A Method for Calculating the Ratio of Each Possible Type of Triglyceride in Natural Fat

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Abstract

A generalized method for calculating the weight ratios or mole fractions of triglycerides in natural fat is developed by applying Vander Wal's method for calculating the mole fractions. In the proposed method a generating function is introduced to calculate the mole fractions of triglycerides.

Introduction

A METHOD FOR CALCULATING the ratio for each triglyceride type in a natural fat was developed and discussed thoroughly by Vander Wal (6,7). Tsuda (4,5) compared several of the existing methods for calculating this ratio and finally evolved a new method for calculation by using a specific set of assumptions. A procedure similar to Vander Wal's method was developed by Gunstone (2). In the present paper a method for calculating the ratio of triglyceride was developed by using a generating function which permitted a more generalized approach to the problem.

Derivation of Formulas

The letters A, B, and C respectively refer to positions 1, 2, and 3 of the triglyceride.

When A_i, B_i, and C_i for each fatty acid, i, are available by chemical analysis of a natural fat, equation 1 can be used to calculate the mole fraction of each possible type of triglyceride.

$$\sum_{i=1}^{n} A_i \sum_{i=1}^{n} B_i \sum_{i=1}^{n} C_i = 1 \qquad (1)$$

In Equation 1 it was assumed that N different types of fatty acids were detected by the chemical analysis. These fatty acids were represented by N different integers 1 through n. In the derivation of Equation 1 the additive law and multiplication law of probabilities were applied (3). It would be worthwhile to mention that no assumption on the distribution of fatty acids was made in Equation 1.

The mole fraction of any possible type of triglyceride can be obtained by selecting the proper term, which has an appropriate combination of symbols, from the expanded right hand side of Equation 1. For example, Q_{jlm} can be obtained by finding the numerical magnitude of A_j, B_l, C_m. In this expression the integers, j, l, or m, representing fatty acids or acyl groups, can be equal to each other.

The existing chemical methods for determining triglycerides do not give separate information on each value of A_i, B_i, or C_i ($i = 1, 2, \ldots n$). Therefore some assumptions must be made to get this information. The simplest assumption is the completely random distribution of acyl groups although this assumption does not produce a satisfactory estimation of the triglyceride composition of a natural fat or oil. By using this assumption, Equation 2 can represent the mole fraction of any acyl group i.

$$A_i = B_i = C_i = ABC_i \quad i = 1, 2, \ldots, n \qquad (2)$$

The mole fraction of any triglyceride can be obtained from Equation 3 when the completely random distribution is applicable.

$$\left[\sum_{i=1}^{n} ABCT_i \right]^2 \cdot \sum_{i=1}^{n} ABCB_i = 1$$

$$\text{where } ABCT_i = ABCB_i = ABC_i \qquad (3)$$

In Equation 3, $ABCT_i$ and $ABCB_i$ are employed, although they are numerically equivalent to ABC_i, because it was necessary to differentiate between the mole fraction of acyl groups at any terminal position and that at position 2. The mole fraction of any triglyceride can be obtained by selecting the numerical value of the terms, which have the appropriate combination of symbols, from the expanded expression of the left side of Equation 3. Therefore the following formulas were obtained for calculating the mole fraction of any triglyceride, after replacing $ABCT_i$ and $ABCB_i$ by ABC_i ($i = 1, 2, \ldots n$).

$$R_{jlm} = 2 \cdot ABC_j \cdot ABC_l \cdot ABC_m$$

$$\text{for } j \neq m \text{ and it is possible that } j = l \text{ or } m = l \qquad (4)$$

$$R_{jlj} = (ABC_j)^2 \cdot ABC_l$$

$$j \text{ can be equal to } l \qquad (5)$$

If the 1,3-random-2-random distribution of fatty acids, which was proposed by Vander Wal (5,6), is applied, the following relationship results, Equation 6.

$$A_i = C_i = AC_i \quad \text{for } i = 1, 2, \ldots, n \qquad (6)$$

The mole fraction of the acyl group i at position 2, B_i, can be calculated from the mole fraction of the acyl group i at positions 1,2, and/or 3, ABC_i, and from the mole fraction of the acyl group i at positions 1 and/or 3, AC_i (1), resulting in Equation 7.

$$B_i = 3 \cdot ABC_i - 2 \cdot AC_i \qquad (7)$$

By entering Equation 6 into Equation 1, Equation 8 is obtained. This is the generating function for calculating the triglyceride composition when the 1,2-random-2-random distribution is applicable.

