70. On the Separation of Glycerides.

Part XIX. The Summarizing Discussion.

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The present writer¹⁾ has been engaged for the past 2 or 3 years, with his several co-workers, in isolating glycerides of natural fats and oils as bromides. Up to this day, 16 kinds of oils, including vegetable oils (2) and oils of marine animal origin (14), have been treated and 84 glycerides have been separated as shown in Table 1.

TABLE 1.

Bromides	M.P.	Occurrences
A. Simple glycerides		
Trizoomarin	Oil	Red salmon, Cuttle-fish, Shark
Triolein	"	Silkworm pupa, Sardine, Shark, Whale (skin)
(C ₂₂ H ₄₁ O) ₃ C ₃ H ₅ O ₃	"	Whale, Sand eel, Red salmon
Trilinolenin	166	Soy bean, Silkworm pupa
Tristearidonin	192 (decomp.)	Whale (skin)
(C ₁₈ H ₂₇ O) ₃ C ₃ H ₅ O ₃	74	Cuttle-fish
Triarachidonin	205 (decomp.)	Sardine, Cod (Sukedo), Shark, Cuttle-fish, Whale (bone)
B. 2 acidic mixed glycerides		
Dizoomaro-palmitin	Oil	Whale
Dizoomaro-stearin	"	Sand eel
Oleo-dipalmitin	"	Shark
Dioleo-palmitin	"	Silkworm pupa
Oleo-dizoomarin	"	Whale (bone)
Dioleo-zoomarin	"	Sand eel
(C ₂₂ H ₄₁ O) ₂ -gadolein	"	Herring
(C ₂₂ H ₄₁ O) ₂ -olein	"	Sardine
(C ₂₂ H ₄₁ O) ₂ -stearin	"	Cod
(C ₂₂ H ₄₁ O) ₂ -arachidonin	"	Sardine
(C ₂₂ H ₄₁ O) ₂ -clupanodonin	"	Sand eel
Linoleo-dizoomarin	"	Cod (liver), Herring, Sand eel, Red salmon, Whale
Dilinoleo-zoomarin	"	Sand eel
Linoleo-diolein	"	Linseed, Soy bean, Whale (bone)
Dilinoleo-olein	"	Linseed, Soy bean
Linoleo-digadolein	"	Herring, Sardine
Linoleno-dizoomarin	"	Cod, Cuttle-fish, Shark, Whale (bone)
Dilinoleno-zoomarin	65	Whale (bone)
Linoleno-diolein	86	Silkworm pupa

1) Proc. **3** (1927), 526-532; **4** (1928), 161-168; **5** (1929), 265-271; **7** (1931), 9-11.

Bromides	M.P.	Occurrences
Dilinoleno-olein	Oil	Soy bean
Linoleno-digadolein	„	Shark
Linoleno-dilinolein	78	Linseed, Soy bean
Dilinoleno-linolein	117	Linseed, Soy bean
Dilinoleno-linolein	158	Linseed
Dilinoleno-isolinolein	133	Silkworm pupa
Dilinoleno-isolinolein	154	Silkworm pupa
Linoleno-diarachidonin	115	Red salmon
Stearidono-dizoomarin	Oil	Cod
Distearidono-zoomarin	168 (decomp.)	Cod (skin)
(C ₁₈ H ₂₇ O) ₂ -linolenin	81	Cuttle-fish
C ₁₈ H ₂₇ O-distearidonin	125	Cuttle-fish
C ₁₈ H ₂₇ O-distearidonin	148	Whale (skin)
(C ₁₈ H ₂₇ O) ₂ -arachidonin	110	Sardine
(C ₁₈ H ₂₇ O) ₂ -arachidonin	126	Sand eel
(C ₁₈ H ₂₇ O) ₂ -clupanodonin	124	Sand eel
C ₁₈ H ₂₇ O-diclupanodonin	125	Cod (liver)
Arachidono-dizoomarin	Oil	*Cod (Sukedo)
Diarachidono-olein	200 (decomp.)	Whale
Diarachidono-olein	216 (decomp.)	Whale
Diarachidono-gadolein	180	Herring
Diarachidono-gadolein	220 (decomp.)	Whale (internal ordans)
(C ₂₂ H ₃₅ O) ₂ -arachidonin	85	Sardine
Diclupanodono-olein	132	Whale
Diclupanodono-linolenin	118	Cod (liver)
Diclupanodono-linolenin	165 (decomp.)	*Cod (Sukedo)
Diclupanodono-stearidonin	125	*Cod (Sukedo)
Diclupanodono-arachidonin	95	*Cod (Sukedo)
Diclupanodono-arachidonin	110	Shark
Clupanodono-diarachidonin	112	Cod (liver), Shark
Clupanodono-diarachidonin	140	Shark

