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• *Letter to the Editor*

The Calculation of Restricted Random Glyceride Distribution[1]

KARTHA (1) has proposed that the fatty acyl groups in triglycerides are distributed at random except that in certain cases a restriction may be placed on the amount of trisaturated glyceride that can be formed. He has given the following equations for calculating the glyceride distribution of fats from random distribution and the amount of trisaturated glyceride found experimentally:

$$(GS_3)_r - GS_3 = F$$

$$GS_2U = (GS_2U)_r + F + \frac{(2/3)(F)(GSU_2)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

$$GSU_2 = (GSU_2)_r - \frac{(2/3)(F)(GSU_2)_r}{(2/3)(GSU_2)_r + (GU_3)_r} + \frac{F(GU_3)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

$$GU_3 = (GU_3)_r - \frac{F(GU_3)_r}{(2/3)(GSU_2)_r + (GU_3)_r}$$

where the subscript r refers to the values calculated by random distribution and GS_3, GS_2U, GSU_2, and GU_3 are the actual amounts of the four glyceride types.

However it is not correct to calculate from one equilibrium state to another by proportions. This is best demonstrated by the fact that the above equations give negative values for GU_3 in cases where the saturated acids exceed 61.8% and the amount of trisaturated glyceride is reduced to its smallest possible value. The other three glyceride types add up to more than 100% in these cases.

A correct equation for the conditions that Kartha has proposed can be derived in the following way. Let the real proportions of GS_3, GS_2U, GSU_2, and GU_3 be a, b, c, and d, respectively. Let the mol proportion of saturated acids be S, then

$$a + b + c + d = 1$$
$$3a + c + 2b = 3S$$

An equilibrium condition may be considered to exist such that

$$GU_3 + GS_2U \rightleftharpoons 2GSU_2$$

and thus

$$db/c^2 = K$$

where K is the equilibrium constant. Since there is no restriction on this equilibrium $K = 1/3$, for in a random distribution there are three ways to form GSU_2 and GS_2U for each way that leads to GU_3. Using these equations to solve for b in terms of S and a,

$$GS_2U = b = (3/2)(1 + S - 2a) - (3/2)(1 - 3S^2 + 2S - 4a + 4Sa)^{1/2}$$

Also

$$GSU_2 = c = 3S - 2b - 3a$$
$$GU_3 = d = 1 + 2a + b - 3S$$

A comparison of the results obtained by Kartha's equation with our equation for various values of S and for the least amount of GS_3 possible indicates that his values may deviate from the correct values by 2% in many places and by 4.5% in one place. These are extreme conditions, and, in general, Kartha's solution will lie closer to the correct value.

The amount of the individual glycerides may be calculated, as Kartha indicated, by multiplying the random value by the proportion in which the glyceride type to which it belongs has changed.

The present method of calculating glyceride distributions from equilibrium considerations is by no means limited to the conditions that Kartha has proposed. It may be used for calculating the glyceride structure when the distribution is believed to be basically a random one which is limited in some specific way, *e.g.*, the type of distribution proposed by Vander Wal (2). However the algebra involved in solving the equations can become complex, and this method may not be the simplest approach.

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