Studies on the Partial Hydrogenation of Fish Oil. VIII. The Constituents of Docosatrienic Acid Produced on Hydrogenating Methyl Clupanodonate.

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In the 6th report(1) of this series, it was pointed out that two isomers, which vary in the degree of absorbing thiocyanogen, existed in docosatrienic acid produced on hydrogenating methyl clupanodonate. The one giving tetrarhodanate was subjected to ozonolysis, and among the resulting decomposition products, the following were identified, as was stated in the 7th report(2): propylaldehyde, propionic acid, succinic acid, succinic acid monomethyl ester, capric acid, adipic acid, nonanedicarboxylic acid, pimelic acid though not assuredly, heptoic or caprylic acid or both, carbon dioxide though in extremely small amount.

Monobasic acids such as propionic acid, capric acid, and heptoic or caprylic acid are to be formed from the terminal group opposite to the carboxyl group of the original acid, so that the formation of such monobasic acids shows that the original acid is not composed of a single compound, but of three or more isomeric acids of different chemical constitutions. The present paper deals with the constitutions of these isomers based on the decomposition products of ozonolysis which were described in the previous paper. Before this experiment, Inoue and Sahashi(3) had made an examination of the partially hydrogenated products of methyl clupanodonate; the products were separated into several fractions as bromides, and by subsequent oxidation with potassium permanganate in acetone, a fraction yielding a hexabromide was designated to be of the combination of the following acids: undecanoic acid (C_{11}), succinic acid (C_4), malonic acid (C_3), and succinic acid (C_4). It shows the existence of $\Delta^{4:5,\,7:8,\,11:12}$-docosatrienic acid in the hydrogenation product of methyl clupanodonate, but no other isomers were mentioned in their description. Thus, they gave to clupanodonic acid a formula having one triple and three double linkings. After that, Toyama and Tsuchiya(4),

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(1) Takano, *J. Soc. Chem. Ind., Japan,* **40** (1937), 165 B.

(2) Takano, *ibid.,* **40** (1937), 166 B.

(3) Inoue and Sahashi, *Proc. Imp. Acad.* (Tokyo), **8** (1932), 371.

(4) Toyama and Tsuchiya, this Bulletin, **10** (1935), 441.

applying ozonolysis to the amyl ester, proposed a formula having five double linkings, and recently⁽⁵⁾, oxidizing the methyl ester with permanganate in acetone and the potassium soap in aqueous solution, they confirmed their conclusion drawn before.

As was stated in the preceding paper, nearly all of the hexabromide of docosatrienic acid produced on bromination of partially hydrogenated clupanodonic acid, associating with tetrabromide, forms a petroleum-ether-insoluble oily substance, and, in general, these bromides can be difficultly separated from one another. Moreover, the docosatrienic acid yielding hexabromide was already found to consist of various isomers, and the oxidation products which were identified by the author markedly differ from those obtained by Inoue and Sahashi; they obtained undecanoic acid and malonic acid among the oxidation products, while in the present experiment, these acids were not formed to a perceptible extent.

Granting that malonic acid occur intermediately, it will, at the very moment of its occurrence, be converted into carbon dioxide and acetaldehyde or acetic acid by a further degradation. However, neither of them was detected in an appreciable amount. The fundamental differences between the author's results and Inoue and Sahashi's gave in conclusion different suggestions for the constituent and the constitution of docosatrienic acid giving hexabromide.

Now concerning the constitutions of isomers which may exist in docosatrienic acid, the author will discuss below.

(I) Ozonide Decomposition Products and Original Constructive Groups. For ozonolysis, 17 grams of methyl ester of docosatrienic acid $C_{22}H_{38}O_2$ giving tetrarhodanate was used, and its decomposition products obtained in usual manner gave some volatile matters (A) which were carried into water and baryta solution. The remaining not volatilized substances were then separated by filtration into two parts: the water-soluble portion (B) and the water-insoluble oily portion (C). From each portion, subsequently treated with petroleum ether, soluble and insoluble substances were obtained. The following oxidation products were identified.

Carbon dioxide. Carbon dioxide is believed to be formed by a secondary decomposition of the intermediate product derived from the group $=CH\text{-}CH_2\text{-}CH=$. However, its amount was extremely small scarcely amounting to 0.1% of the original sample, so that the isomer having this group may be an exceedingly minor constituent.

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(5) Toyama and Tsuchiya, this Bulletin, **11** (1936), 745, 751.

Propylaldehyde and propionic acid. Propylaldehyde, contaminated with propionic acid, was detected in aqueous solution of volatile matters (A). To determine its content, the solution was analysed by using $NaHSO_3$ and iodine solution. A greater part of propionic acid was obtained as barium-salt from the petroleum-ether-soluble substance of the not volatilized water-soluble portion (B). Both of these products seem to be derived from the same group CH_3-CH_2-$CH=$. Assuming that one such group exists in the original ester, the theoretical yield as propionic acid is 21.4%, while the experiment yielded only 3%, all being calculated as the acid. Hence, the presence of isomer I containing this group may be less than 10% of the total.

