THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. III. THE ISOLATION AND CONSTITUTION OF MOROCTIC ACID $C_{18}H_{28}O_2$.*

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In the first paper(1) of this series it was shown concerning the highly unsaturated C_{18}-acids of sardine oil that the sardine oil contained an octadecatetraenoic acid $C_{18}H_{28}O_2$, and also the occurrence of an octadecatrienoic acid $C_{18}H_{30}O_2$ was indicated. In this paper the results of our further experiments concerning the octadecatetraenoic acid are described. Whilst this acid could not be isolated in the previous experiments, we have this time achieved its isolation by using a large quantity of sardine oil. Although the occurrence of octadecatetraenoic acid in sardine oil and in other marine animal oils has hitherto been stated by various authors, the acids described as an octadecatetraenoic acid by earlier authors represented, in some cases, a mixture of several highly unsaturated acids, and no octadecatetraenoic acid appears to have been isolated with certainty before our experiments. We designate the octadecatetraenoic acid isolated from sardine oil as moroctic acid.(2)

In order to determine the constitution of moroctic acid, methyl moroctate was oxidised by the ozonide method in the first place. Among the decomposition products of the ozonide, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde, acetic acid, acetaldehyde, carbon dioxide, methyl hydrogen succinate and the corresponding semi-aldehyde were recognised; the presence of malonic acid was also indicated. Of these decomposition products, propionic acid and propyl aldehyde are derived from the $CH_3{\cdot}CH_2{\cdot}CH{=}$ group, while succinic acid and its semi-aldehyde from the $=CH{\cdot}(CH_2)_2{\cdot}CH{=}$ group, and it was found from the yield of succinic acid and its semi-aldehyde that methyl moroctate contained two of the $=CH{\cdot}(CH_2)_2{\cdot}CH{=}$ group. The presence of acetic acid, acetaldehyde, carbon dioxide together with malonic acid is explainable

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* Translated from the paper published in Japanese in the Report of Tokyo Imperial Industrial Research Laboratory, **27** (1932), No. 2.

(1) Toyama and Tsuchiya, this Bulletin, **4** (1929), 83.

(2) The name is derived from "Morokuti" (Japanese) which is one of a few other names given to Japanese sardine.

on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group which on oxidation yields primarily malonic acid and the corresponding aldehyde, from which acetic acid, acetaldehyde and carbon dioxide are formed by the secondary decompositions thus: $HOOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COOH + CO_2$ or $HOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COH + CO_2$. Finally the methyl hydrogen succinate and the corresponding semi-aldehyde are derived from the $=CH\cdot (CH_2)_2\cdot COOCH_3$ group, showing that free moroctic acid has the $=CH\cdot (CH_2)_2\cdot COOH$ group. From these results, moroctic acid is found to contain the following groups: $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot CH_2\cdot CH=$, $=CH\cdot (CH_2)_2\cdot CH=$ (two), and $=CH\cdot (CH_2)_2\cdot COOH$. Accordingly its constitution is expressed by one of the following formulae:

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

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

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

In order to determine which of these formulae is correct, we have successfully applied the principle of selective addition of thiocyanogen to the poly-ethylenic acids.(3) After having found by determining the thiocyanogen value of methyl moroctate that thiocyanogen adds selectively to two of the four ethylenic linkings in methyl moroctate, yielding a tetrathiocyanate, we have prepared tetrathiocyanate of methyl moroctate and subjected the latter to ozonolysis. Among the decomposition products, propionic acid, propyl aldehyde, acetic acid, acetaldehyde, carbon dioxide and an oily substance containing thiocyano-groups were recognised; also malonic acid seemed to be present. Of these products, propionic acid and propyl aldehyde are derived from the $CH_3\cdot CH_2\cdot CH=$ group, and acetic acid, acetaldehyde and carbon dioxide together with malonic acid are considered to come from the $=CH\cdot CH_2\cdot CH=$ group. It is seen from these results that the two groups, $CH_3\cdot CH_2\cdot CH=$ and $=CH\cdot CH_2\cdot CH=$, in methyl moroctate remained unsaturated when thiocyanogen was allowed to act upon methyl moroctate. Of the three formulae given above, only the formula (I) is consistent with these facts, and it should be concluded that tetrathiocyanate of methyl moroctate is formed by the selective addition of thiocyanogen to the two ethylenic linkings (4:5 and 8:9) lying near the carboxyl group in the formula (I), leaving the other two ethylenic linkings (12:13 and 15:16) unsaturated. The oily substance formed on ozonolysis of tetrathiocyanate had still thiocyano-groups. It must, therefore, contain monomethyl ester of 3,4,7,8-tetrathiocyano-

