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Research Article

Free Energy Contribution to Gas Chromatographic Separation of Petroselinate and Oleate Esters

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The ease of separation by gas chromatography between petroselinic and oleic acids depends on the alcohol moieties of their esters. The esters of higher molecular weight alcohols tend to be better separated on a 90%-biscyanopropyl-10%-cyanopropylphenyl polysiloxane capillary column (30 m × 0.25 mm i.d.). By analysis of free energies contribution from different parts of the molecules, it is tentatively concluded that the interaction between the double bond and the column stationary phase is interfered by the bulky alkyl group, and it is the major driving force for the separation of the two fatty acids.

1. Introduction

Petroselinic acid (18:1Δ6*cis*) is a major fatty acid in the seed oils of most of the members of the Apiaceae (Umbelliflerae), Araliaceae, Garryaceae species, Acer (Aceraceae), and Geraniaceae [1–4]. Petroselinic acid is an interesting oleochemical for food, cosmetics, and pharmaceutical industries [5]. Coriander seed oil, which contained about 70% petroselinic acid, showed a significant hypolipidomic effect on animals [6]. High petroselinic acid diets found to lower the n-6 long-chain fatty acids of the phospholipids [7]. Hence, petroselinic has become more and more important in industry and human health. In 1997, Santinelli and Damiani [8] pointed out that petroselinic acid was always accompanied by some oleic acid (18:1Δ9*cis*), and there was no single chromatographic technique suitable for their separation and quantitation. However, methods for its separation from oleic acid have gradually been improved. Lin et al. [9] and Liu and Hammon [10] reported the separation of these two positional isomers by reversed phase liquid chromatography. Kim et al. [11] were able to separate and quantitate petroselinic and oleic acids in coriander tissues as their methyl esters by gas chromatography (GC) on a 5%-phenyl-95%-methylpolysiloxane capillary column. In addition, Thies [12] reported the use of butyl esters for the separation of these two positional isomers at 220°C with a total run time of 13 min. Thies saw good resolution of the butyl esters under these conditions, but they were not baseline separated. On the other hand, with a highly polar column (100%-cyanopropyl polysiloxane) of 50 meters, the two isomers could almost be baseline separated as their isopropyl esters [13, 14]. These two isomers in coriander seed oil could also be separated and quantitated on a 30 m of 100%-cyanopropyl polysiloxane with two steps temperature program [15], but how well they were separated was not reported. Near-baseline separations of methyl petroselinate and oleate on 100%-cyanopropyl polysiloxane columns from two different manufacturers at 180°C were reported [16]. A recent report [17] showed that methyl petroselinate and oleate could be separated on ionic liquid stationary phase [1,9-di(3-vinyl-imidazolium) nonane bis-(trifluoromethyl) sulfonyl imidate] columns, with the lengths of 12 (the microbore capillary), 30, and 100 meters.

A detailed study on the effects of alcohol chain lengths and branched chain on the separations of petroselinic and oleic acid esters was reported by Isbell [18]. Analyses were conducted on a 30 m of 100%-cyanopropyl polysiloxane column. The authors found that 2-ethyl-1-hexyl esters were

promising derivatives for quantitative analysis of the oils containing the mixture of petroselinic and oleic acids. With the 2-ethyl-1-hexyl esters, the interaction of the polar carboxyl group with the stationary phase was sterically masked. Therefore, the main interaction would be that between the small polarity differences of the olefins and the polar stationary phase of the column, which caused the separation.

However, methyl esters of these two acids could also be separated on a 100 m of 100%-cyanopropyl polysiloxane capillary column [19].

In this study, oils containing petroselinic and oleic acids are transesterified with alcohols of different chain lengths. The gas chromatographic separations of these two positional isomers are discussed in term of their standard free energy of transfer from solution to gas ($\Delta^g_{s\ln}G^o$). Thus, a general knowledge of GC related to $\Delta^g_{s\ln}G^o$ is briefly reviewed.

In gas-liquid chromatography, the solute (at infinite dilution) partitioning between the stationary and the mobile phases is assumed to be at equilibrium or very close to equilibrium state. Thus, the change in $\Delta^g_{s\ln}G^o$ directly relates to its equilibrium constant (K). The $\Delta^g_{s\ln}G^o$, on the other hand, can be divided into $\Delta^g_{s\ln}G_f$ and $\delta^g_{s\ln}G$ [20] as described in the following:

$$\Delta^g_{s\ln}G^o = \Delta^g_{s\ln}G_f + z\delta^g_{s\ln}G, \tag{1}$$

where z is the number of carbon atoms. If $z = 0$, $\Delta^g_{s\ln}G_f = \Delta^g_{s\ln}G^o$, that is $\Delta^g_{s\ln}G_f$ is the free energy contributed from the hypothetical molecule of zero carbon atom or may be simply understood as the functional group. Differentiating (1) with respect to z, one obtains $\delta^g_{s\ln}G = \delta\Delta^g_{s\ln}G^o/\delta z$. Thus, $\delta^g_{s\ln}G$ is the change in $\Delta^g_{s\ln}G^o$ per carbon atom. In addition, equation (1) can be expanded as described below [21].

From basic thermodynamics,

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0, \\ \ln k &= -\frac{\Delta G^0}{RT} - \ln\beta, \end{aligned} \tag{2}$$

where ΔH^0 and ΔS^0 are the changes in standard enthalpy and entropy, respectively. T is the absolute temperature, k is the retention factor, β is column phase ratio, and R is the universal gas constant. Equation (3) is obtained by substitution of (2) into (1),

$$\ln k = -\frac{\Delta^g_{s\ln}H_f}{RT} + \frac{\Delta^g_{s\ln}S_f}{R} - \frac{z\delta^g_{s\ln}H}{RT} + \frac{z\delta^g_{s\ln}S}{R} - \ln\beta \tag{3}$$

or

$$\ln\frac{t_R - t_M}{t_M} = a + bz + \frac{c}{T} + z\frac{d}{T}, \tag{4}$$

where

$$\begin{aligned} a &= -\ln\beta + \frac{\Delta^g_{s\ln}S_f}{R}, \qquad b = \frac{\delta^g_{s\ln}S}{R}, \\ c &= -\frac{\Delta^g_{s\ln}H_f}{R}, \qquad d = -\frac{\delta^g_{s\ln}H}{R}. \end{aligned} \tag{5}$$

