Equivalent Chain Lengths of Methyl Octadecadienoates and Octadecatrienoates[1]

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ABSTRACT

Equivalent chain lengths (ECL) have been determined for a number of methyl octadecadienoates and octadecatrienoates with different stationary phases, including Apiezon L, polyphenyl ether, diethylene glycol succinate, XF 1150, 100% cyanoethyl silicone and tetracyanoethylated pentaerythritol. ECL values for unconjugated esters are slightly larger than calculated by adding the ECL increments over stearate found for octadecenoates with the same position and configuration of double bonds. In general, differences are greater for methylene-interrupted double bonds and for *trans* double bonds. They are greater for more polar columns. Average corrections can be added so that calculated ECL values agree well with the determined values. ECL increases with polarity of the stationary phase. The relative ECL pattern on different stationary phases changes little with position of double bonds in the isomers, but it is affected by double bond configuration. For esters with the same double bond positions isomers with *trans* double bonds tend to have lower ECL values than *cis* on polar stationary phases and higher ECL values on nonpolar. ECL's of conjugated octadecadienoates are always higher than unconjugated and increase in the order *cis,cis*; mono-*trans*; and *trans,trans*.

INTRODUCTION

Numerous values have been published for gas chromatographic equivalent chain lengths (ECL) (1) of methyl linoleate and linolenate, but values are few for less readily available methyl octadecadienoate and octadecatrienoate isomers. Hofstetter et al. (2) published values for several positional isomers; Christie (3), for all the methylene-interrupted *cis,cis*-octadecadienoates; and Gunstone and Jie (4), for a number of *cis,cis*- and *trans,trans*-octadecadienoates. Several sets of values have appeared for geometric and conjugated esters, mostly for isomers derived from linoleic and linolenic acids (5-9).

Obviously, ECL values will not be determined for all the 338 possible nonconjugated nonallenic octadecadienoates; however, a general understanding of the elution pattern of these compounds and the factors influencing their elution order is desirable. Methods have been proposed (10-12) for correlating and predicting retention characteristics in terms of separation factors or ECL's. These methods have been developed mainly for naturally occurring esters of different chain length and unsaturation but with *cis* double bonds separated by single methylene groups and composing families of esters with the same end carbon chain. They have not generally been applied to esters with *trans* or widely separated double bonds, such as those produced by partial hydrogenation of oils.

We have determined ECL values for a number of octadecadienoate methyl esters on capillary columns coated with several stationary phases. We point out the relation of these values to those for the octadecenoate series.

EXPERIMENTAL PROCEDURES

Most of the esters used were produced at our Laboratory in the course of other work. The *cis,cis*-5,12-; -6,10-; -6,11-; -6,12-; -7,12- and -8,11-methyl octadecadienoates were furnished by Dr. Gunstone. The 9,11 series was obtained by dehydration of ricinoleic and ricinelaidic acids (13). Methyl *trans*-10,*cis*-12-octadecadienoate was prepared by crystallization of esters from alkali-isomerized linoleic acid (14). The former was isomerized with iodine to give a mixture of the other 10,12 isomers assuming the double bond positions are not changed. The *cis*-12,*trans*-14- and *trans*-13,*cis*-15-octadecadienoates were in a mixture prepared by alkali isomerization of a 9,12- and 12,15-octadecadienoate mixture (15).

TABLE I

Columns Used for Determination of ECL[a] Values

Coating	Temperature, C	Pressure, psi	Length, ft
Apiezon L	200	45-55	200
PPE 6 ring	190	40	150
DEGS	165	45	200
GE XF1150	170	30	200
100% CN	200	20	200
TCPE	160	45	200

[a]Abbreviations: ECL, equivalent chain length; PPE, polyphenyl ether; DEGS, diethylene glycol succinate; 100% CN, 100% cyanoethyl silicone; TCPE, tetracyanoethylated pentaerythritol.

