12 lower than the level of our other columns. These low values are not included in our data presented here.

With the 100% cyanoethyl silicone column our values for oleate and elaidate agree with those of Litchfield et al. (13).

We know of no other ECL values published for polyphenyl ether columns. Kuemmel and Chapman (14) obtained excellent separations of *cis* monoenes, but they used temperature programming and did not obtain isothermal ECL values.

Although levels of ECL values differ, the patterns are similar for different substrates, and also similar to those found by Gunstone for other substrates (3). Consequently, we would expect that ECL values of *cis*-2- and 3- and both 16-monoenes not included here would follow a similar pattern to that found by Gunstone. For monoenoic esters, except for 2- and 3-isomers which have high values, ECL generally increased with distance of the double bond from the ester group but with less change from the 6- to 10-position. Differences are smaller among isomeric *trans* than *cis* monoenes, except that the *trans*-2-monoene is much higher. The difference in level for *cis* and *trans* monoenes varies with polarity of the substrate. On the more polar DEGS and cyanoethyl silicone, *cis* esters are eluted last, with the difference between *cis* and *trans* being greater on the cyanoethyl silicone. On polyphenyl ether, *trans* is eluted last, except for the 15-isomer.

With methyl octadecynoates there is a greater, more regular increase in ECL as the triple bond moves away from the ester group. The level of ECL values for DEGS and cyanoethyl silicone is reversed from the *cis*-octadecenoates, with ECL for DEGS being higher from positions 5 through 12. Our values for 6-, 7-, 8-, 9- and 11-octadecynoates on DEGS are lower than those of Hofstetter et al. (4); this difference may again be a temperature effect.

Our best separations have been obtained with the polyphenyl ether column. These results are partly caused by the physical characteristics of the column with a large number of theoretical plates and long retention times. The curves also exhibit less tailing than many others; our columns show slight reverse tailing, with the trailing edge of a peak steeper than the leading edge. However, caution must be used in quantitative interpretation of polyphenyl ether chromatograms. We have previously noted (15) that in mixtures of *cis*-9- and *cis*-12-octadecenoates with stearate, correction factors were necessary to correct area per cent to mole per cent. We have also found that a mixture containing equal amounts of oleate and elaidate, both by weight and by infrared analysis, gives 60 area % methyl elaidate on a polyphenyl ether column. Among saturated esters those of higher molecular weight give lower area per cent than on packed or capillary columns with other substrates.

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