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(3) P. H. Kaufmann, *Arch. Pharm.*, **263** (1925), 675.

decane- 1,10-dicarboxylic acid. This was verified by the fact that on elimination of thiocyanogen from the oily substance followed by hydrolysis, there was obtained a decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid) which yielded on hydrogenation decane-dicarboxylic acid. From these results, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid expressed by the formula (I).

Of the unsaturated C_{18}-acids found in the natural fats and oils, the most widely distributed acids are oleic ($\Delta^{9:10}$), linolic ($\Delta^{9:10,\ 12:13}$), and linolenic ($\Delta^{9:10,\ 12:13,\ 15:16}$) acids. Comparing these acids with moroctic acid, there exist the following relations between the positions of respective ethylenic linkings. Thus the 9:10 ethylenic linking is common to oleic, linolic and linolenic acids, but it does not occur in moroctic acid; the 12:13 ethylenic linking is common to linolic, linolenic and moroctic acids, while the 15:16 ethylenic linking is common to linolenic and moroctic acids. Although there are found, besides the above-mentioned acids, petroselinic ($\Delta^{6:7}$), vaccenic ($\Delta^{11:12}$), γ-linolenic ($\Delta^{6:7,\ 9:10,\ 12:13}$),(4) and elaeostearic ($\Delta^{9:10,\ 11:12,\ 13:14}$) acids as naturally occurring unsaturated C_{18}-acids, neither 4:5 nor 8:9 ethylenic linking occurs in these acids except moroctic acid.

Experimental.

1. **The Isolation and Properties of Moroctic Acid and its Methyl Ester.** The ethyl esters (60 kg.) obtained by ethanolysis of sardine oil were subjected to distillation, and the distillate (28.5 kg.) boiling below 215°/10 mm. was collected separately. This was converted into free fatty acids, and the latter were dissolved in 85% methanol and cooled to separate crystalline solids which were filtered off. An aqueous solution of lithium hydroxide was added to the filtrate, and the insoluble lithium soaps were filtered. From the filtrate, the remaining fatty acids (7.5 kg.) were recovered and converted into methyl esters, from which a fraction (5.9 kg.) boiling below 215°/15 mm. was obtained on distillation. This was brominated in ethereal solution, and the ether insoluble bromides obtained were separated by means of benzene. The details of the above experiments were already described in the previous report(5) in which the benzene soluble bromides (1.5 kg.) were worked up for the isolation of hiragonic acid. In this paper the benzene insoluble bromides (900 g.) were debrominated and the product was fractionated to yield methyl moroctate. The debromination of the benzene insoluble bromides was carried out as follows: to the mixture of 100 g. of the bromides and 50 g. of zinc powder, 150 c.c. of alcohol was added. Unlike the case with the benzene soluble bromides described in the previous report, no appreciable heat evolution occurred. The mixture was gently refluxed by heating on the

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(4) A. Eibner, L. Widenmayer and E. Schild, *Chemische Umschau Fette, Oele, Wachse und Harze*, **34** (1927), 312.