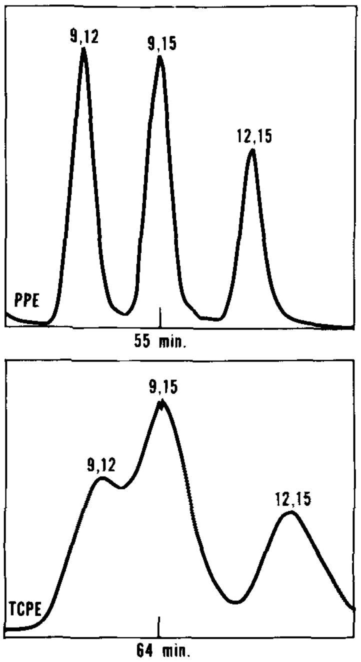

FIG. 1. Gas chromatograms of *cis,cis*-9,12-, -9,15- and -12,15-methyl octadecadienoates on polyphenyl ether and tetracyanoethylated pentaerythritol.

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TABLE II

ECL[a] of Methyl Octadecadienoates and Octadecatrienoates

Ester	ECL					
	Apiezon L	PPE	DEGS	XF1150	110% CN	TCPE
Cis-5,*cis*-12		18.04				
Cis-6,*cis*-10		18.06				
Cis-6,*cis*-11		18.01				
Cis-6,*cis*-12		18.10				
Cis-7,*cis*-12		18.05				
Cis-8,*cis*-12		18.15				
Cis-9,*cis*-12	17.50	18.19	19.06	19.08	19.16	19.49
Cis-9,*trans*-12	17.59	18.35		18.95	18.96	19.36
Trans-9,*cis*-12		18.43				19.42
Trans-9,*trans*-12	17.65	18.41	19.00	18.67	18.69	19.14
Cis-9,cis-15	17.66	18.32	19.24	19.22	19.29	19.59
Cis-9,*trans*-15	17.60	18.30	19.04	18.89		19.32
Trans-9,*cis*-15	17.75	18.45	19.18	19.05		19.46
Trans-9,*trans*-15	17.68	18.40	18.98	18.68		19.13
Cis-12,*cis*-15	17.83	18.46	19.45	19.41	19.48	19.82
Cis-12,*trans*-15		18.51	19.30			19.56
Trans-12,*cis*-15		18.61	19.38			19.68
Trans-12,*trans*-15	17.85	18.55	19.23			19.34
Cis-9,*cis*-12,*cis*-15		18.52	19.91	19.90	20.00	20.49
Cis-9,*trans*-12,*cis*-15		18.55		19.91	19.80	
Trans-9,*cis*-12,*trans*-15		18.79		19.50	19.52	20.15
Trans-9,*trans*-12,*trans*-15		18.83	19.75	19.14	19.12	19.91

[a] Abbreviations: see Table 1.

All chromatograms were run on a Barber-Coleman Model 20 instrument with a Radium D argon ionization detector and 0.01 in. ID stainless-steel capillary columns. The columns and experimental conditions are listed in Table I.

Apiezon L and diethylene glycol succinate have been used as gas chromatograph column coatings by many investigators to separate fatty acid esters. Polyphenyl ether was used by Kuemmel and Chapman (16) and gave good resolution for us with *cis* octadecenoates (17). The 100% cyanoethyl silicone is the General Electric experimental nitrile silicone 238-149-99 used by Litchfield et al. (6) and by us (17) for octadecenoates. General Electric XF1150 was suggested to us by D.I. Zeman as having been used by I. Forman and J. Stekla to separate *cis* and *trans* esters.

The technique was the same as used for octadecenoates (17) with each unsaturated ester compared with two saturated esters run at the same time in a mixture with it.

RESULTS

ECL values for unconjugated methyl octadecadienoates and octadecatrienoates are listed in Table II. The data show that generally all-*cis* esters with the double bond nearest the terminal methyl have the largest ECLs. On the less polar columns *cis*-containing esters tend to be eluted before the corresponding *trans* esters; on the more polar columns they are eluted last.