$$\left[\sum_{i=1}^{n} AC_i \right]^2 \cdot \sum_{i=1}^{n} B_i = 1 \qquad (8)$$

The mole fraction of any triglyceride can be obtained by finding the numerical magnitude of the term with the appropriate combination of symbols after expanding the left side of Equation 8. For example, P_{jlm} is obtained by finding the numerical values of terms $AC_j \cdot AC_m \cdot B_l$. After expanding the left side of Equation 8, Equations 9 and 10[1] are obtained for calculating the triglyceride composition.

$$P_{jlm} = 2 \cdot AC_j \cdot AC_m \cdot B_l$$

for $j \neq l$ and j and m or m and l could be equal (9)

$$P_{sls} = (AC_s)^2 \cdot B_l$$

s and l could be equal (10)

The number of different types of terms, which are obtained by expanding a generating function, gives the number of possible types of triglycerides. When the completely random distribution of acyl groups is applicable, the number, N_c, of possible types of triglycerides can be calculated by Equation 11, which is obtained from Equation 3.

$$N_c = n^2 (n + 1) / 2 \qquad (11)$$

When the 1,3-random 2-random distribution of acyl groups is applicable, the number, N_v, of possible types of triglycerides can be obtained from Equation 8. If α terms of AC_i (i = 1,2, ..., n) and β terms of B_i (i = 1, 2, ... n) are nil, N_v can be calculated by Equation 12.

$$N_v = (n - \alpha) \cdot (n - \beta) \cdot (n - \alpha + 1) / 2 \qquad (12)$$

When the weight ratio of each fatty acid has been determined, this ratio can be converted to the mole fraction by using Equations 13, 14, and 15.

$$ABC_v = WABC_v / \{ W_v \cdot \sum_{i=1}^{n} WABC_i / W_i \} \qquad (13)$$

$$AC_v = WAC_v / \{ W_v \cdot \sum_{i=1}^{n} WAC_i / W_i \} \qquad (14)$$

$$B_v = WB_v / \{ W_v \cdot \sum_{i=1}^{n} WB_i / W_i \} \qquad (15)$$

If the molecular weight of each component fatty acid varies slightly, W_v and W_i in Equations 13, 14, and 15 will essentially cancel out each other. The weight ratio then approximately equals the mole fraction, that is,

$$ABC_v \cong WABC \qquad (13\text{–}1)$$

$$AC_v \cong WAC_v \qquad (14\text{–}1)$$

$$B_v \cong WB_v \qquad (15\text{–}1)$$

By entering Equations 14 and 15 into Equations 9 and 10 respectively, the formulas are obtained for calculating the mole fraction of triglyceride when the weight ratios of component fatty acids are given.

The weight ratio W_{jlm} of any triglyceride can be calculated by Equation 16 for any combination of j, l, and m when the 1,3-random-2-random distribution is applicable.

$$W_{jlm} = (38.05 \cdot U_{jlm} + E_{jlm}) / (38.05 \cdot \sum_{x,y,z} U_{xyz} + 1) \qquad (16)$$

The following expressions define all terms employed in Equation 16.

[1] Vander Wal (7) shows formulas similar to this equation on page 245 of his paper. A clear definition of symbols used in his formula is not given in the paper. They should be interpreted as follows: symbols with numeral 1, such as *A*1—the percentage of a type of acyl group located in position 1 and/or 3 to all acyl groups at positions 1 and/or 3; symbols with numeral 2, such as *A*2—the percentage of a type of acyl group located at position 2 to all acyl groups at position 2; symbols with numeral 3, such as *A*3—the percentage of a type of acyl group located at position 1 and/or 3 to all acyl groups at positions 1 and/or 3.

The multiplication factor 2 in the equation for % *ABA* on page 245 of his paper (7) should be deleted as he has indicated in his personal communication with the author.