C. 3 acidic mixed glycerides

Oleo-zoomaro-stearin	Oil	Whale (bone)
Linoleo-zoomaro-stearin	„	Whale (bone), *Cod (Sukedo)
Linoleo-oleo-stearin	„	Linseed, Sardine
Linoleno-oleo-palmitin	„	Silkworm pupa
Linoleno-zoomaro-stearin	„	Whale (bone), Herring
Linoleno-oleo-stearin	„	Linseed
Linoleno-C ₂₂ H ₃₅ O-gadolein	105	Herring
Stearidono-gadoleo-palmitin	Oil	Whale
Stearidono-linoleno-cetolein	172	Whale (skin)
Stearidono-C ₁₈ H ₂₇ O-zoomarin	135	Sardine
Stearidono-C ₁₈ H ₂₇ O-linolenin	122	Whale (skin)
Stearidono-C ₂₂ H ₃₅ O-zoomarin	120	Sardine
Stearidono-C ₂₂ H ₃₅ O-zoomarin	150	Herring
Arachidono-linoleo-zoomarin	255 (decomp.)	Cod
Arachidono-stearidono-zoomarin ..	148	Herring
Arachidono-linoleno-olein	145	Whale (bone)
Arachidono-linoleno-linolein	103	Red salmon
Arachidono-C ₁₈ H ₂₇ O-linolein	153	Sand eel
Clupanodono-linoleno-zoomarin	131	Cod, Whale (bone)
Clupanodono-stearidono-zoomarin ..	193	Whale (internal organs)
Clupanodono-C ₁₈ H ₂₇ O-zoomarin	220 (decomp.)	Cod (liver)

Bromides	M.P.	Occurrences
Clupanodono-arachidono-zoomarin .	105	Cod (liver)
Clupanodono-arachidono-zoomarin .	152 (decomp.)	Herring
Clupanodono-arachidono-olein	95	Whale (bone)
Clupanodono-arachidono-linolenin...	117	Shark
Clupanodono-C ₂₂ H ₄₁ O-linolenin	123	Whale (bone)
Clupanodono-C ₂₂ H ₃₅ O-linolenin	105	Whale (internal organs)

*Cod (Sukedo) *Theragra chalcogramma*.

Let us consider, for comparison, the glycerides of marine fishes. They are built of 1, 2 or 3 kinds of 13 fatty acids, including zoomaric, cetoleic,¹⁾ gadoleic, linolic, linolenic, stearidonic,²⁾ C₁₈H₂₈O₂,²⁾ arachidonic, C₂₂H₃₆O₂,²⁾ clupanodonic, palmitic and stearic acids. Of these 13 fatty acids, some 73 kinds of glycerides are composed. How these acids combine together in almost all possible ways in the glycerides of the table will be seen more clearly in Fig. 1. Acids connected with line occur simultaneously, once at least, in a glyceride.

The number of oils analyzed is very small, but even in these few cases, already, it is observed that the fatty acids occur as glycerides in almost every combination. When more cases were studied, it will be seen, with all probabilities, that ordinary fatty acids are coupled together

with other acids in every possible combination. In nature, there are almost innumerably different kinds of fats and oils composed of a comparatively few fatty acids and the fact is accounted for only by assuming that the acids are connected with glycerol in every possible combination and palmitation. Fig. 1 proves how this assumption is well founded.

The fact that fatty acids occur in glycerides in a free combination does not necessarily mean that the tissue of plants and animals synthesize them non-selectively. On the contrary, in surveying, again, Table 1, we will notice that the glycerides which occur in more than two

Fig. 1.

1) C₂₂H₄₂O₂ in Table 1 is most probably cetoleic acid.

2) These 3 acids are newly found by us. c.f. Proc. 4 (1928), 167; 5 (1929), 272-273.

oils are rather few, whereas most of them are found in only one oil and lacking in others. This selectiveness of the synthesis of organisms is shown more comprehensively in Table 2.

We found 10 and 11 acids respectively in herring and sardine oils, among them 8 acids (zoomaric, cetoleic, gadoleic, linolic, stearidonic, arachidonic, $C_{22}H_{38}O_2$, clupanodonic and stearic acid) are common to both, and 13 glycerides are built of the acids.

TABLE 2.

Heering	Sardine
Dicetoleo-gadolein	Triarachidonin
Linoleo-dizoomarin	Linoleo-digadolein
Linoleo-digadolein	($C_{22}H_{35}O$) ₂ -arachidonin
Diarachidono-gadolein	Stearidono- $C_{22}H_{35}O$ -zoomarin (M.P. 120)
Linoleno- $C_{22}H_{35}O$ -gadolein	
Stearidono- $C_{22}H_{35}O$ -zoomarin (M.P. 150)	
Arachidono-stearidono-zoomarin	
Clupanodono-arachidono-zoomarin (150 decomp.)	
Clupanodono-arachidono-zoomarin (152 decomp.)	

Identity or non-identity of the two linoleo-digadolein of both the oils has not been verified as the bromides were oily substances. The two clupanodono-arachidono-zoomarin decomposed at almost the same degree but their behaviors toward solvents were different.

The sardine and the herring belong to the same family and by far the larger part of the fatty acids are common to both the oils, and yet the glycerides built of these common acids are almost all different. This should be an example of the selectiveness of microorganisms in synthesizing fatty oils.

In the preceeding paper, the author, together with two others, set forth the view that the very fresh preparation of natural fats and oils is optically active and that the easy racemization of the glycerides is responsible for embarrassing the investigators, thus the matter whether fats and oils are active or not being hidden in ambiguity. Now that the activities of natural oils are verified, the author considers that it is an ample proof of the preferential occurrence of one antipode of a glyceride in a tissue of organisms as it is the case in carbohydrates and proteins.

In conclusion, we lay stress upon the facts that in living organisms either of the two antipodes of glycerides is selectively synthesized and that, by complicated combinations of fatty acids, a large number of glycerides are formed from a few basal units, the fats and oils being no exception among other biological constituents, with respect to these points.