Succinic acid and its monomethyl ester. Succinic acid was obtained from the petroleum-ether-insoluble part of the not volatilized portion (B). Formation of this acid evidently shows the existence of the group $=CH$-$(CH_2)_2$-$CH=$, and if one such group exists in the original ester, the isomer having this group should be 33.5% of the original ester. In view of the fact that the experimental content of succinic acid is by far greater than is calculated theoretically on the assumption, that there exists only one such group in each isomer, there seems to exist some isomer which has two such groups. On saponifying the not volatilized water-insoluble portion (C), petroleum-ether-insoluble succinic acid was liberated, whereby succinic acid monomethyl ester was suggested to exist in the portion mainly. Taking a little operative loss into consideration, the amount of this ester altogether seems to be 30–35% of the original sample. This is derived from the group $=CH$-$(CH_2)_2$-$COOCH_3$, and if one such group in average exists in the original sample, it should be 37.9%. Therefore, the existence of one group may be supposed in every isomer.

Monobasic acids of higher molecular weights excepting propionic acid. In the petroleum-ether-soluble part of the not volatilized water-soluble oily portion (C), there was suggested the existence of either heptoic acid or caprylic acid, otherwise, both of these acids. On distilling the collected substances, two fractions were obtained; the one having lower boiling point gave neutralisation value 395.5 and the other having higher boiling point 340.7, respectively. Accordingly, these monobasic acids proved to be contained in the former fraction, and a small portion of the acids mixed with propionic acid will possibly remain in the petroleum-ether-soluble part of the water-soluble portion (B). Heptoic and caprylic acids are derived from CH_3-$(CH_2)_5$-$CH=$ and CH_3-$(CH_2)_6$-$CH=$, respectively. If either of these groups is to be contained in a proportion of one group to the original ester, it will be found in a range of 37–40%. Eventually, isomer II giving either heptoic or caprylic acid seemed to be the most plentiful, amounting to a half of the original sample. The component of the latter fraction having higher boiling point mainly consisted of capric acid. Its amount was by far smaller than that of the acids which were contained in the former fraction. The presence of capric acid indicates the existence of isomer III having the group $CH_3\text{-}(CH_2)_8\text{-}CH=$. The quantity of this isomer (III) seemed to be somewhat greater than that of isomer I.

Dibasic acids of higher molecular weights. Adipic acid together with nonanedicarboxylic acid was found in the petroleum-ether-insoluble substances of not volatilized water-soluble portion (C). This acid is evidently derived from the group $=CH\text{-}(CH_2)_4\text{-}CH=$, and from one such group contained in the original ester, 40% is to be obtained. The existence of pimelic acid was recognized, though not assuredly, in the same portion as adipic acid. Therefore, it shows the presence of the group $=CH\text{-}(CH_2)_5\text{-}CH=$. Nonanedicarboxylic acid, being inferred to exist in a smaller extent than adipic acid, was found also in the same fraction as before. This acid is produced obviously from the group $=CH\text{-}(CH_2)_9\text{-}CH=$, and taking into consideration the theoretical yield from one such group existed in the original sample, an isomer having this group seems to exist in a range of 5–10%.

(II) Kinds of Isomers and Their Chemical Constitutions. Clupanodonic acid is already known to be a normal chain compound by the fact that it is converted into behenic acid having a series connection of 22 carbon atoms on complete hydrogenation. Hence every isomer of docosatrienic acid which is produced from clupanodonic acid by partial hydrogenation will be also normal chain compound. The terminal group opposite to the carboxyl group always gives monobasic acid for every isomer. Of the isomers, which are suggested by the production of the monobasic acids, the existence of the following isomers will be most probable: isomer I giving propionic acid; isomer II which gives either heptoic or caprylic acid or both; isomer III giving capric acid.

The group on the side of the carboxyl group is identical giving the same succinic acid for every isomer. These isomers are also proved to have three double linkings in different positions. It may be considered, therefore, that each of the three isomers described above contains, besides two terminal groups already mentioned, two more groups which give respective dibasic acids in the middle position of the carbon chain. One of the two dibasic acids which come from the middle of the respective chain is succinic acid, the other being adipic acid, nonanedicarboxylic acid, and probably succinic acid, respectively. Consequently, the following distribution is proposed regarding the variety of combinations of the derived acids, counting their yields and arranging the numbers of their carbon atoms so as to make 22 in total:

Isomer	Monobasic	Dibasic	Dibasic	Dibasic
I (C_{22})	propionic (C_3)	nonanedicarboxylic (C_{11})	succinic (C_4)	succinic (C_4)
II (C_{22})	heptoic (C_7)	pimelic (C_7)	succinic (C_4)	succinic (C_4)
	caprylic (C_8)	adipic (C_6)	succinic (C_4)	succinic (C_4)
III (C_{22})	capric (C_{10})	succinic (C_4)	succinic (C_4)	succinic (C_4)

For isomer II, two combinations are made, viz. $C_8C_6C_4C_4$ and $C_7C_7C_4C_4$. Furthermore in respect to isomers I and II, the following combinations may be possible:

I: $C_3C_4C_{11}C_4$; II: $C_8C_4C_6C_4$ and $C_7C_4C_7C_4$.

