SOME OBSERVATIONS ON THE CHEMISTRY OF GLYCERIDES—PART I

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THE investigation of the glyceride composition of a large number of fats by the more modern methods led Professor Hilditch[1] to suggest the rule of even distribution. The depot fats of the mammalia and various other land animals, a group of vegetable fats containing large proportions of C_{14} and lower saturated acids and the mammalian milk fats fall outside the scope of this rule. An attempt[2] has been made to explain this divergence on the basis of bio-hydrogenation followed by selective absorption to give depot fats; and a different mechanism to give mammalian milk fats.[3] Smith and Dastur[4] found a decrease of about 90% in the lower fatty acids of milk with an equivalent increase of oleic acid during fasting of cows. The finding was interpreted to indicate that the lower fatty acids represent intermediate products in the synthesis of oleic acid (see reference 24 for a similar idea). So far no attempt seems to have been made to account for the divergence in the group of vegetable fats.

Fractional crystallisation studies showed that the proportion of fully saturated glycerides in fats from different sources differ widely even when they have the same saturated-unsaturated acid ratio. Cacao butter,[5] *Garcina indica* fat[9] Borneo tallow[7] were found to contain not more than traces of fully saturated glycerides; whereas beef and mutton tallows[8] of similar saturated acid content and a Laurel kernal fat[9] of the same saturated-unsaturated acid ratio were found to contain 16% and 30% respectively of saturated glycerides. Further, Bailey[10] has shown that even those animal fats which contain fully saturated glycerides in proportions close to those required by chance distributions and which Longenecker[11] has suggested might probably be containing the other glyceride types also in proportions required by chance distribution, do not seem to fit into any established order. On interesterification of such fats,[12] fats differing greatly from the originals as regards physical properties resulted.

The synthesis of body fats and their transport by blood is also important in this connection. Parry and Smith[13] made the interesting observation that ox blood contains a high proportion of C_{20} and C_{22} unsaturated acids.

These acids must have a bio-synthetic origin as they are absent in the usual foodstuffs and consequently absent from the depot fats of the animals. Esterification of polyhydric alcohols[14] with mixtures of saturated and unsaturated acids produce fats with chance distribution of glyceride types. Since fats perform a number of vital functions[15] the formation of natural fats *in vivo* requires further study.

The GS_3 content in various natural fats are known with a reasonable degree of accuracy and in this contribution we are recording certain interesting conclusions regarding them. We have made use of published data[16] regarding GS_3-content and for other glyceride groups (forthcoming publication) we shall be drawing on our own results. Hilditch and Jones[17] pointed out an increase in the molar proportion of GS_3 corresponding to an increase in the proportion of saturated to unsaturated acids and that GS_3 varies as the cube of the molar percentage of saturated acids. It has also been pointed out[18, 19] that animal fats rich in stearic acid appear to be similar in GS_3-content and the mammalian milk fats resemble stearic rich animal fats as far as their GS_3 content is concerned. Whole tallows show GS_3-content higher than S^3, oleo-oils show consistently lower values, Bababssn fat[20] shows approximate identity; and so far as we know these constitute all the published references to the subject and is clearly limited to statements of approximate similarity of GS_3 to S^3 in certain groups of natural fats.

The relationship existing between GS_3 and S^3 may be expressed either as $GS_3 = K \times S^3$ or $S^3 \pm K$, where K is a constant. In the former case GS_3/S^3 remains a constant and in the latter $GS_3 - S^3$ is a constant. The mechanism involving the addition or elimination of a fixed quantity of fully saturated glycerides, irrespective of the saturated acid content, appears much less probable than one where a definite fraction of the fully saturated glyceride is always functioning. If the proportion of the trisaturated glyceride is related to the saturated acid content, the most likely relationship would be $GS_3 = K.S^3$.

We have already published a note[21] regarding one aspect of the question and a detailed examination of published data shows that K shows a maximum value in *Laurus nobilis* kernal fat,[22] where GS_3 is 41 and S^3 is 20·5 giving 2·02 as the value of K. Regarding the lower limit, it may be stated that it tends towards zero. Natural fats containing large proportions of myristic and lower saturated acids possess values for K in the neighbourhood of one, and are frequently of the positive type: the six palmæ fats showing a value for K within 1·05 ± 0·02, or the cow milk fats which give an average value of 1·11 for K. The internal depot fats of the land animals often belong to the positive group, although they do not generally contain any appreciable proportions of lower saturated acids.