Ackman and Burgher (18) and Haken (11) have related retention times of esters in terms of separation factors:

$$t'_{R_1} = rt'_{R_2}$$

where r is the separation factor and $t_{R_1}' = rt_{R}2'$ are adjusted retention times of esters and

$$t'_{R(s+x+y)} = t'_{Rs} \times r_x \times r_y$$

where s denotes a saturated ester and x and y two noninteracting double bonds at positions x and y. Jamieson and Reid (12) have pointed out that if the equation involving separation factors is put in logarithmic form

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

where x refers to chain length and y to number of double bonds. In this equation k_I is equivalent to Miwa's ECL of functional groups for a double bond (19). Ackman (20) has used fractional chain lengths in a similar way to calculate ECLs of multiple branched fatty acids, and Gunstone and Jie (4) have applied the same calculation to methyl *cis,cis*- and *trans,trans*-octadecadienoates.

These correlations have been applied mainly to naturally occurring esters of varying chain length and unsaturation with double bonds separated by single methylene groups which can be grouped according to end-carbon chain length. It seems that if ECLs of the requisite monoenes were known, it should be possible to relate them to ECL's of derived polyunsaturates, and we have attempted to show such a relationship for the values reported in Table II.

Viewed another way, the process of converting a saturated ester to an unsaturated homolog may be considered as removing an ethylene group, $-CH_2CH_2-$, with an ECL value of 2 from the chain and replacing it by an ethene group, $-CH{=}CH-$, with a different ECL value. If the effects of the double bonds were isolated, this additive approach should enable ECLs for polyunsaturated esters to be obtained from those of the related monoenes.

As an example, we showed earlier (17) that on polyphenyl ether ECL of methyl *cis*-9-octadecenoate is 18.01 and methyl *cis*-12-octadecenoate is 18.13. The calculated ECL for methyl *cis*-9,*cis*-12-octadecadienoate would be 18.00 + 0.01 + 0.13 = 18.14. The experimental value is 18.19. Similar calculations (not reported) for all ECL values

TABLE III

ECL[a] of Methyl Octadecenoates

Ester	ECL		
	Apiezon L	XF1150	TCPE
Cis-9	17.66	18.42	18.54
Trans-9	17.73	18.25	18.39
Cis-12	17.76	18.57	18.72
Trans-12	17.79	18.40	18.52
Cis-15	17.96	18.79	18.96
Trans-15	17.88	18.49	18.65

[a] Abbreviations: see Table 1.

TABLE IV

Corrections to be Added in Calculating ECL[a] of Methyl Octadecadienoates and Range of Differences Between Measured and Calculated ECL Values

	Group A		Group B	
Coating	Correction	Range of measured ECL values minus calculated ECL values	Correction	Range of measured ECL values minus calculated ECL values
Apiezon L	0.15	-0.01, 0.03	0.07	-0.03, 0.04
PPE	0.14	-0.04, 0.06	0.02	-0.08, 0.04
DEGS	0.20	-0.04, 0.06	0.07	-0.02, 0.06
XF1150	0.08	-0.06, 0.05	0.01	-0.07, 0.08
100% CN	0.24	-0.02, 0.01	0.11	-0.02, 0.01
TCPE	0.23	-0.06, 0.08	0.13	-0.04, 0.10

[a]Abbreviations: see Table I.

in Table II showed that the effects of the double bonds are not completely independent and that actual ECL values are nearly always slightly greater than calculated. This difference between actual and calculated ECL values was also found by Gunstone and Jie (4) for *cis,cis* esters on Apiezon L. Our ECL values for methyl octadecenoates used in the calculations have been published for polyphenyl ether, diethylene glycol succinate and the 100% cyanoethyl silicone (17). For the other columns they are given in Table III. The differences between experimental and calculated values are so small that it is difficult to detect significant trends, but the differences seem to be greater for more polar columns; they seem to be greater for *trans*-containing esters than for all-*cis* and greater for single methylene-interrupted double bonds than for more isolated double bonds.

