105. *Unsaturated Fatty Acids and Their Derivatives.*

Part VIII. The Constitution of Clupanodonic Acid.

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In 1928, Tsujimoto¹⁾ investigated the constitution of clupanodonic acid by the ozonizing method and concluded that the acid should have either one of the constructions,

isolating, as oxidative fission products, CO_2 , acetaldehyde, propionic aldehyde and succinic acid and adopting the premise that one of the 5 ethenoid linkages will lie between the carbons 11 and 12, the fact of which Toyama²⁾ verified in the construction of cetoleic acid. The authors started the present study to affirm Tsujimoto's work by using the method of partial hydrogenation which one of the authors (Inoue) learned, together with B. Suzuki,³⁾ to be convenient and fruitful in similar cases. Our experimental results, however, have not been conformable with the construction proposed by Tsujimoto and clupanodonic acid has been shown to be docosa-4-in-11, 15, 18-trien-22-acid

For the procedures of hydrogenation, the previous Parts³⁾ are to be referred to and for the oxidation, Armstrong and Hilditch's⁴⁾ method has been exclusively adopted.

The clupanodonic acid used for the study had been prepared following Tsujimoto's⁵⁾ method but the distillation was carried out under the diminished pressure of 0.018–0.02 mm which is much lower than that used by Tsujimoto. The distillation was repeated several times and finally a fraction which distilled over at 174–175° C was gathered and used. To show the several constants; $d_4^{20}=0.9290$, $n_D^{20}=1.4868$, Br of the bromide 69.90% (10 atoms Br). It (10 g) was oxidized and the products, shown in the Table 1, were isolated and identified.

1) Bull. Tokyo Imp. Ind. Lav. **23** (1928), No. 3, 1.

2) J. Soc. Chem. Ind. Japan, **30** (1927), 597.

3) Proc. **6** (1930), 266; **7** (1931), 15.

4) J. Soc. Chem. Ind., **44** (1925), 43; 180.

5) J. Soc. Chem. Ind. Japan, **23** (1920), 272.

TABLE 1.

Acid	Yield (g)	m.p. (°C)	C (%)	H %	Reference
Butyric	2.0		39.63 (40.09)	5.92 (5.89)	as Zn-salt
Pimelic.....	2.5	104-105	52.38 (52.47)	8.08 (7.56)	
Succinic	2.5	185	40.71 (40.66)	5.38 (5.12)	
Adipic	0.1	149	48.99 (49.29)	6.59 (6.90)	
Malonic	0.5	132	34.38 (34.60)	4.09 (3.88)	
Oxalic	0.5	101	19.31 (19.04)	4.56 (4.80)	as (COOH) ₂ ·2H ₂ O

Tsujimoto obtained propionic aldehyde as mentioned above. Keeping this fact in mind, we searched exhaustively for propionic acid but no trace of it had been found. Adipic and oxalic acid were formed, presumably, by the secondary oxidation of pimelic and malonic acid respectively. We can count, therefore, butyric, pimelic, succinic and malonic acid as primary oxidation products, the total number of carbons of the products amounting, thus, to 18. If we assume that an atomic group of 4 carbons repeats twice in the chain, then the chain of 22 carbons will be completed. In this connection, it is noteworthy that the yield of succinic acid has been comparatively large. By this assumption, the total number of saturated carbon chain being 5, only 4 unsaturation centres are possible to exist. The brominations show, on the other side, definitely that decabromobehenic acid is obtained from clupanodonic acid, so that, if all unsaturation linkages be ethylenic, 5 of them should exist in the chain. What will be the centre in the construction which causes this seemingly contradicted phenomenon?

One of the striking properties of clupanodonic acid is that its iodine value is smaller than that calculated from Br content of the bromides. While theory requires 368.9, the estimated values were 340 (after 22 h) by Rosenmund's and 338.01 (after 24 h) by Wij's method. These values come between those to be given by 4 and 5 double bonds. This fact suggests to us that one of the unsaturation centres, at least, is not a simple ethylenic bond.