The most interesting aspect of the study is the constant K, the value of which is so specific, that the nature and proportions of saturated or unsaturated acids, or the position of the source in the scale of evolution or the special functions which fats are likely to have, does not seem to affect it. Vegetable seed fats, which have been considered as excellent examples of the operation of the rule of even distribution, show this relationship well. The fruit-coat fats do not generally obey the rule of even distribution as regards the proportion of fully saturated glycerides or the variations due to differences in saturated acid content. However, stilling asebifera fats typical fruit coat fat show the GS_3/S^3 relationships, K being 0·75. *Myristica molabarica* fat was considered to be anomalous, but on the basis of the present conception it shows K to be 0·92. It is clear from the tabulated data that irrespective of the theory[23] concerning their origin, the depot fats show the GS_3/S^3 characteristics. The cow milk fats give the most important confirmation of our hypothesis and provide the widest variation in saturated acid content for the same fat from the same biologic source so far examined. The manner of variation of fully saturated glycerides with saturated acid content, considered a very special and characteristic relationship exhibited by mammalian milk-fats, should be explained in any theory concerning the genesis of these fats. Graham, Houchin, Peterson and Turner[24] have suggested that fat metabolism in the mammary gland probably takes the form of synthesis rather than breakdown. A close examination shows that milk-fats show no outstanding peculiarity demanding a special theory, the fully saturated glyceride content of cow milk-fats[24] is given by the equation $(1 \cdot 12 \pm 0 \cdot 02).S^3$, for buffalo milk-fat the constant is 0·98 and for sheep milk-fat 0·90. It is interesting to note that the abnormality in the fatty acid composition, due to ingestion[25, 26] of foreign fats in the diet, does not affect the constant; and it is clear that it is not necessary to assume anything fundamentally characteristic of the origin of mammalian milk-fats to explain the peculiar trisaturated glyceride: saturated acid ratio; as it is now clear that the mammalian milk-fats do not form any exception to the ordinary rules obeyed by all the other natural fats.

SUMMARY

A critical analysis of the trisaturated glyceride content of fats shows that the natural fats are characterised by definite numerical relationships between the proportions of GS_3 experimentally determined and those possible according to chance distribution and that the ratio between these is a specific characteristic of the source.

Name of Fat	S	GS_3	S^3	K	Group
1. *Cocos nucifora*[16] ..	93·9	86·0	82·8	1·04	Positive
	92·9	84·0	80·2	1·05	do
2. He goat–back tissue fat[27] ..	63·1	29·2	25·1	1·16	do
She goat– do ..	63·8	30·8	25·8	1·19	do
Mutton tallow[16] ..	61·0	26·6	22·7	1·17	do
3. Cow Milk Fat[16]—					
(*a*) English spring pasture ..	61·9	27·2	23·7	1·16	do
(*b*) do autumn feed ..	63·0	29·1	25·0	1·16	do
(*c*) do stall feed, soybean ..	70·0	38·2	34·3	1·11	do
(*d*) do do cocoanut cake ..	72·4	41·3	37·9	1·09	do
(*e*) New Zealand spring pasture ..	70·2	39·6	34·6	1·15	do
(*f*) Control ..	71·4	40·4	36·4	1·11	do
(*g*) Control ..	64·1	34·2	33·0	1·04	do
(*h*) Linseed oil in diet ..	61·3	24·8	23·0	1·08	do
(*i*) Rape oil in diet ..	59·4	25·3	21·0	1·20	do
(*j*) Cod-liver oil in diet ..	51·5	17·2	15·3	1·12	do
	50·6	14·6	12·9	1·13	do
4. Buffalo milk-fats– Sample 1[29] ..	74·9	41·7	42·0	0·99	do
2 ..	62·9	24·3	24·8	0·98	do
3 (Ref. 30) ..	70·1	34·3	34·5	0·99	do
5. *Manicraria saccifera*[16] ..	91·6	82·0	76·86	1·07	do
6. *Abrocomia sclerocarpa*[16] ..	86·3	69·0	64·27	1·07	do
7. *Astrocoryum tucama*[16] ..	88·0	73·0	68·16	1·07	do
8. *Eloeis guinonsis*[16] ..	85·3	66·0	62·0	1·06	do
9. Babassu kernal fat[20] ..	86·7	67·3	65·2	1·03	do
10. *Myristica malabartca*[16] ..	59·2	19·0	20·7	0·92	Negative
	56·2	16·0	17·7	0·91	do
11. *Stillingia sebifcra*[16] ..	72·5	28·4	38·0	0·75	do
	68·4	23·9	32·0	0·75	
12. Rat fat[16] ..	34·5	2·5	4·0	0·63	do
	37·0	3·5	5·0	0·70	do
13. Indian ox depot: Calcutta[28] ..	67·5	28·0	30·75	0·91	do
Bombay ..	72·9	36·0	38·7	0·93	do
14. *Shorea stenoptera*[16] ..	62·9	5·1	24·9	0·20	do
	62·8	4·5	24·8	0·18	do

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