(5) This Bulletin, **10** (1935), 192.

water-bath, and 150 c.c. of 5 N alcoholic solution of hydrogen chloride was added in the course of 2.5 hours, another 50 g. of zinc powder being added in several portions. When all the alcoholic solution of hydrogen chloride has been added, heating was continued for one hour more, after which the alcoholic solution was removed by decantation. The residual insoluble substance was again refluxed with alcohol and zinc powder, and alcoholic solution of hydrogen chloride was added as before. The alcoholic solution was filtered, and the final residue was washed with alcohol. From the united alcoholic solution, the debrominated products were separated on addition of a large quantity of water, and extracted with ether. Since the products obtained from the ethereal solution were suspected to contain unsaponifiable substance, though it might have been a minute amount, they were saponified and the resulting soap solution was extracted with ether to remove unsaponifiable substance, after which the soap solution was decomposed with hydrochloric acid to yield the free fatty acids, and then the latter were reconverted into methyl esters. From 900 g. of the bromides there were obtained 220 g. of debrominated methyl esters. These were repeatedly fractionated, and a fraction (48 g.) boiling at 208–213°/15 mm. was finally obtained as methyl moroctate; d_4^{15} 0.9174, d_4^{20} 0.9140, n_D^{15} 1.4849, n_D^{20} 1.4829, mol. refr. 90.66 (calc. for $C_{19}H_{30}O_2\lvert\overline{\overline{4}}$: 89.73), saponification value 193.3 (calc. 193.3), iodine value by the Rosenmund-Kuhnhenn method 344.6 (calc. 349.8), thiocyanogen value 173.1 (calc. for the formation of tetrathiocyanate $C_{19}H_{30}O_2(SCN)_4$: 174.9). On brominating methyl moroctate in ethereal solution, it yielded 57% of ether insoluble bromide which melted at about 215° to a tar-like substance (Found: Br, 68.65. Calc. for $C_{19}H_{30}O_2Br_8$: Br, 68.78%).

Moroctic acid liberated from its methyl ester in the usual way had the following constants (Found: C, 78.12; H, 10.25. Calc. for $C_{18}H_{28}O_2$: C, 78.20; H, 10.22%): d_4^{15} 0.9334, d_4^{20} 0.9297, n_D^{15} 1.4930, n_D^{20} 1.4911, mol. refr. 86.00 (calc. for $C_{18}H_{28}O_2\lvert\overline{\overline{4}}$: 84.99),(6) neutralisation value 201.7 (calc. 203.1), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 372.6 and 361.9 respectively (calc. 367.6). On brominating moroctic acid in ethereal solution, it yielded 58% of ether insoluble bromide which melted at about 220° to a tar-like substance (Found: Br, 69.72. Calc. for $C_{18}H_{28}O_2Br_8$: Br, 69.83%). The hydrogenation product of moroctic acid yielded, after recrystallisation from 95% alcohol, a pure stearic acid; neutr. value 196.7 (calc. 197.4), m.p. and mixed m.p. 69.5–70°.

2. **Ozonolysis of Methyl Moroctate.** Methyl moroctate (5 g.) was dissolved in chloroform (50 c.c.), cooled with ice-salt, and a current of ozonised oxygen was passed through the solution until it became saturated, after which the chloroform was distilled by heating on the water-bath under diminished pressure. As it was found by a preliminary experiment that the ozonide was exceedingly unstable and decomposed explosively on undue heating, the temperature of water-bath was kept at about 40°C. When most of the chloroform was driven off, the distillation was stopped since there was a danger of frothing of the residue. The ozonide remained as a light yellow viscous liquid which is probably not a normal ozonide but an ozonide peroxide. From

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(6) It should be noted here that moroctic acid and its methyl ester, like hiragonic acid, showed a slight exaltation of mol. refr. This was also observed with decadienedicarboxylic acid which was obtained in the experiments of the ozonolysis of tetrathiocyanate described below. The cause of this exaltation of mol. refr. is unknown to us.