TABLE I
The Mole Fraction of Component Fatty Acids

i	Component acids	W_i	ABC_i	AC_i	B_i
1	Palmitic	256.4	0.128	0.194	0.004(0)
2	Stearic	284.5	0.019	0.030	−0.003(0)
3	Oleic	282.5	0.287	0.281	0.299(0.297)
4	Linoleic	280.4	0.560	0.486	0.708(0.703)
5	Linolenic	278.4	0.006	0.009	0

$$U_{xyz} = E_{xyz} / (W_x + W_y + W_z)$$
for any combination of x, y, and z (16a)

$$U_{jlm} = E_{jlm} / (W_j + W_l + W_m)$$
for any combination of i, l, and m (16b)

$$E_{xyz} = 2 \cdot WAC_x \cdot WAC_z \cdot WB_y$$
for $x \neq z$ and x and y, or y and z could be equal (16c)

$$E_{jlm} = 2 \cdot WAC_j \cdot WAC_m \cdot WB_l$$
for $j \neq m$ and j and or l and m could be equal (16d)

$$E_{sys} = (WAC_s)^2 \cdot WB_y$$
s and y could be equal (16e)

$$E_{tlt} = (WAC_t)^2 \cdot WB_l$$
t and l could be equal (16f)

The constant 38.05 in Equation 16 is obtained by the following calculation.

$$\begin{pmatrix}\text{The molecular weight}\\ \text{of glycerol}\end{pmatrix} - 3 \cdot \begin{pmatrix}\text{The molecular weight}\\ \text{of water}\end{pmatrix} = 38.05$$

If the molecular weights of the component fatty acids differ slightly, Equation 17 is obtained for any combination of j, l, and m.

$$W_{jlm} \cong E_{jlm} \cong P_{jlm} \qquad (17)$$

Example of Calculation

The more fractions of fatty acids (Table I) in corn oil are calculated from their weight ratios (7) by using Equations 13 and 14. For example, the value for ABC_1 is calculated as follows:

$$ABC_1 = \frac{\dfrac{0.118}{256.4}}{\dfrac{0.118}{256.4} + \dfrac{0.019}{284.5} + \dfrac{0.291}{282.5} + \dfrac{0.564}{280.4} + \dfrac{0.008}{278.4}} = 0.128$$

TABLE II
The Mole Fractions of Triglycerides of All Possible Types in Corn Oil

Fatty acid[a] at the following position			Mole fraction	Fatty acid[a] at the following position			Mole fraction
terminal	2	terminal		terminal	2	terminal	
1	3	1	0.0112	2	4	4	0.0205
1	4	1	0.0265	2	3	5	0.00016
1	3	2	0.0034	2	4	5	0.00038
1	4	2	0.0082	3	3	3	0.0235
1	3	3	0.0324	3	4	3	0.0555
1	4	3	0.0766	3	3	4	0.0811
1	3	4	0.0560	3	4	4	0.1920
1	4	4	0.1326	3	3	5	0.0015
1	3	5	0.0010	3	4	5	0.0036
1	4	5	0.0025	4	3	4	0.0702
2	3	2	0.00027	4	4	4	0.1660
2	4	2	0.00063	4	3	5	0.0026
2	3	3	0.0050	4	4	5	0.0062
2	4	3	0.0119	5	3	5	0.000024
2	3	4	0.0087	5	4	5	0.000057

[a] Each fatty acid is represented by the following integer: 1—palmitic acid, 2—stearic acid, 3—oleic acid, 4—linoleic acid, 5—linolenic acid.

The negative values for B_1 and B_2 are probably a result of an analytical error and are replaced by zeros in the following calculation. In order to get unity for the sum of B_i, the values for B_3 and B_4 are modified respectively to 0.297 and 0.703. By modifying these numerical values, unity for the sum of mole fractions of all possible triglycerides is ensured. These modifications thus provide a means for checking the numerical calculations of the mole fractions.

If the 1,3-random-2-random distribution is applicable, the number of possible triglycerides in corn oil is determined by Equation 12 as follows:

$$\text{with } n = 5, \alpha = 0, \beta = 3$$

$$N_v = (5 - 0) \cdot (5 - 3) \cdot (5 - 0 + 1)/2 = 30$$

By using Equations 9 and 10, the mole fraction of all possible triglycerides in corn oil have been calculated (Table II). In these calculations the 1,3-random-2-random distribution is assumed.

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SUPPLEMENTARY DETAIL

A_i — Mole fraction of fatty acid *i* located at position 1 to the total numbers of moles of all fatty acids located at this position.

A_j — Same as A_i. However the mole fraction is referred to fatty acid *j*.

ABC_i — Mole fraction of fatty acid i located at positions 1,2, and/or 3 to the total number of moles of all fatty acids located at positions 1,2, and/or 3.

ABC_j, ABC_l, ABC_m, ABC_v, ABC_1 — Same as ABC_i. However the mole fractions are referred to fatty acids *j, l, m, v*, and 1 respectively.