$\Delta^g_{s\ln}H_f$ and $\Delta^g_{s\ln}S_f$ are the changes in standard enthalpy and entropy of transfer from solution to gas of an hypothetical molecule of $z = 0$, respectively. $\delta^g_{s\ln}H$ and $\delta^g_{s\ln}S$ are the increments in standard enthalpy and entropy of transfer from solution to gas per carbon atom; t_R and t_M are retention times of the solute and unretained gas, respectively

At constant z, equation(4) is reduced to (6) or Vant' Hoff's equation.

$$\ln\frac{t_R - t_M}{t_M} = a'' + \frac{c''}{T}, \tag{6}$$

where

$$\begin{aligned} a'' &= a + bz, \\ c'' &= c + dz. \end{aligned} \tag{7}$$

It was reported that all the four numeric values of (4) (a, b, c, and d) remained unchanged when the column was broken or cut into different lengths [22]. They were still valid for predicting t_R of fatty acid methyl esters (FAMEs) with good accuracy. On the other hand, for columns of the same stationary phase but differing in the inside diameters, only the numeric value of a was changed while the other three remained unchanged [23]. The β value is approximately equal to column inside diameter/(4 × film thickness), while the other coefficients are thermodynamic parameters and depend on type of solute and solvent (stationary phase) pair.

For linear aliphatic solutes (RH and RX), having the same number of carbon atoms but differing in the X functional groups, the difference in the retention indices of R_z X and R_z H is called homomorphic factor [24]. When the solutes are fatty acid alkyl esters (FAAEs) of different alcohols, the general structure would be R_1COOR_y, where R_z = R_1COO- and X = R_y. In this study, the homomorphic factors of fatty esters of different alcohols are evaluated in term of thermodynamic parameters. Furthermore, the free energy of transfer from solution gas of the double bond ($\Delta^g_{s\ln}G_u$) is postulated, and the relative change in $\Delta^g_{s\ln}G_u$ is responsible for the separations of 18:1Δ6 and 18:1Δ9 esters of different alcohols.

2. Experimental

2.1. Materials. Coriander seeds were obtained from a plant grower (Bangkok, Thailand). Olive oil was from local supermarket in Bangkok (Thailand). Fatty acid methyl esters (C16–C20) and oleic acid methyl ester were obtained from Sigma-Aldrich Chem. Co. (St. Loius, MO). C1–C3 alcohols and solvents were reagent grade obtained from Lab Scan Co. (Bangkok, Thailand). Higher alcohols (C4–C8) were from Sigma-Aldrich Chem. Co. (St. Loius, MO).

2.2. Extraction of Coriander Seed Oil. One gram of coriander seed kernel was ground in a mortar. The paste was transferred to a 4 mL vial, and 1 mL of toluene was added. The mixture was intermittently vortexed for 1 min. The toluene layer was decanted into a new vial and transesterified as described in the next section.

2.3. Transesterification. Transesterification of FAMEs with other alcohols (C2–C8) was carried out via a microreactor as described by Kaewkool et al. [25]. A disposable syringe (3 mL) was plugged with a small piece of cotton wool. NaOH (0.5 g) was rapidly ground and packed into the disposable syringe.

Five hundred microliters of a standard mixture of FAMEs (C16–C20) in toluene, about 2 mg/mL each, were mixed with 0.5 mL of the desired alcohol (C2–C8). Transesterification was started by passing the mixture through the microreactor gravitationally. Elution rate was controlled manually by the plunger, such that the mixture was eluted out in 30–45 s. Another 1 mL of the toluene-alcohol (1 : 1 v/v) mixture was added to wash the microreactor. The wash time was about 20 s. The combined eluent was acidified with 0.1 mL glacial acetic acid and washed with 1 mL of water. The organic layer was separated and dried over anhydrous Na_2SO_4. Transesterification and soap formation were checked by a liquid chromatography-based method according to Kittiratanapiboon and Krisnangkura [26].

For coriander seed oil an equal amount of olive oil, was mixed in order to increase the oleate peak in the chromatogam. The oil was similarly transesterifed as described above. For secondary octanols, alkaline catalyst was not suitable due to its slow reaction rate and soap formation. Acid catalysis was performed according to Kalayasiri et al. [27].

2.4. Gas Chromatography (GC). Gas chromatographic analysis was carried out on a Shimadzu gas chromatograph model 2010 (Shimadzu Inc., Tokyo, Japan) and equipped with an FID, a split-splitless injector, a data processor (CBM 102), and a 90%-biscyanopropyl-10%-cyanopropylphenyl polysiloxane (Rtx-2330) capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; from Restek International, Bellefonte, PA). The chromatographic conditions were as follows: Nitrogen carrier gas flow, 1 mL/min; nitrogen makeup gas flow, 30 mL/min; detector/injector, 230°C; split ratio, about 50 : 1. Oven temperatures were set isothermally at 5°C intervals between 180°C and 200°C, for determination of the column coefficients (a, b, c, and d) and 180°C for the separation of petroselinic and oleic esters.

2.5. Determination of the Four Coefficients of (4) *for Fatty Acid Butyl Esters (FABEs).* FABEs, which are approximately half way between methyl and octyl esters, were chosen as the references. The four numeric coefficients for FABEs were determined as described by Krisnangkura et al. [21].

At constant absolute temperature (T), equation (4) is reduced to (8), the well-known Martin's equation

$$\ln \frac{t_R - t_M}{t_M} = a' + b'z, \tag{8}$$

where

$$a' = a + \frac{c}{T},$$
$$b' = b + \frac{d}{T} \tag{9}$$

Thus, plotting a' against $1/T$ would result in a straight line with a slope of c and an intercept of a. Plotting b' against $1/T$ would also result in a straight line with a slope of d and an intercept of b.

The mixture of FABEs (C16–C20) was chromatographed at 5°C intervals between 180°C and 200°C. The four column coefficients were solved by Microsoft Office Excel 2007.

2.6. Determination of the Four Coefficients of (4) *for Fatty Acid Esters of Other Alcohols.* The difference in retention indices of RX and RH (R = alkyl, X is functional group) is called homomorphic factor. According to (1), $\Delta^g_{s\ln}G_f$ is the free energy contributed from the characteristic functional group, X. $z\delta^g_{s\ln}G$ is the free energy contributed from the hydrocarbon chain of z carbon atoms. Thus, the difference in $\Delta^g_{s\ln}G^o$ between RX and RH would simply arise from the $\Delta^g_{s\ln}G_f$ of the two molecules, which have the same alkyl, R, group. Similarly, two fatty acid esters having the same z but differing in the alcohol moieties, the difference in $\Delta^g_{s\ln}G^o$ of the two fatty acid esters would be the difference in $\Delta^g_{s\ln}G_f$. When (1) is expanded to (4), the numeric values of b and d would remain unchanged. Only the a and c, derived from $\Delta^g_{s\ln}G_f$, are changed. Therefore, the numeric values b and d of FABEs are assigned for other fatty acid esters. The values of a and c were obtained by solving two simultaneous equations, at different temperatures. The numeric values of a and c for each fatty acid ester are averaged from 25 data (5 different temperature pairs and 5 fatty acids).