20 g. of methyl moroctate, there was obtained 35 g. of ozonide (175%) which was not thoroughly freed from chloroform. The calculated yields for normal ozonide $C_{19}H_{30}O_{41}$ and ozonide peroxide $C_{19}H_{30}O_{15}$ are 165.9 and 171.4%, respectively. Water (200 c.c.) was then added to the ozonide in a flask, and the liquid was heated for about 30 minutes on the water-bath in a current of hydrogen. In order to recover the volatile decomposition products carried over with hydrogen, the flask was attached by a delivery tube to another three flasks which were connected in succession, the first **(a)** being filled with 200 c.c. of water and cooled with ice, the second **(b)** and the third **(c)** being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The products of ozonolysis were thus separated into two parts: (i) volatile decomposition products and (ii) decomposition products which were not carried over with hydrogen.

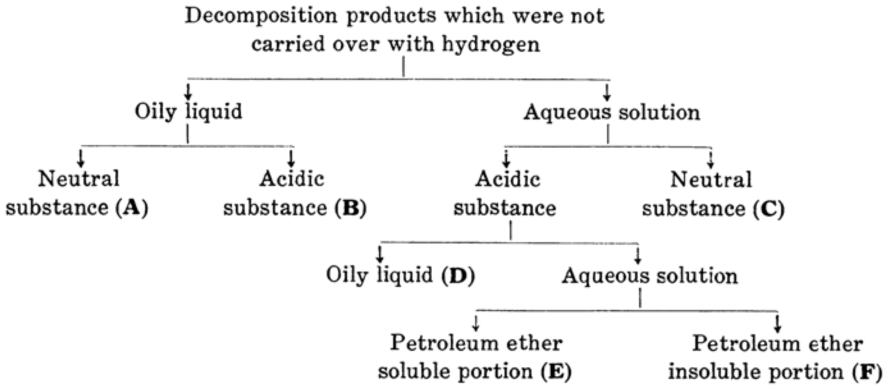
(i) *Volatile decomposition products.* These were collected in three flasks (**a**, **b** and **c**) as stated above. The aqueous solution in the flask **(a)** gave a pink colouration with Schiff's reagent and indicated the presence of acetaldehyde by a deep blue colouration produced on adding diethylamine and sodium nitroprusside. On adding phenylhydrazine, it yielded an oily phenylhydrazone which, after being washed with acetic acid, was heated with zinc chloride to 180°, when a smell of scatol was recognised, and consequently the presence of propyl aldehyde in the aqueous solution in the flask **(a)** was indicated. In order to effect a partial separation of acetaldehyde and propyl aldehyde, 50 c.c. of the aqueous solution was heated in a flask $(\mathbf{a}_1)$ to 45°, and a current of carbon dioxide was passed through the solution to drive off the volatile portion at 45°; it was then caught by means of passing through an ice-cold water in another flask $(\mathbf{a}_2)$ which was connected to the flask $(\mathbf{a}_1)$ by a delivery tube. The solution remained in the flask $(\mathbf{a}_1)$ precipitated, on adding *p*-nitrophenylhydrazine and hydrochloric acid, 0.7 g. of *p*-nitrophenylhydrazone which on recrystallisation from 50% alcohol yielded an impure *p*-nitrophenylhydrazone of propyl aldehyde in orange yellow needles; m.p. 121.5–122° (Found: N, 21.82. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask $(\mathbf{a}_2)$ yielded 0.5 g. of *p*-nitrophenylhydrazone which, on fractional crystallisation from 50% alcohol, gave 1st crop with m.p. 116.5–117°, 2nd crop with m.p. 115.5–116° and 3rd crop with m.p. 113–113.5°. The 1st crop was found to consist of a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde by analysis (Found: N, 22.83. Calc. for $C_9H_{11}O_2N_3$: N, 21.76. Calc. for $C_8H_9O_2N_3$: N, 23.46%).

The solution in the flask **(a)** showed also acid reaction. On neutralising this solution (100 c.c.) with barium hydroxide and evaporating to dryness, there remained 0.25 g. of barium salt which was found to be barium acetate by analysis (Found: Ba, 53.30. Calc. for $C_4H_6O_4Ba$: Ba, 53.73%).