The partial hydrogenation did not run as smoothly as in the case of linolic or linolenic acid, 4 or 5 acids contaminating always one another. Naturally great pains were taken over the work of isolating each mixing component. It was found finally, however, that the object is attained by bromination method. The hydrogenated mixture was brominated in a suitable solvent and the bromides were isolated by treating with several solvents. As an example, a case, in which clupanodonic acid 2/5 hydrogenated (assuming 5 ethenoid linkages) was used, is shown:

If clupanodonic acid has 5 common ethenoid linkages, there is no reason for not expecting to encounter the octabromide in some stages of hydrogenation. With this consideration, the preparation of clupanodonic acid had been variously hydrogenated but in no case the desired substance had been found to be formed. Finally we arrived at the conclusion that, under our experimental conditions, clupanodonic acid does not stop at the 4/5 hydrogenated stage, the hydrogenation proceeding a step further.

The bromides were debrominated as usual, the debrominated acids were oxidized and the products were identified as follows:

From dibromide —stearic, succinic (1)
 tetrabromide —pentadecylic, malonic (2), oxalic (2), succinic (2)
 hexabromide —undecylic, malonic (3), oxalic (3), succinic (3)

The analyses of the products are

Acid	m.p. (°C)	C (%)	H (%)	Reference
Oxalic (2)	101	19.43 (19.04)	5.22 (4.80)	as (COOH) ₂ ·2H ₂ O
Oxalic (3)	101	19.62	4.99	"
Malonic (2)	132	34.14 (34.60)	4.42 (3.88)	
Malonic (3)	131-132	34.44	3.65	
Succinic (1)				identified with mix. test
Succinic (2)	184	41.11 (40.66)	5.45 (5.12)	
Succinic (3)	184	40.87	4.95	
Undecylic	27-27.5	51.48 (52.00)	7.90 (8.34)	Ba: 27.35 (27.06)
(as Ba-salt)	(free)			
Pentadecylic	69-70	58.65 (58.08)	9.32 (9.43)	Ba: 22.63 (22.16)
(as Ba-salt)	(free)			
Stearic	123-125	55.21 (55.84)	9.61 (9.12)	
(as Pb-salt)				

The molar proportion of the yield of succinic acid and the sum of those of malonic and oxalic acid, in the case of 3/5 hydrogenated acid, was 1.0:0.8 while, in more unsaturated acids, the proportion were about 2.2:1.0. We consider, therefore, that we are justified to suppose two maternal atomic groups of succinic acid in the latter cases, but only one for malonic acid. Then, to arrange the oxidation products in order,

Hydrogenated	The oxidation products					Br of bromide
0	butyric C:4	pimelic C:7	succinic	malonic	succinic	10
2/5	undecylic C:11		succinic C:4	malonic	succinic	6
3/5	pentadecylic C:15			malonic C:3	succinic	4
4/5	stearic C:18				succinic C:4	2
5/5	behenic C:22					0

From 2/5 hydrogenated acid, undecylic acid is obtained as above and, as it is a monobasic acid, the maternal atomic group should be situated in the left end of the chain. By the oxidation of clupanodonic acid, on the other hand, butyric and pimelic acid were formed from the corresponding unsaturated carbon chain so that we can assume, among 11 carbons concerned, only one unsaturation centre and it takes 4 atoms of Br. As unsaturated linkages which give anomalous iodine value, conjugated and accumulated double bonds are counted besides acetylenic bond. If the occurrence of the former bonds be the case, the oxidation products should be different, naturally, from those we obtained. Especially the existence of a conjugated double bond is out of probability for clupanodonic acid is not reducible by Na and alcohol. Accordingly, we have to choose, as the most possible case, the acetylenic linkage.

From the above considerations, we are able to deduce the following constitutions:

The further properties of the triple bond of clupanodonic acid are being studied, and we hope to be able to prove the existence of it from other sides.

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