3. Results and Discussion

3.1. The Homomorphic Factor of Fatty Acid Esters. As pointed out in Section 2.6, the homomorphic factor is the difference in retention indices of RX and RH. According to (1), two FAAEs (R_1COOR_y) having the same R_1but differing in the alcohol moieties (R_y), $\Delta^g_{s\ln}G_f$ would be characteristic of the homomorphic factor. In this section, attempts are made to prove that FAAEs of different alcohols would differ in $\Delta^g_{s\ln}G_f$, while the $\delta^g_{s\ln}G$ values are unchanged.

3.1.1. The Numeric Values for FAAEs. The four numeric coefficients for FAAEs were determined as described in Section 2.6 and solved by Microsoft Office Excel 2007. The numeric values and the standard deviations (sd) of 95% confidence for a, b, c, and d are listed in Table 1. Although, only 4 significant numbers are shown in Table 1, it should be pointed out that the higher decimal number would give better agreement between the predicted and experimental values. Hence, unrounded values of the 4 coefficients were used in the calculations.

The average values of a and c for FAAEs and their sd are summarized in Table 1. The values of a are more negative as the carbon numbers of the alcohols are increased. The plot of a and carbon numbers of alcohols yield a straight line with the slope of −0.580 and intercept of −6.265. The r^2, sd of intercept, and slope are 0.941, 0.298, and 0.059, respectively. On the other hand, the values of c increase positively as the carbon numbers of the alcohols are increased. The plot of

Table 1: Numeric values of the coefficients of (4) for different alkyl esters. Numbers in the bracket are standard deviation.

FAAE	a	b	c	d
FAME	−7.169 (0.154)	−0.596 (0.003)	1007 (80.43)	401.3 (1.323)
FAEE	−7.459 (0.143)	−0.596 (0.003)	1175 (68.58)	401.3 (1.323)
FAPrE	−7.978 (0.115)	−0.596 (0.003)	1523 (54.78)	401.3 (1.323)
FABE	−8.392 (0.051)	−0.596 (0.003)	1825 (23.89)	401.3 (1.323)
FAPeE	−8.398 (0.103)	−0.596 (0.003)	1936 (49.86)	401.3 (1.323)
FAHxE	−10.02 (0.042)	−0.596 (0.003)	2837 (20.20)	401.3 (1.323)
FAHpE	−10.55 (0.019)	−0.596 (0.003)	3198 (9.014)	401.3 (1.323)
FAOE	−11.05 (0.052)	−0.596 (0.003)	3571 (24.69)	401.3 (1.323)
sd (intercept)	0.298	—	157.7	—
sd (slope)	0.059	—	31.22	—

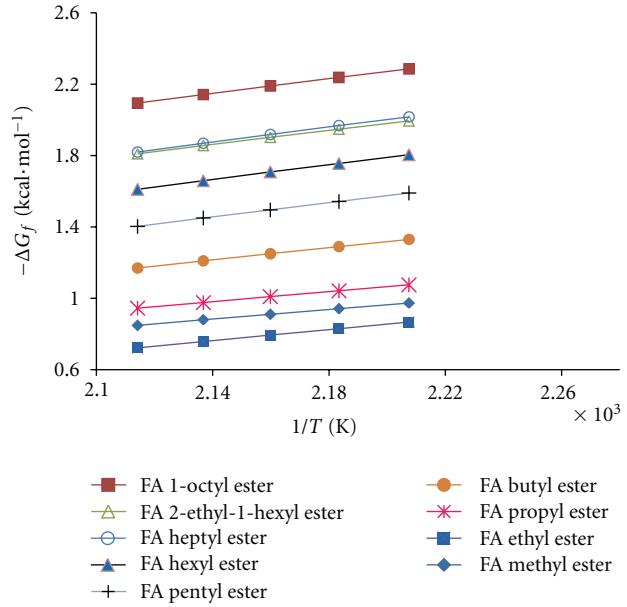

Figure 1: The change in $\Delta^g_{s\ln}G_f$ with $1/T$.

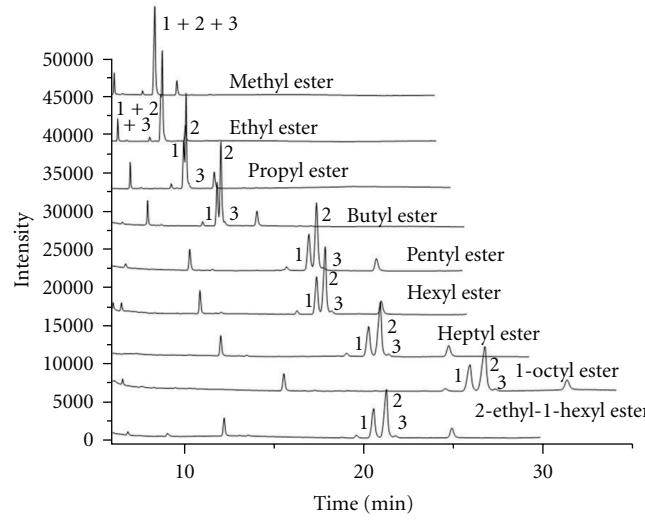

Figure 2: 2 Alignment of gas chromatograms of different alkyl esters of coriander seed oil + olive oil at 180°C. Peaks identification: 1, 18:1Δ6*cis*; 2, 18:1Δ9*cis*; 3, 18:1Δ11*cis*.

c and carbon numbers of alcohols give a straight line with the slope and intercept, of 382.1 and 416.7, respectively. The r^2, sd of intercept and slope are 0.961, 157.7, and 31.22, respectively.

$\Delta^g_{s\ln}G_f$ is the difference between $\Delta^g_{s\ln}H_f$ and $T\Delta^g_{s\ln}S_f$. The values of $\Delta^g_{s\ln}G_f$ for each fatty acid ester at any temperature can be estimated from the coefficients a and c (in Table 1, with the nominal β value of 250). The value of $\Delta^g_{s\ln}G_f$, for each fatty acid ester, at constant temperature, increases negatively as the carbon numbers of the alcohols are increased (Figure 1). However, the transformation of a solute in solution to gas involves two physical phenomena. The interaction between the solute and the column stationary phase is measured by free energy of solution, (Δ_sG_f), and the vaporization of the solute is measured by free energy of vaporization, $\Delta^g_lG^o$, [28, 29]. Therefore, the increment in $\Delta^g_{s\ln}G_f$ with R_y may involve Δ_sG_f or $\Delta^g_lG^o$ or both of them, and the separation between 18:Δ6*cis* and 18:Δ9*cis* cannot be ascribed to Δ_sG_f at this moment.