The barium hydroxide solution in the flask **(b)** was found to contain precipitate of barium carbonate, which was also formed in a smaller amount in the solution of the flask **(c)**. The quantity of carbon dioxide formed by the ozonolysis is calculated from the quantity of the barium carbonate as 2.58 g. or 12.9% of the methyl moroctate used for ozonolysis. The formation of carbon dioxide in such a large amount is explainable on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group. The latter on ozonolysis yields malonic acid and its semi-aldehyde which, however, undergo secondary decompositions with the formation of carbon dioxide together with acetaldehyde and acetic acid, and the yield of carbon dioxide is 15.2% of methyl moroctate when the secondary decompositions take place to a quantitative extent. The reason why the yield of carbon dioxide was not quantitative in this experiment may be attributed to the fact that a part of the primary decomposition products escaped the secondary decomposition and remained unchanged.

(ii) *Decomposition products which were not carried over with hydrogen.* A portion of these products separated under aqueous solution as an oily liquid. This was neutralised with sodium carbonate solution, the resulting solution was extracted with ether, and after distilling off the ether from ethereal solution, there remained a neutral substance (**A**). The neutralised solution, separated from ethereal extracts, was acidified with hydrochloric acid and an acidic substance (**B**) liberated was taken up with ether. The aqueous solution, separated from the oily liquid, was shaken with 2 l. of ether in order to extract the decomposition products thoroughly from the aqueous solution. The ethereal solution was concentrated to about 200 c.c., and then shaken with sodium carbonate solution to remove the acidic substance as sodium salts. The ethereal solution left behind a neutral substance (**C**) on distilling off ether. The carbonate solution containing the sodium salts of acidic substance was acidified, and the acidic substance liberated was taken up with ether. After distilling off the ether, 60 c.c. of water was added to the residue; a portion remained undissolved as an oily liquid (**D**) which was separated by filtration. The aqueous solution which contained dissolved substances was extracted with ether, and the product obtained on distilling off the ether was then treated with petroleum ether in order to effect a separation into petroleum ether soluble portion (**E**) and petroleum ether insoluble portion (**F**). The portions obtained by these separative operations are shown in Table 1.

Table 1.



Neutral substance (**A**). Yield 0.7 g. It had saponif. value 477.4 which is close to the saponif. value 483.4 for methyl ester of succinic semi-aldehyde $C_5H_8O_3$. After saponification it was subjected to oxidation with potassium permanganate in alkaline solution, and the crystalline product obtained on acidification showed, after being washed with a little ether, neutr. value 948.1 (calc. for succinic acid $C_4H_6O_4$: 950.6) and m.p. 180–180.5° which was not lowered when the substance was admixed with a pure specimen of succinic acid, m.p. 182.5–183°.

Acidic substance (**B** and **D** united). Yield 6.3 g., neutr. value 422.9, saponif. value 830.5 Although the neutr. value agrees with the calculated value for methyl hydrogen succinate $C_5H_8O_4$ (neutr. value 424.9; saponif. value 849.7), and the saponif. value is also close to the calculated value for methyl hydrogen succinate, the acidic substance obtained is an oily liquid at the ordinary temperature and it is considered to contain some other compounds besides methyl hydrogen succinate, since the melting point of the latter is recorded as 58° by Bone, Sudborough, and Sprankling.(7) The free acid obtained on saponification followed by acidification yielded, however, a pure succinic acid with neutr. value 948.5 and m.p. 182–183° after being recrystallised from ethyl acetate.

Neutral substance obtained from aqueous solution (**C**). Yield 1.2 g. It consisted of an orange yellow liquid and had saponif. value 380.4. After saponification, it was subjected to the permanganate oxidation in alkaline solution, and the crystalline product obtained on acidification showed neutr. value 940.9 and m.p. 178.5–179° after being washed with a little ether, and it was considered to be an impure succinic acid. Accordingly, this portion seems to contain methyl ester of succinic semi-aldehyde and in addition succinic aldehyde (or its polymerised products).

