Some Deviations from 1,3-Random 2-Random Distribution in Natural Fats

Sir: According to the 1,3-random 2-random hypothesis (1), the component fatty acids are distributed at random in each of the three glyceryl positions. The 1- and 3-positions are identical and hold identical kinds and proportions of fatty acid groups, and the 2 positions may be occupied by the same fatty acids in the same proportions or by another combination.

That some natural fats do not conform to this hypothesis is demonstrated by the data in Table I. In all but the last of the series, the data in the first line, headed 1,3-random 2-random distribution, represent the molecular composition as calculated on the assumption of 1,3-random 2-random distribution of the fatty acids.

The data in the line headed, specific restricted random distribution, represent the molecular composition calculated on the assumption that the distribution is in accord with the specific restricted random distribution theory (4). According to this theory, specific esterification takes place in the sequence $\alpha \rightarrow \alpha' \rightarrow \beta$, and formation of S_3 is limited to the quantity which can exist in a fluid state in vivo. When this limit is reached, the percentage of S_3 remains constant and the excess of S forms S_2U and SU_2 only. Specific restricted random values can be calculated from the percentages of S, S_3, and S combined at the 2-position, found by analysis (4).

In the present instance, the same values have been derived directly from the 1,3-random 2-random data (line one) and the experimental S_3 contents (line three) by a new calculation technique (Appendix). In line three are comparative experimental data derived, for the most part, from fat samples other than those represented in line one. The comparative experimental data were adjusted in each case to the same level of saturated acid content as the sample analyzed for S combined at the 2-position by calculation, using the "GS_3 Constant" [the ratio of S_3 present to S_3 by random distribution, a factor which appears characteristic for a particular biological source (2)]

TABLE I

The Structures of Some Natural Fats as Reproduced by Different Fatty Acyl Group Distribution Hypotheses

	Fat	% Mol							
		S_3	SUS	S_2U	SSU	USU	SU_2	UUS	U_3
1.	Phulwara butter, Sm-62.8[a]								
	1,3 random 2 random (5)	3.5	80.4	81.1	0.7	0.0	14.6	14.6	0.7
	Specific restricted random	1.2	82.8	85.7	2.9	0.1	12.5	12.4	0.6
	Comparative experimental data (7)[b,c]	1.2		87.0			10.8		1.0
2.	Kokum butter, I, Sm-62.7								
	1,3 random 2 random (6)	3.6	80.9	81.5	0.6	0.0	14.3	14.3	0.6
	Specific restricted random	0.3	84.2	88.1	3.9	0.0	11.0	11.0	0.6
	Comparative experimental data (3,2,8)	0.3		88.7			10.0		1.0
3.	Kokum butter, II, Sm-59.3								
	1,3 random 2 random (1)	2.8	73.1	73.9	0.8	0.0	21.6	21.6	1.6
	Specific restricted random	0.3	75.5	78.5	3.0	0.2	19.8	19.6	1.3
	Comparative experimental data (3,2,8)	0.3		78.7			19.0		2.0
4.	Cocoa butter, I, Sm-62.0								
	1,3 random 2 random (5)	2.7	81.8	82.3	0.5	0.0	15.3	15.3	0.7
	Specific restricted random	0.0	83.5	86.5	3.0	0.1	13.9	13.8	0.6
	Comparative experimental data (9)[c]	0.0		87.0			12.0		1.0
5.	Cocoa butter, II, Sm-59.9								
	1,3 random 2 random (1)	7.1	65.0	67.5	2.5	0.2	23.3	23.1	2.1
	Specific restricted random	0.0	71.7	81.0	9.3	0.6	17.7	17.1	1.3
	Comparative experimental data (9)[c]	0.0		81.0			18.0		1.0
6.	*Vateria indica* seed fat, Sm-57.3								
	1,3 random 2 random (6)	3.5	66.0	67.5	1.5	0.1	26.4	26.3	2.6
	Specific restricted random	0.2	69.3	73.8	4.5	0.4	23.7	23.3	2.3
	Comparative experimental data (3,2,8)	0.2		74.8			22.0		3.0
7.	Palm oil, Sm-50.1								
	1,3 random 2 random (5)	8.2	34.8	43.5	8.7	2.2	38.7	36.5	9.6
	Specific restricted random	6.2	36.8	47.2	10.4	2.7	37.5	34.8	9.1
	Comparative experimental data (3)	6.2		48.5			34.5		10.8
8.	Shea butter, Sm-45.2								
	1,3 random 2 random (5)	1.6	42.2	43.7	1.5	0.4	43.6	43.2	11.1
	Specific restricted random	0.0	43.8	46.8	3.0	0.7	42.4	41.7	10.9
	Comparative experimental data (10)[c]	0.0		49.0			38.0		13.0
9.	Mowrah oil, Sm-45.7								
	1,3 random 2 random (6)	2.8	39.7	42.7	3.0	0.8	43.2	42.4	11.3
	Specific restricted random	0.3	41.4	46.4	5.0	1.2	42.2	41.0	10.6
	Comparative experimental data (3,2,8)	0.3		50.0			36.7		13.0
10.	Neen oil, Sm-40.5								
	1,3 random 2 random (6)	1.6	30.5	32.8	2.3	0.9	47.7	46.8	17.9
	Specific restricted random	0.0	32.1	35.3	3.2	1.8	47.7	45.9	17.0
	Comparative experimental data (3,2,8)	0.0		41.0			41.0		18.0
11.	Ox depot fat, I, Sm-68.0								
	1,3 random 2 random (5)	28.8	32.8	48.6	15.8	2.2	20.1	17.9	2.5
	Specific restricted random	22.0	38.4	61.0	22.6	2.3	15.7	13.4	1.3
	Comparative experimental data (3,2,8)	22.0		60.0			18.0		0.0
12.	Ox depot fat, II, Sm-53.5								
	1,3 random 2 random (1)	12.6	30.6	43.7	13.1	3.4	35.3	31.9	8.4
	Specific restricted random	11.0	32.2	46.7	14.3	3.7	34.4	30.7	8.1
	Comparative experimental data (3,2,8)	11.0		48.3			32.2		8.5
13.	*Cassia auriculata* seed fat, Sm-28.1								
	1,3 random 2 random, maximum for S_2U and U_3	0.0		18.2			48.2		33.6
	Experimental (11)	0.0		28.2			27.7		44.1