3.1.2. Evaluation of Coefficients in (4). The four numeric values (a, b, c, and d) for FAAEs of different alcohols are summarized in Table 1. The validations of these values were indirectly verified by comparing the calculated retention times ($t_{R(\text{cal})}$) with the experimental values ($t_{R(\text{exp})}$). Both $t_{R(\text{cal})}$ and $t_{R(\text{exp})}$ values are summarized in Table 2. All the $t_{R(\text{cal})}$ are very close to the $t_{R(\text{exp})}$ values. The greatest difference is 1.56% for methyl arachidate. There are only 3 $t_{R(\text{cal})}$ values which differed greater than ±1.00% from the $t_{R(\text{exp})}$ values. Forty one data points (21.0%) have the differences between 0.50 and 1.00. The rest (155 data points or 77.5%) have the differences less than 0.50%. The good agreement between the $t_{R(\text{cal})}$ and $t_{R(\text{exp})}$ values suggests that all the coefficients are valid for prediction retention times of FAAEs. The slopes, intercepts, r^2 and standard deviations of the plots between $t_{R(\text{cal})}$ and $t_{R(\text{exp})}$ for each FAAE are summarized in Table 3. The r^2, values of all the FAAE are greater than 0.997, and the slopes (the ratios of $t_{R(\text{cal})}/t_{R(\text{exp})}$) are very close to 1.00, except that of FAME.

Table 2: Comparison of the $t_{R(cal)}$ with the $t_{R(exp)}$ for fatty acids of different alkyl esters between temperatures 180 and 200°C, at 5°C interval.

	180°C			185°C			190°C			195°C			200°C		
FAME	$t_{R(cal)}$	$t_{R(exp)}$	%Δ[a]	$t_{R(cal)}$	$t_{R(exp)}$	%Δ	$t_{R(cal)}$	$t_{R(exp)}$	%Δ	$t_{R(cal)}$	$t_{R(exp)}$	%Δ	$t_{R(cal)}$	$t_{R(exp)}$	%Δ
16	5.09	5.14	−0.97	4.76	4.79	−0.63	4.48	4.50	−0.44	4.25	4.28	−0.70	4.09	4.10	−0.24
17	5.81	5.85	−0.68	5.34	5.36	−0.37	4.95	4.96	−0.20	4.63	4.66	−0.64	4.40	4.41	−0.23
18	6.77	6.78	−0.15	6.11	6.10	0.16	5.56	5.56	0.00	5.13	5.14	−0.19	4.80	4.80	0.00
19	8.06	8.01	0.62	7.13	7.07	0.85	6.37	6.35	0.31	5.78	5.76	0.35	5.32	5.31	0.19
20	9.77	9.64	1.35	8.48	8.35	1.56	7.43	7.33	1.36	6.61	6.56	0.76	5.99	5.95	0.67
FAEE															
16	5.18	5.21	−0.58	4.80	4.84	−0.83	4.50	4.51	−0.22	4.27	4.28	−0.23	4.06	4.07	−0.25
17	5.95	5.96	−0.17	5.41	5.45	−0.73	4.99	5.00	−0.20	4.67	4.68	−0.21	4.39	4.40	−0.23
18	6.97	6.97	0.00	6.23	6.25	−0.32	5.64	5.64	0.00	5.19	5.19	0.00	4.81	4.81	0.00
19	8.34	8.30	0.48	7.30	7.29	0.14	6.49	6.47	0.31	5.87	5.85	0.34	5.35	5.34	0.19
20	10.16	10.08	0.79	8.72	8.68	0.46	7.60	7.55	0.66	6.75	6.70	0.75	6.04	6.01	0.50
FAPrE															
16	5.89	5.91	−0.34	5.29	5.34	−0.94	4.99	4.98	0.20	4.65	4.65	0.00	4.37	4.38	−0.23
17	6.89	6.90	−0.14	6.07	6.12	−0.82	5.62	5.61	0.18	5.16	5.15	0.19	4.78	4.79	−0.21
18	8.22	8.21	0.12	7.10	7.16	−0.84	6.45	6.42	0.47	5.82	5.81	0.17	5.31	5.31	0.00
19	9.99	9.97	0.20	8.46	8.52	−0.70	7.54	7.49	0.67	6.68	6.65	0.45	5.99	5.98	0.17
20	12.37	12.30	0.57	10.26	10.33	−0.68	8.97	8.89	0.90	7.79	7.74	0.65	6.86	6.84	0.29
FABE															
16	6.82	6.84	−0.29	6.17	6.15	0.33	5.61	5.59	0.36	5.14	5.14	0.00	4.77	4.77	0.00
17	8.12	8.14	−0.25	7.20	7.17	0.42	6.43	6.40	0.47	5.79	5.79	0.00	5.29	5.29	0.00
18	9.86	9.88	−0.20	8.57	8.53	0.47	7.50	7.46	0.54	6.63	6.62	0.15	5.95	5.96	−0.17
19	12.17	12.21	−0.33	10.37	10.31	0.58	8.90	8.85	0.56	7.72	7.71	0.13	6.81	6.81	0.00
20	15.27	15.32	−0.33	12.76	12.68	0.63	10.74	10.68	0.56	9.14	9.12	0.22	7.91	7.92	−0.13
FAPeE															
16	8.11	8.17	−0.73	7.13	7.16	−0.42	6.37	6.38	−0.16	5.80	5.78	0.35	5.26	5.28	−0.38
17	9.86	9.91	−0.50	8.49	8.51	−0.24	7.44	7.44	0.00	6.64	6.61	0.45	5.93	5.94	−0.17
18	12.20	12.23	−0.25	10.29	10.31	−0.19	8.84	8.83	0.11	7.74	7.69	0.65	6.78	6.79	−0.15
19	15.32	15.34	−0.13	12.68	12.67	0.08	10.67	10.65	0.19	9.17	9.10	0.77	7.87	7.89	−0.25
20	19.48	19.51	−0.15	15.83	15.71	0.76	13.07	13.05	0.15	11.02	10.94	0.73	9.28	9.31	−0.32
FAHxE															
16	9.79	9.83	−0.41	8.45	8.46	−0.12	7.41	7.41	0.00	6.61	6.60	0.15	5.92	5.93	−0.17
17	12.10	12.13	−0.25	10.23	10.32	−0.87	8.80	8.78	0.23	7.70	7.67	0.39	6.76	6.77	−0.15
18	15.19	15.21	−0.13	12.60	12.58	0.16	10.63	10.59	0.38	9.11	9.07	0.44	7.86	7.86	0.00
19	19.32	19.34	−0.10	15.73	15.71	0.13	13.02	12.97	0.39	10.95	10.90	0.46	9.26	9.28	−0.22
20	24.83	24.93	−0.40	19.86	19.87	−0.05	16.15	16.12	0.19	13.33	13.30	0.23	11.07	11.11	−0.36
FAHpE															
16	11.98	12.01	−0.25	10.17	10.16	0.10	8.72	8.72	0.00	7.64	7.63	0.13	6.74	6.75	−0.15
17	15.03	15.05	−0.13	12.51	12.48	0.24	10.52	10.50	0.19	9.04	9.02	0.22	7.83	7.83	0.00
18	19.11	19.11	0.00	15.60	15.56	0.26	12.87	12.85	0.16	10.86	10.82	0.37	9.22	9.22	0.00
19	24.55	24.61	−0.24	19.69	19.69	0.00	15.96	15.96	0.00	13.22	13.18	0.30	11.01	11.04	−0.27
20	31.81	32.05	−0.75	25.11	25.18	−0.28	20.01	20.09	−0.40	16.28	16.29	−0.06	13.32	13.40	−0.60
FAOE															
16	15.30	15.27	0.20	12.63	12.67	−0.32	10.71	10.68	0.28	9.14	9.15	−0.11	7.98	7.98	0.00
17	19.46	19.38	0.41	15.77	15.79	−0.13	13.13	13.07	0.46	11.00	10.99	0.09	9.42	9.40	0.21
18	25.03	24.92	0.44	19.93	19.95	−0.10	16.30	16.21	0.56	13.40	13.38	0.15	11.27	11.24	0.27
19	32.46	32.43	0.09	25.43	25.54	−0.43	20.45	20.39	0.29	16.52	16.53	−0.06	13.65	13.63	0.15
20	42.38	42.60	−0.52	32.71	33.03	−0.97	25.89	25.94	−0.19	20.58	20.69	−0.53	16.72	16.75	−0.18