For determining average corrections to be added in calculating ECL of methyl octadecadienoates, we have placed esters containing single methylene-interrupted double bonds at least one of which is *trans* in one group (group A) and all others in another group (group B). This is an empirical arrangement; although more extensive data might suggest a different classification, no more elaborate grouping seems justified based on the data we now have. Average corrections for these groups are summarized in Table IV, as calculated from the data in Table II. The correction for methyl *cis*-9,*cis*-12-octadecadienoate with polyphenyl ether is 0.02; therefore the calculated ECL would be 18.00 + 0.01 + 0.13 + 0.02 = 18.16 instead of 18.14 shown above.

With our limited number of octadecatrienoate values results were best by adding approximately 1.5 times the appropriate dienoate correction.

Our values for conjugated methyl octadecadienoates are given in Table V. The *cis*-12,*trans*-14- and *trans*-13,*cis*-15-isomers could not be identified separately but were present in mixture from alkali isomerization of *cis*-12,*cis*-15- and *cis*-9,*cis*-12-octadecadienoic acids. Beerthuis et al. (21) showed that conjugated diene esters are eluted after unconjugated and gave retention data for several conjugated dienes. Body and Shorland (9) established that *cis,cis* conjugated diene is eluted between mono-*trans* and *trans, trans* isomers and gave ECL data for the 9,11 series. Several other retention values have been reported for conjugated esters; one of the most complete sets is that by Strocchi et al. (7). Our results confirm that conjugated esters are eluted after unconjugated and in the order mono-*trans*, *cis,cis* and *trans,trans*. Our data showing the *cis*-12,*trans*-14 and *trans*-13,*cis*-15 eluting before the 9,11 and 10,12 series on polar columns represent an exception to the rule that esters with double bonds near the methyl end of the chain are eluted later than those with double bonds nearer the middle of the chain.

TABLE V

ECL[a] of Conjugated Methyl Octadecadienoates

	ECL			
Ester	PPE	DEGS	XF1150	TCPE
Cis-9,*cis*-11	19.31	20.32		20.87
Cis-9,*trans*-11	19.04	20.10	20.10	20.60
Trans-9,*cis*-11			20.15	20.65
Trans-9,*trans*-11	19.60	20.70	20.59	21.19
Cis-10,*cis*-12	19.32			
Cis-10,*trans*-12	19.07			
Trans-10,*cis*-12	19.16	20.30	20.24	20.77
Trans-10,*trans*-12	19.61	20.72	20.57	21.16
Cis-12,*trans*-14	19.59	19.68		20.00
Trans-13,*cis*-15	19.70	19.82		20.16

[a]Abbreviations: see Table I.

From the retention data that both previous workers and we obtained, it appears there are two kinds of variations in retention among 18 carbon esters. First, there are those esters that have the same relative order regardless of the type of column coating. One example is the pattern for octadecenoates where the change of ECL with double bond position is similar for all columns. A second is the longer retention time of conjugated esters. Terry and Wheeler (22) have reported that conjugated esters distill at higher temperatures than unconjugated. Body and Shorland (9) confirm this report and indicate that there is some separation of individual conjugated esters on distillation. Likely, other variations of this kind may also be ascribed to differences in vapor pressure. Sometimes retention order reverses with change in column coating. It is generally known that on Apiezon—a nonpolar coating—more unsaturated esters come off first; on polar coatings they come off last. On less polar coatings *cis* esters come off before *trans*; on more polar coatings the order is reversed. Such variations in retention must seemingly be ascribed to interactions between ester and stationary phase.

We should also point out that the coating which gives greatest difference in ECL values does not necessarily always give the best separations. This aspect is illustrated in Fig. 1, which shows separations of *cis,cis*-9,12-, 9,15- and 12,15-methyl octadecadienoates on polyphenyl ether and tetracyanoethylated pentaerythritol. Although the differences in ECL's are either similar or greater for tetracyanoethylated pentaerythritol, the separations are much better with polyphenyl ether. For the 12,15-isomer, values of 4800 theoretical plates were calculated for tetracyanoethylated pentaerythritol and 18,000 for polyphenyl ether. In future research the possibility of increasing resolution is probably greater by attempting to improve column efficiency than by attempting to find stationary phases of greater selectivity.

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