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[Received August 21, 1956]

Letter to Editor

A Note on Glyceride Structure: Specific, Random, and Restricted-Random Distribution

KARTHA (1) has advanced the theory that the fatty acyl groups in all natural fats are distributed at random among the triglyceride molecules unless the quantity of GS_3 so produced exceeds that which can exist in a fluid state *in vivo*. In this event the excess of saturated acids is distributed at random among the remaining glyceride types, GS_2U , GSU_2 , and GU_3 . This form of dispersion is known as "restricted-random distribution." He assumes that the acyl groups are all equally reactive and in dynamic equilibrium among all the triglyceride molecules that are in a fluid state and that all positions in the molecules are equivalent.

The theoretical proportions of GS_2U , GSU_2 , and GU_3 present in a fat which is in restricted random distribution can be calculated from the proportions of GS_3 and the saturated acids found by analysis. The molar percentages of the four glyceride types found in cacao butter by Hilditch and Stainsby (2) and those for GS_2U , GSU_2 , and GU_3 calculated by Kartha (1) from their data in accord with the restricted-random distribution theory are presented in the table. Included are the results of analyses by Meara (3) and Amberger and Bauch (4), as reinterpreted by Lewkowitsch (5).

The Glyceride Type Composition of Cacao Butter

	GS_3	GS_2U	GSU_2	GU_3
Hilditch and Stainsby (experimental)	2	77	21	...
Kartha (calculated)	2	80	17	1
Meara (experimental)	2.5	83	13.5	1
Amberger and Bauch (experimental)	...	80	20	...

Examination of the table shows clearly that the results of the calculations by Kartha based on the restricted-random distribution theory agree with the experimental results of the others.

Calculations from other data from various sources on other fats give similar results. The glyceride-type composition of lard, which does not agree with the theory (6), would do so if the latter were amended to permit, in some instances, restriction in the formation of GS_2U as well as that of GS_3 . In this event the excess of acyl groups must perforce appear in the GSU_2 fraction.

Kartha has determined the proportions of the glyceride types in several natural fats of various kinds, the S content of which varied from 8 to 99 mol per cent, by direct analysis. The results are in close agreement with those calculated in accord with the restricted-random distribution theory.

The evidence points to the conclusion that the proportions of the glyceride types in many fats are, at least approximately, in agreement with the theoretical values based on the restricted-random distribution theory. Included are those in which the glyceride types are present in the proportions in which they would occur if fatty acid distribution were at random (1, 6, 9, 10, 11).

STRICT ADHERENCE to Kartha's theories would require that the fatty acids constituting individual mixed triglycerides be distributed among the three positions at random. It is likely however that in some or all fats the fatty acids are not distributed within the individual mixed glyceride molecules at random. In lard, for instance, saturated acids appear to occupy predominantly the 2-position in the mixed glycerides. In cacao butter, on the other hand, the 2-position is said to be occupied almost exclusively by unsaturated acids. The earlier work has been reviewed by Hilditch (7), and more evidence has appeared recently from several sources (8). It has been suggested by Lutton (8) that triglycerides of specific constitution are characteristic of natural fats rather than triglycerides formed by random fatty acid distribution.

Kartha's data do not disagree with this view. In his calculations and analyses he dealt with saturated and/or unsaturated acyl groups combined in groups of three as triglycerides. He made no attempt to show by experiment that these acyl groups were distributed at random within the triglyceride molecules. His analyses and the calculations based on chance by which his results could have been predicted do appear to show that, in several fats at least, the three saturated and/or unsaturated long chain acyl groups constituting each triglyceride molecule become parts thereof by chance. Under some circumstances this chance association results in random distribution of the glyceride types. Under other circumstances, chance association results in a certain kind of nonrandom, or "restricted random," distribution of the glyceride types.

Perhaps, in many natural fats, long-chain saturated and/or unsaturated groups become associated by chance in those triglyceride molecules formed but are not distributed within each molecule at random. These may prove to be facts related to the mechanics by which triglycerides in general are synthesized *in vivo*. They may provide clues to the nature of these mechanisms. They also may be related to the processes by which fatty acids are synthesized *in vivo*.

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