[a]percent different between $t_{R(exp)}$ and $t_{R(cal)}$.

Table 3: Correlation of $t_{R(cal)}$ and $t_{R(exp)}$ of FAAEs. Numbers in parentheses are standard deviation.

FAAE	Slope	Intercept	r^2
FAME	0.970 (0.004)	0.162 (0.021)	0.997
FAEE	0.987 (0.002)	0.086 (0.015)	0.999
FAPrE	0.995 (0.002)	0.034 (0.013)	0.999
FABE	1.001 (0.003)	0.025 (0.023)	0.999
FAPnE	0.999 (0.002)	0.004 (0.025)	0.999
FAHxE	1.003 (0.002)	−0.044 (0.021)	0.999
FAHpE	1.008 (0.001)	−0.112 (0.021)	0.999
FAOE	1.007 (0.002)	−0.121 (0.038)	0.999

The anomaly of the C1 series was observed on other phenomenon, such as gas holdup time [30, 31]. Hence, they are additional information, which supports that all the column coefficients are valid for predicting the retention times of FAAEs. Therefore, it may conclude that when the alcohols are changed, the numeric values of $\delta^g_{s\ln}H$ of and $\delta^g_{s\ln}S$ remain unchanged, accordingly the $\delta^g_{s\ln}G$ value does not change. It would also imply that the interaction between the saturated hydrocarbon chain and the stationary phase is not affected by the alcohol moieties. Thus, the homomorphic factor is verified for fatty acid esters of different alcohols.

3.2. GC Separation of Octadecenoic Acid Alkyl Esters of Different Alcohols and Free Energy Contribution from the Double Bond. Figure 2 is the aligned chromatograms of FAAEs (with different alcohols) of a mixture of coriander seed and olive oils, separated on a 90%-biscyanopropyl-10%-cyanopropylphenyl polysiloxane (Rtx-2330) capillary column at 180°C. The methyl and ethyl esters of petroselinic and oleic are coeluted. Partial separations of these two acid esters are observed when the alkyl groups have 3–6 carbon atoms. FAAEs of higher alcohols (FAHpE, FAOE, and FAEHE) are baseline resolved. Results agree well with the report of Isbell et al. [18]. In Figure 2, the octyl esters show approximately the same resolution as those of the 2-ethyl-1-hexyl esters in separations of 18:1Δ6 and 18:1Δ9. However, the 2-ethyl-1-hexyl esters are eluted faster than the octyl esters. The retention times of the 2-ethyl-1-hexyl esters are comparable to those of the heptyl esters. The bulky 2-ethyl-1-hexyl group was ascribed for lowering the interaction between the polar carboxyl and the polar stationary phase. Therefore, the interaction between the small polarity differences of the olefin and the polar stationary phase became apparent and caused the separation [18]. Although the discussion of Isbell et al. [18] was theoretically sound, it lacked the supported evidence. On the contrary, results in Figure 1 show that $\Delta^g_{s\ln}G_f$ values increase as the alcohol groups are larger, which contradicted to the explanation of Isbell et al. [18]. Therefore, a new free energy term is proposed, and it is expected that it would be able to find the cause of the separation between petroselinic and oleic esters.

Martin [20] were the first to divide a molecule into different parts, and a free energy term was assigned to each of them as shown in (1). Subsequently, different free energy terms were assigned to describe interactions between column stationary phase and different functional groups of the molecule [32, 33]. Hence, the free energy concept of Kollie and Poole [32] and Golovnya [33] was extended, in this work, to investigate the interaction between the double bond and the column stationary phase. The new free energy is called free energy of transfer from solution to gas of the double bond ($\Delta^g_{s\ln}G_u$). Equation (10) is obtained by inserting the $\Delta^g_{s\ln}G_u$ into(1)

$$\Delta^g_{s\ln}G^o_2 = \Delta^g_{s\ln}G_f + z\delta^g_{s\ln}G^o_1 + \Delta^g_{s\ln}G_u, \tag{10}$$

where the subscripts 1 and 2 stand for saturated and unsaturated fatty acids, respectively.