The double linkings suggested from these forms show multifarious positions, so that they are inconvenient to judge of the constitution of the clupanodonic acid. The distribution given first is more convenient to explain the positions of double linkings in clupanodonic acid; the distribution shows that the two double linkings near the carboxyl group in each isomer are identically situated at the positions 4:5 and 8:9, accordingly it will be concluded that these isomers are derived from the clupanodonic acid having double linkings at the position 4:5 and 8:9. Eventually, among the isomers of docosatrienic acid produced by hydrogenation of methyl clupanodonate, four following isomers should be suggested:

I: $CH_3\cdot CH_2\cdot CH{=}CH\cdot (CH_2)_9\cdot CH{=}CH\cdot (CH_2)_2\cdot CH{=}CH\cdot (CH_2)_2\cdot COOH$

II: (a) $CH_3\cdot (CH_2)_6\cdot CH{=}CH\cdot (CH_2)_4\cdot CH{=}CH\cdot (CH_2)_2\cdot CH{=}CH\cdot (CH_2)_2\cdot COOH$

(b) $CH_3\cdot (CH_2)_5\cdot CH{=}CH\cdot (CH_2)_5\cdot CH{=}CH\cdot (CH_2)_2\cdot CH{=}CH\cdot (CH_2)_2\cdot COOH$

III: $CH_3\cdot (CH_2)_8\cdot CH{=}CH\cdot (CH_2)_2\cdot CH{=}CH\cdot (CH_2)_2\cdot CH{=}CH\cdot (CH_2)_2\cdot COOH$

Of these acids, isomer II seemed to be of the largest quantity and isomer I the smallest, the yields of their decomposition products being taken into account. Supposing that these isomers are the main components of docosatrienic acid, the existence of two double linkings at the positions 4:5 and 8:9 throughout every isomer will show that these linkings, originally contained in clupanodonic acid, must have remained unattacked, though they are easily attacked by thiocyanogen. Moreover, from the above formulæ, assuming that no displacement of unsaturated linkings occurred during hydrogenation, it may be suggested that there is possibility of the existence of such double linkings as 12:13, 14:15, 15:16 and 19:20 in the clupanodonic acid. Judging from the result of the investigation of the oxidation products, a form, which keeps both of the double linkings 14:15 and 15:16, is impossible to exist in clupanodonic acid. Therefore, the suggestion is that, an existence of either combination 12:13, 14:15, 19:20 or 12:13, 15:16, 19:20 is possible, and that, one of the double linkings 14:15 and 15:16 is formed by the displacement of the other. Two following formulæ are made for clupanodonic acid from the above combinations.

(a) $\Delta^{4:5,\ 8:9,\ 12:13,\ 14:15,\ 19:20}$-docosapentenic acid;

(b) $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenic acid.

Concerning its constitution, the formulæ described below were hitherto proposed:

$\Delta^{4:5,\ 7:8,\ 11:12,\ 15:16,\ 19:20}$-docosapentenic acid or $\Delta^{4:5,\ 8:9,\ 11:12,\ 15:16,\ 19:20}$-docosapentenic acid by Tsujimoto(6);

$$CH_3\cdot(CH_2)_2\cdot C{\equiv}C\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$$

by Inoue and Sahashi, also maintained by Inoue and Kato(7);

$$CH_3\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot CH_2\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot CH{=}CH\cdot(CH_2)_2\cdot COOH$$

by Toyama and Tsuchiya, who established this formula by further investigations(5).

Of the formulæ described by the present author, (b) is quite identical with that proposed by Toyama and Tsuchiya. In compliance with this formula, it will be understood that the double linking 14:15 was formed by a displacement of 15:16 in the course of hydrogenation. It was already pointed out in the previous report that the hydrogenation always tends to take place selectively in the unsaturated linking which hardly absorbs thiocyanogen. Toyama and Tsuchiya(8) had subjected the clupanodonic acid to selective absorption of thiocyanogen in various graduations for the purpose of investigation of its constitution, whereby its tetrarhodanate indicated an absorption of thiocyanogen in unsaturated linkings near the carboxyl group; i.e. 4:5 and 8:9. It is evident through this experiment that the unsaturated linkings 4:5 and 8:9 which absorb

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(6) Tsujimoto, this Bulletin, **3** (1928), 299.

(7) Inoue and Kato, *Proc. Imp. Acad.* (Tokyo), **10** (1934), 463.

(8) Toyama and Tsuchiya, *Repts. Tokyo Imp. Ind. Research Inst. Lab.*, **30** (1935), No. 6.

thiocyanogen show more difficulties than the other in hydrogenation, while, on the contrary, the unsaturated linkings 12:13, 15:16 and 19:20 which are unattacked by thiocyanogen are comparatively easily hydrogenated.

The docosatrienic acid together with docosadienic acid is an important component which occurs in the course of hydrogenation of clupanodonic acid; this amounts to half quantities of the total products, when all the original clupanodonic acid just disappeared by hydrogenation, and it is noticeable that this acid has somewhat great drying property, though in a little less degree than linolenic acid which belongs to the same series and is found in vegetable drying oils.

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