Petroleum ether soluble portion (**E**). On distilling off the petroleum ether from the solution, the distillate showed acid reaction. The barium salt prepared from the distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.01. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (2.7 g.) obtained on distilling off petroleum ether was a reddish orange liquid. On heating in an oil bath, about 1 g. of colourless distillate was obtained between 120–180° (temperature of bath). The distillate was neutralised with sodium hydroxide solution, and silver nitrate solution was added to precipitate silver salts fractionally; those were found to be a mixture of silver acetate and silver propionate by analyses (Found for 1st precipitate: Ag, 60.61. Found for 2nd precipitate: Ag, 62.45. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

Petroleum ether insoluble portion (**F**). Yield 15.4 g. This portion consisted of a reddish orange liquid and a crystalline solid. On oxidation with alkaline permanganate, there was obtained, after acidification, a white crystalline product which yielded succinic acid on recrystallisation from ethyl acetate; neutr. value 948.1, m.p. 182.5–183°. On concentrating the mother liquor, a further quantity of succinic acid separated, and after all the ethyl acetate being driven off, there remained a soft solid. A little water was added to the residue, a small portion of insoluble substance was removed, and the aqueous solution was shaken with ether in order to extract the substance dissolved in aqueous solution. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.8 g., neutr. value 1010, m.p. 124.5–125°), which decomposed on heating at 140–150° with the formation of carbon dioxide, and it was considered to contain malonic acid (neutr. value 1079, m.p. 133°). From these results, the petroleum ether insoluble portion is found to consist principally of succinic acid and its semi-aldehyde though a little malonic acid was contained in addition to these compounds. Whilst the maximum yield of succinic acid is 40.67% if methyl moroctate has only one $=CH\cdot(CH_2)_2\cdot CH=$ group, the yield of petroleum ether insoluble portion obtained in these experiments is 77% of the methyl moroctate

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(7) *J. Chem. Soc.*, **85** (1904), 539.

used for ozonolysis. Accordingly, methyl moroctate must have two of the $=CH\cdot(CH_2)_2\cdot CH=$ group.

3. **Ozonolysis of Methyl Tetrathiocyano-moroctate.** Methyl moroctate (5 g.) was dissolved in 50 c.c. of glacial acetic acid, and 350 c.c. of 1/2 N thiocyanogen solution in glacial acetic acid was added. After being allowed to stand for 24 hours, the excess of thiocyanogen was removed by sodium thiosulphate solution. Methyl tetrathiocyano-moroctate was extracted with chloroform, and the chloroform solution was washed with water, dehydrated, and then concentrated to about 50 c.c. A current of ozonised oxygen was passed through the solution cooled with ice-salt until it became saturated. After distilling off chloroform from the solution, the ozonide remained as a reddish orange syrup. The last traces of chloroform could not be driven off owing to the frothing of the residual ozonide. Fifteen g. of methyl moroctate yielded 35 g. of ozonide (probably ozonide peroxide), from which the chloroform was not thoroughly removed. The calculated yield for ozonide peroxide $C_{19}H_{30}O_9(SCN)_4$ is 32.8 g. Water (150 c.c.) was added to the ozonide thus obtained, and the liquid was heated on the water-bath for 30 minutes. During heating, a current of hydrogen was passed through the flask containing the ozonide, and the volatile substance was carried over with hydrogen into another three flasks which were connected in succession, the first (**a**) being filled with 150 c.c. of water, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The decomposition products remained in the initial flask consisted of aqueous solution and insoluble oil which separated under aqueous layer. By these treatments, the decomposition products of ozonide were separated into three portions: (i) volatile substance, (ii) aqueous solution and (iii) oily substance.