Equation (10) can also be derived as follows:

$$\begin{aligned}\Delta^g_{s\ln}G^o_1 &= -RT\ln K_1,\\ \Delta^g_{s\ln}G^o_2 &= -RT\ln K_2.\end{aligned} \tag{11}$$

Equation (12) is the difference between (11).

$$\Delta^g_{s\ln}G_u = \Delta^g_{s\ln}G^o_2 - \Delta^g_{s\ln}G^o_1 = -(RT\ln K_2 - RT\ln K_1). \tag{12}$$

Equation (10) is obtained by substituting (1) into (12).

$\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ is the difference between $\Delta^g_{s\ln}G^o_{2(\Delta9)}$ of 18:1Δ9 and $\Delta^g_{s\ln}G^o_{2(\Delta6)}$ of 18:1Δ6 as shown in .

$$\begin{aligned}\Delta^g_{s\ln}G^o_{2(\Delta9)} - \Delta^g_{s\ln}G^o_{2(\Delta6)} &= \Delta^g_{s\ln}G_{u(\Delta9)} - \Delta^g_{s\ln}G_{u(\Delta6)}\\ &= \Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}.\end{aligned} \tag{13}$$

The $\Delta\Delta^g_{s\ln}G^o_{2(\Delta9-\Delta6)}$ will be used as a tool to investigate the interaction of the double bond with the stationary phase of the column. The $\Delta^g_{s\ln}G^o_2$ of petroselinic and oleic (and vaccenic 18:1Δ11*cis*) acid esters at 180°C are summarized in Table 4. The C1–C3 esters are not well separated from each other, and they are not listed in the table. The $\Delta^g_{s\ln}G_u$ values of these three esters at 180°C are approximately −151, −133, and 128 cal·mol^{-1}, respectively. Partial separations are observed for FABEs. Separations of FAAE are gradually improved as the carbon numbers of the alcohols are increased.

According to Isbell et al. [18], the bulky alkyl group interfered the interaction of the carboxyl group to the column stationary phase. The interference did not extend to the hydrocarbon chain. Hence, the relative changes in $\Delta^g_{s\ln}G^o$ should be the same for both saturated and unsaturated FAAEs. However, the $\Delta^g_{s\ln}G_u$ values of petroselinic, oleic, and vaccenic esters (Table 4) become less negative as the alkyl sizes are increased, suggesting that the alkyl groups interfere the interaction between the hydrocarbon chain and the stationary phase, and the degree of interferences increases as the carbon numbers of the alcohols are increased.

The $\Delta^g_{s\ln}G_u$ values of the butyl esters of 18:1Δ6, Δ9, and Δ11 are −102.4, −120.1, and −145.4 cal·mol^{-1}, respectively. The values become less negative as the alkyl groups are larger. 2-Ethyl-1-hexyl esters have the lowest $\Delta^g_{s\ln}G_u$ compared with other alkyl esters. Their $\Delta^g_{s\ln}G_u$ values for 18:1Δ6, Δ9, and Δ11 are −36.7, −61.4, and −90.5 cal·mol^{-1}, respectively.

Table 4: The $\Delta^g_{sln}G_u$(cal·mol^{-1}) of esters of C18:1Δ6, C18:1Δ9, and C18:1Δ11.

	$\Delta^g_{s\ln}G_u$(cal·mol^{-1})					
Fatty acids	FABE	FAPnE	FAHxE	FAHpE	FAOE	FAEHE
18:0	0.0	0.0	0.0	0.0	0.0	0.0
18:1△6	−102.4	−82.0	−78.7	−68.8	−61.4	−36.7
18:1△9	−120.1	−103.8	−102.2	−92.1	−85.9	−61.4
18:1△11	−145.4	−134.3	−131.7	−122.1	−113.1	−90.5
			$\Delta\Delta^g_{s\ln}G_u$ (cal·mol^{-1})			
(18:1Δ9) – (18:1Δ6)	−17.7	−21.8	−23.5	−23.3	−24.5	−24.7
(18:1Δ11) – (18:1△9)	−25.3	−30.5	−29.5	−30.0	−27.2	−29.1

Table 5: Separations of petroselinic and oleic octyl esters on Rtx 2330 at 190°C.

					$\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$	
Octanol	t_{R1}(min)[a]	t_{R2} (min)	k_1	k_2	(cal·mol^{-1})	Rs
1-octanol	17.27	17.71	6.19	6.35	−24.5	1.26
2-octanol	12.67	12.97	4.51	4.64	−25.8	1.15
3-octanol	12.00	12.29	4.00	4.12	−25.1	1.17
4-octanol	11.41	11.69	3.74	3.84	−25.1	1.20

[a]the subscripts 1 and 2 represent petroselinate and oleate, respectively.

Therefore, the interaction of the double bond with the column stationary phase increases when the double bond is far away from the carboxyl group, that is, interference from the bulky alkyl group decreases along the distant.

The difference in $\Delta^g_{s\ln}G_u$ of 18:1Δ9 and 18:1Δ6 ($\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$) of butyl, pentyl, hexyl, heptyl, octyl and 2-ethylhexyl esters is −17.7, −21.8, −23.5, −23.3, −24.5, and −24.7 cal·mol^{-1}, respectively. The increases in $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ as the alkyl groups increased suggest that the relative interactions of the double bonds of the two acid esters with the stationary phase are increased. Thus, it may conclude that $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ is the driving force for the separation of the two isomers. However, the $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ values level after C6, implying that the resolution of these two positional isomers may not be further increased by simply increasing the size of the alcohol.

The $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ of 2-ethyl-1-hexyl esters is −24.7 cal·mol^{-1}. It is estimated that a column of about 65,000 required plate numbers (N_{req}) would be able to baseline separate the two positional isomers, while the butyl esters, whose $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ is −17.7 cal·mol^{-1}, would require up to 180,000 plate numbers. The $\Delta^g_{s\ln}G_u$ of 18:1△9 and △11 have similar trend as the 18:1△6 and 18:1△9 pair, and discussion is not necessary.

Petroselinic acid has a double bond closer to the carboxyl group than oleic acid. The interference from the bulky alkyl group should be stronger than that to the oleic acid. Similar observation was reported by Kuningas et al. [34] that the separation of geometric isomers (alkenes) depended on the differences in free energy.

The $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ the adjacent pairs of octadecenoic esters would reflect on the ease of separation for each pair. Results in Table 4 show that the separation of 18:1△9 and 18:1△11 is much simpler than the separation of 18:1△6 and 18:1△9.