[a] Sm = Saturated acids, molecules percentage.
[b] References under comparative experimental data denote source of original data for agreement with Glyceride Type Distribution Rule and GS_3 constants.
[c] S_3 contents were recalculated from original acetone crystallization data for calculating the GS_3 constants.

and the Glyceride Type Distribution Rule, to which the samples experimentally investigated for glyceride type structure conformed (3). Such adapted values are believed adequate for purposes of comparison.

The data for *Cassia auriculata* seed fat do not correspond completely with those for the other fats because pancreatic lipolysis data are lacking.

It will be observed that, for Samples 1–12, the 1,3-random 2-random figures (line one) are higher than the comparative values for S_3 (line three) by 1.6–6.9%, and for SU_2 (USU + UUS) by 2–10%. Those for S_2U (SUS + SSU) are lower than the comparative values by 5–14%. The U_3 values are too small for accurate comparison. In this series the total percentage of S is greater than 40.

In Sample 13 (*Cassia auriculata* seed fat), which has an S content of less than 30%, the maximum S_2U and U_3 possible by 1,3-random 2-random distribution (line one) are less than the experimental values (line two), and the minimum possible SU_2, according to this theory (line one), is higher than the experimental value (line two).

It is evident that there is consistent agreement between the molecular compositions in terms of S_3, S_2U, SU_2, and U_3 calculated on the assumption of specific restricted random distribution and the adjusted experimental values. It is equally evident that there is a consistent lack of agreement between the corresponding 1,3-random 2-random values and those mentioned.

It appears therefore that, in terms of S_3, S_2U, SU_2, and U_3, the specific restricted random values are more nearly accurate than those calculated according to the 1,3-random 2-random hypothesis. There is no positive evidence that the proportions of the isomeric forms of SUS-SSU and of USU-UUS are correct by either hypothesis, but the evidence favors the specific restricted random theory.

Appendix

The specific restricted random distribution values, calculated from the 1,3-random 2-random distribution (T) values and S_3 found, follow. a) Interchange randomly the S combined at the 2 position in the function [S_3(T) − S_3 found] with U combined at the 2 position in SUU(T) and U_3(T) so as to produce SSU from SUU and USU from U_3. This gives Derived Structure I. b) Interchange randomly the S combined at the 1 position in the function [S_3(T) − S_3 found] with U combined in the 1 and 3 positions in SUU(T), USU(T), and U_3(T) so as to produce SUS from SUU, USS from USU, and SUU from U_3. This gives Derived Structure II. c) Two-thirds of each component in Derived Structure I is to be combined with one-third of each component in Derived Structure II to give the specific restricted random distribution values.

A. R. S. KARTHA
Division of Chemistry
Indian Agricultural
Research Institute
New Delhi, India

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