$ABCB_i$ — Same as ABC_i. It is employed to signify the mole fraction of fatty acid *i* located at position 2 to all fatty acids located at this position.

$ABCT_i$ — Same as ABC_i. It is employed to signify the mole fraction of fatty acid *i* located at position 1 and/or 3 to all fatty acids located at position 1 and/or 3.

AC_i — Mole fraction of fatty acid *i* located at positions 1 and/or 3 to the total number of moles of all fatty acids located at positions 1 and/or 3.

AC_j, AC_m, AC_s, AC_v — Same as AC_i. However the mole fractions are referred to fatty acid *j, m, s*, and *v* respectively.

B_i — Mole fraction of fatty acid *i* located at position 2 to the total number of moles of all fatty acids located at this position.

B_l, B_v, B_1, B_2, B_3, B_4 — Same as B_i. However the mole fractions are referred to fatty acids *l, v*, 1, 2, 3, and 4 respectively.

C_i — Mole fraction of fatty acid *i* located at position 3 to the total number of moles of all fatty acids located at this position.

C_m — Same as C_i. However the mole fraction is referred to fatty acid *m*.

E_{jlm}, E_{sys}, E_{tlt}, E_{xyz} — Expressions defined by equations 16d, 16e, 16f, and 16c respectively.

i, j, l, m, n — Integers which represent fatty acids or acyl groups.

N — Number of different types of fatty acids obtained by chemical analysis of triglyceride.

N_c — Number of all possible types of triglycerides when the completely random distribution is applicable.

N_v — Number of all possible types of triglycerides when the 1,3-random-2-random distribution is applicable.

P_{jlm} — Mole fraction of triglyceride, which has acyl group *j* at a terminal position, acyl group *m* at another terminal position, and acyl group *l* at position 2. In the calculation of P_{jlm} the 1,3-random-2-random distribution is assumed.

P_{sls} — Mole fraction of triglyceride, which has acyl group *s* at terminal positions and acyl group *l* at position 2. In the calculation of P_{sls} the 1-3-random-2-random distribution is assumed.

Q_{jlm} — Mole fraction of triglyceride, which has acyl group *j* at position 1, acyl group *l* at position 2, and acyl group *m* at position 3.

R_{jlm} — Mole fraction of triglyceride, which has acyl group *j* at a terminal position, acyl group *m* at another terminal position, and acyl group *l* at position 2. In the calculation of R_{jlm} the completely random distribution is assumed.

R_{jlj} — Mole fraction of triglyceride, which has acyl group *j* at the terminal positions and acyl group *l* at position 2. In the calculation of R_{jlj} the completely random distribution is assumed.

R_{jjj} — Mole fraction of triglyceride, which has acyl grouj *j* at all positions. In the calculation of R_{jjj} the completely random distribution is assumed.

s, t — Integers which represent fatty acids or acyl groups.

U_{jlm} — Expression defined by equation 16b.

U_{xyz} — Expression defined by equation 16a.

W_i, W_j, W_l, W_m, W_v, W_x, W_y, W_z — Molecular weights of fatty acids *i, j, l, m, v, x, y*, and *z* respectively.

W_{jlm} — Weight ratio of triglyceride, which has acyl group *j* at a terminal position, acyl group *m* at another terminal position, and acyl group *l* at position 2.

$WABC_i$ — Weight ratio of fatty acid *i* located at positions 1,2, and/or 3 to the total weight of fatty acids located at positions 1,2, and/or 3.

$WABC_v$ — Same as $WABC_i$. However the weight ratio is referred to fatty acid *v*.

WAC_i — Weight ratio of fatty acid *i* located at positions 1 and/or 3 to the total weight of fatty acids located at positions 1 and/or 3.

WAC_j, WAC_m, WAC_s, WAC_t, WAC_v, WAC_x, WAC_z — Same as WAC_i. However the weight ratios are referred to fatty acids *j, m, s, t, v, x*, and *z* respectively.

WB_i — Weight ratio of fatty acid *i* located at position 2 to the total weight of fatty acids located at position 2.

WB_l, WB_v, WB_y — Same as WB_i. However the weight ratios are referred to *l, v*, and *y* respectively.

x, y, z — Integers which represent fatty acids or acyl groups.

α — Number of AC_i terms the numercial values of which are nil.

β — Number of B_i terms the numerical values of which are nil.