3.3. Separation of Octadecenoic Acid Octyl Esters. As discussed in Section 3.2, the lowering in $\Delta^g_{s\ln}G_u$ was ascribed to the reduction in the interaction between the double bond in the FAAEs and the column stationary phase. 1-Octyl and 2-ethy-1-hexyl esters are two of the best derivatives for separation of petroselinic and oleic acids. However, esters of secondary octyl alcohols have not been reported (to our knowledge). Thus, they were investigated for their interferences to the interaction of the double bond with the stationary phase. The retention times, retention factors, $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$, and resolution (Rs) between secondary octyl petroselinate and oleate are summarized in Table 5. The $\Delta\Delta^g_{s\ln}G_{u(\Delta9-\Delta6)}$ values of secondary octyl esters of petroselinate and oleate range from −24.5 to −25.8 cal·mol^{-1}. The resolutions of these two acid secondary octyl esters (1.15-1.26) are close to that of the 1-octyl ester (1.26). However, more symmetric or compact alcohol had the shorter retention time. The order of elution for the esters is 4-octyl, 3-octyl, 2-octyl, and 1-octyl, respectively.

4. Conclusion

When the alcohol moieties of FAAE are changed, the $\delta^g_{s\ln}G$ does not change. It implies that the interaction between the saturated hydrocarbon chain and the stationary phase is not affected by the alcohol moieties. On the other hand, petroselinic and oleic have one cis-double bond in the hydrocarbon chain; its interaction with the column stationary phase would differ from that of the saturated hydrocarbon. Therefore, $\Delta^g_{s\ln}G_u$ is introduced and it would provide an insight into the interaction of the double with the column stationary phase. The bulky alkyl group attached to the carboxyl group affects the interaction between the double bond and the stationary phase. The steric effect decreases along the distance. In addition, for FAAEs having the same

carbon numbers, the more compact is alcohol moiety, the shorter is the retention time, while the resolutions of the adjacent positional isomers are approximately the same. For petroselinic and oleic acids, the driving force for their separation is the difference in $\Delta^{g}_{s\ln}G_u$ of the two geometrical isomers.

5. Symbols and Abbreviation

Fatty Acids

18:1Δ6*cis*: Petroselinic acid
18:1Δ9*cis*: Oleic acid
18:1Δ11*cis*: Vaccenic acid.

Thermodynamics

$\Delta^{g}_{s\ln}G^{o}$: Standard free energy of transfer from solution to gas
$\Delta^{g}_{s\ln}H^{o}$: Standard enthalpy of transfer from solution to gas
$\Delta^{g}_{s\ln}S^{o}$: Standard entropy of transfer from solution to gas
$\Delta^{g}_{s\ln}G_f$: Free energy of transfer from solution to gas of a hypothetical molecule of zero carbon atom or simply called free energy of the functional gr
$\Delta^{g}_{s\ln}H_f$: Enthalpy of transfer from solution to gas of a hypothetical molecule of zero carbon atom
$\Delta^{g}_{s\ln}S_f$: Entropy of transfer from solution to gas of a hypothetical molecule of zero carbon atom
$\Delta^{g}_{s\ln}G_u$: Free energy of transfer from solution to gas of a double bond
$\delta^{g}_{s\ln}G$: Change in free energy of transfer from solution to gas per carbon atom
$\delta^{g}_{s\ln}H$: Change in enthalpy of transfer from solution to gas per carbon atom
$\delta^{g}_{s\ln}S$: Change in entropy of transfer from solution to gas per carbon atom
$\Delta\Delta^{g}_{s\ln}G_{u(\Delta 9-\Delta 6)}$: The difference in free energy of transfer from solution to gas of two unsaturated FAAE (Δ9 and Δ6).

General

β: Column phase ratio
FAAE: Fatty acid alkyl ester
FABE: Fatty acid butyl ester
FAEE: Fatty acid ethyl ester
FAEHE: Fatty acid 2-ethylhexyl ester
FAHpE: Fatty acid heptyl ester
FAHxE: Fatty acid hexyl ester
FAME: Fatty acid methyl ester
FAPnE: Fatty acid pentyl ester
FAPrE: Fatty acid propyl ester
FAOE: Fatty acid octyl ester
k: Retention factor
R: Universal gas constant
Rs: Resolution
sd: Standard deviation
t_R: Retention time of a solute
t_M: Hold up time
T: Absolute temperature
z: Carbon number.

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References

[1] R. Kleiman and G. F. Spencer, "Search for new industrial oils: XVI. Umbelliflorae-seed oils rich in petroselinic acid," *Journal of the American Oil Chemists' Society*, vol. 59, no. 1, pp. 29–38, 1982.
[2] C. Y. Hopkins, A. W. Jevans, and M. J. Chisholm, "Fatty acids of Aceraceae seed oils," *Canadian Journal of Biochemistry*, vol. 46, no. 9, pp. 999–1002, 1968.
[3] F. Destaillats, J. Arul, J. E. Simon, R. L. Wolff, and P. Angers, "Dibutyrate derivatization of monoacylglycerols for the resolution of regioisomers of oleic, petroselinic, and cis-vaccenic acids," *Lipids*, vol. 37, no. 1, pp. 111–116, 2002.
[4] N. Tsevegsuren, K. Aitzetmuller, and K. Vosmann, "*Geranium sanguineum* (Geraniaceae) seed oil: a new source of petroselinic and vernolic acid," *Lipids*, vol. 39, no. 6, pp. 571–576, 2004.
[5] P. Avato, F. P. Fanizzi, and I. Rosito, "The genus Thapsia as a source of petroselinic acid," *Lipids*, vol. 36, no. 8, pp. 845–850, 2001.
[6] M. F. Ramadan, M. M. A. Amer, and A. E.-S. Awad, "Coriander (*Coriandrum sativum* L.) seed oil improves plasma lipid profile in rats fed a diet containing cholesterol," *European Food Research and Technology*, vol. 227, no. 4, pp. 1173–1182, 2008.
[7] N. Weber, I. Kiewitt, and K. D. Mukherjee, "Modulation of brain lipids of rats by various dietary oils: sunflower, high-oleic sunflower, olive, rapeseed or coriander oil," *Nutrition Research*, vol. 19, no. 7, pp. 997–1007, 1999.
[8] F. Santinelli and P. Damiani, "A simple and rapid method for concurrent determination of petroselinic and oleic acids in oils," *Journal of the American Oil Chemists' Society*, vol. 74, no. 8, pp. 935–938, 1997.
[9] J.-T. Lin, T. A. McKeon, and A. E. Stafford, "Gradient reversed-phase high-performance liquid chromatography of saturated, unsaturated and oxygenated free fatty acids and their methyl esters," *Journal of Chromatography A*, vol. 699, no. 1-2, pp. 85–91, 1995.
[10] L. Liu and E. G. Hammond, "Phenylethyl esters of fatty acids for the analytical resolution of petroselinate and oleate," *Journal of the American Oil Chemists' Society*, vol. 72, no. 6, pp. 749–751, 1995.
[11] S.-W. Kim, M.-K. Park, K.-S. Bae, M.-S. Rhee, and J.-R. Liu, "Production of petroselinic acid from cell suspension cultures of *Coriandrum sativum*," *Phytochemistry*, vol. 42, no. 6, pp. 1581–1582, 1996.
[12] W. Thies, "Petroselinic Acid Content in Seeds of *Coriandrum sativum* by Gas Liquid Chromatography," *Fat Science and Technology*, vol. 95, p. 20, 1993.
[13] R. L. Wolff and F. Vandamme, "Separation of petroselinic (cis -6 18:1) and oleic (cis -9 18:1) acids by gas-liquid

chromatography of their isopropyl esters," *Journal of the American Oil Chemists' Society*, vol. 69, no. 12, pp. 1228–1231, 1992.

[14] R. L. Wolff and C. C. Bayard, "Improvement in the resolution of individual trans-18:1 isomers by capillary gas-liquid chromatography: Use of a 100-m CP-Sil 88 column," *Journal of the American Oil Chemists' Society*, vol. 72, no. 10, pp. 1197–1201, 1995.

[15] M. F. Ramadan and J.-T. Mörsel, "Oil composition of coriander (*Coriandrum sativum* L.) fruit-seeds," *European Food Research and Technology*, vol. 215, no. 3, pp. 204–209, 2002.

[16] W. M. N. Ratnayake, S. L. Hansen, and M. P. Kennedy, "Evaluation of the CP-Sil 88 and SP-2560 GC columns used in the recently approved AOCS Official Method Ce 1h-05: Determination of c/s-, trans-, saturated, monounsaturated, and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method," *Journal of the American Oil Chemists' Society*, vol. 83, no. 6, pp. 475–488, 2006.

[17] C. Ragonese, P. Q. Tranchida, P. Dugo et al., "Evaluation of use of a dicationic liquid stationary phase in the fast and conventional gas chromatographic analysis of health-hazardous C18 cis/trans fatty acids," *Analytical Chemistry*, vol. 81, no. 13, pp. 5561–5568, 2009.

[18] T. A. Isbell, L. A. Green, S. S. DeKeyser, L. K. Manthey, J. A. Kenar, and S. C. Cermak, "Improvement in the gas chromatographic resolution of petroselinate from oleate," *Journal of the American Oil Chemists' Society*, vol. 83, no. 5, pp. 429–434, 2006.

[19] K. Msaada, K. Hosni, M. Ben Taarit, T. Chahed, M. Hammami, and B. Marzouk, "Changes in fatty acid composition of coriander (*Coriandrum sativum* L.) fruit during maturation," *Industrial Crops and Products*, vol. 29, no. 2-3, pp. 269–274, 2009.

[20] A. J. P. Martin, "Some theoretical aspects of partition chromatography," *Biochemical Society Symposia (Partition Chromatography)*, vol. 3, p. 4, 1950.

[21] K. Krisnangkura, A. Tancharoon, C. Konkao, and N. Jeyashoke, "An alternative method for the calculation of equivalent chain length or carbon number of fatty acid methyl esters in gas chromatography," *Journal of Chromatographic Science*, vol. 35, no. 7, pp. 329–332, 1997.

[22] S. Nilratnisakorn, N. Jeyashoke, and K. Krisnangkura, "Effect of column—programmed gas chromatography," *Science Asia*, vol. 251, p. 173, 1999.

[23] K. Aryusuk and K. Krisnangkura, "Prediction of gas chromatographic retention times of capillary columns of different inside diameters," *Journal of Separation Science*, vol. 26, no. 18, pp. 1688–1692, 2003.

[24] V. Pacakova and L. Feltl, *Chromatographic Retention Indices—An Aid to Identification of Organic Compounds*, Ellis Horwood, New York, NY, USA, 1992.

[25] P. Kaewkool, K. Kittiratanapiboon, K. Aryusuk, and K. Krisnangkura, "Micro-reactor for transesterification of plant seed oils," *European Journal of Lipid Science and Technology*, vol. 111, no. 5, pp. 474–480, 2009.

[26] K. Kittirattanapiboon and K. Krisnangkura, "Separation of acylglycerols, FAME and FFA in biodiesel by size exclusion chromatography," *European Journal of Lipid Science and Technology*, vol. 110, no. 5, pp. 422–427, 2008.

[27] P. Kalayasiri, N. Jeyashoke, and K. Krisnangkura, "Survey of seed oils for use as diesel fuels," *Journal of the American Oil Chemists' Society*, vol. 73, no. 4, pp. 471–474, 1996.

[28] A. Srisaipet, K. Aryusuk, S. Lilitchan, and K. Krisnangkura, "The relationship between vapour pressure, vaporization enthalpy, and enthalpy of transfer from solution to gas: An extension of the Martin equation," *Journal of Chemical Thermodynamics*, vol. 39, no. 7, pp. 1077–1084, 2007.

[29] J. S. Chickos, S. Hosseini, and D. G. Hesse, "Determination of vaporization enthalpies of simple organic molecules by correlations of changes in gas chromatographic net retention times," *Thermochimica Acta*, vol. 249, no. 1-2, pp. 41–62, 1995.

[30] M. S. Wainwright, J. K. Haken, and D. Srisukh, "A comparative study of mathematical dead-time and methane retention," *Journal of Chromatography A*, vol. 179, no. 1, pp. 160–166, 1979.

[31] M. S. Wainwright and J. K. Haken, "Effective carbon number of methane in gas chromatography," *Journal of Chromatography A*, vol. 256, no. C, pp. 193–199, 1983.

[32] T. O. Kollie and C. F. Poole, "Influence of solute size and the non-polar interaction term on the selection of test solutes for the classification of stationary phase selectivity in gas chromatography," *Journal of Chromatography*, vol. 556, no. 1-2, pp. 457–484, 1991.

[33] R. V. Golovnya, "Universal system for liquid stationary phase classification on the basis of thermodynamical data," *Chromatographia*, vol. 12, no. 8, pp. 533–538, 1979.

[34] K. Kuningas, S. Rang, and T. Kailas, "Gas-chromatographic study of the thermodynamic properties of systems containing linear alkenes and alkynes," *Chromatographia*, vol. 27, no. 11-12, pp. 544–548, 1989.