(i) *Volatile substance.* The volatile substance collected in three flasks (**a, b** and **c**) was examined. In the aqueous solution of the flask (**a**), the presence of acetaldehyde was indicated by a deep blue colouration exhibited on adding diethylamine and sodium nitroprusside. Also the presence of propyl aldehyde was indicated by preparing phenylhydrazone and heating the latter with zinc chloride to 180°, when a smell of scatol was recognised. A partial separation of two aldehydes was attempted by passing carbon dioxide through the solution (50 c.c.) in a flask ($\mathbf{a}_1$) which was kept at 45°, and by collecting the volatilised portion, carried over with carbon dioxide, in another flask ($\mathbf{a}_2$) containing ice-cold water. The solution remained in the initial flask ($\mathbf{a}_1$) yielded 0.6 g. of crystalline *p*-nitrophenylhydrazone which melted at 121–121.5° after recrystallising from 50% alcohol and was considered to be an impure *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.94. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask ($\mathbf{a}_2$) yielded 0.5 g. of *p*-nitrophenylhydrazone which melted at 115.5–116° after recrystallising from 50% alcohol and was considered to be a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde (Found: N, 22.73. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask (**a**) contained also acetic acid which was identified by preparing the barium salt (Found: Ba, 53.51. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%).

The barium hydroxide solution in the flask (**b**) was found to contain a precipitate of barium carbonate which was also precipitated in the solution of the flask (**c**) in a smaller amount. The quantity of carbon dioxide formed by the ozonolysis is calculated from the quantity of the precipitate of barium carbonate as 12.1% of the methyl moroctate used in these experiments.

(ii) *Aqueous solution.* The decomposition products dissolved in water were extracted with 2 l. of ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether in order to separate it into petroleum ether soluble portion and petroleum ether insoluble portion. The petroleum ether which was driven off from the solution had the odour of acetic acid. The barium salt prepared from the petroleum ether distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.42. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (1.8 g.) obtained after distilling off petroleum ether was heated in an oil bath, and there was obtained about 0.5 g. of a colourless liquid distilling below 136°. The silver salts fractionally precipitated from the distillate were found to be a mixture of the silver salts of acetic and propionic acids (Found for 1st precipitate: Ag, 60.48. Found for 2nd precipitate: Ag, 62.58. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

The petroleum ether insoluble portion consisted of a soft solid (0.8 g.). On adding a little water, a portion remained insoluble and was removed, and the aqueous solution was extracted with ether. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.3 g., neutr. value 1020, m.p. 125–126°), which decomposed at about 140° forming carbon dioxide and was considered to consist mainly of malonic acid.

(iii) *Oily substance.* Yield 21 g. For the elimination of thiocyano-groups, 30 c.c. of alcohol and 20 g. of zinc powder were added to the oily substance, the mixture gently refluxed, and 30 c.c. of 5 N alcoholic solution of hydrogen chloride gradually added. The product was extracted with ether, and after distilling off ether from ethereal solution, the residue was saponified and the resulting soap solution was shaken with ether in order to remove the unsaponifiable portion. On acidification of soap solution, a reddish orange oil was obtained. This was converted into methyl ester and the latter was fractionated, yielding a fraction boiling at 170–180°/10 mm., from which a free acid consisting of decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid) was liberated in the usual way (Found: C, 63.57; H, 8.13. Calc. for $C_{12}H_{18}O_4$: C, 63.68; H, 8.02%). It had d_4^{20} 0.9989, n_D^{20} 1.4535, mol. refr. 61.25 (calc. for $C_{12}H_{18}O_4\overline{|\!=}_4$: 59.76), neutr. value 495.0 (calc. 496.2), iodine value by the Rosenmund-Kuhnhenn method 220.1 (calc. 224.5). On hydrogenation it yielded decane-1,10-dicarboxylic acid after recrystallising from 50% alcohol; neutr. value 484.8 (calc. for $C_{12}H_{22}O_4$: 487.5), m.p. 124.5–125°. Nördlinger(8) gives m.p. 124.5–125.5°; Chuit(9) gives m.p. 127.5–128°.

Summary.

Moroctic acid $C_{18}H_{28}O_2$ has been isolated from a large quantity of Japanese sardine oil. For the determination of its constitution, methyl moroctate was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde,

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(8) *Ber.*, **23** (1890), 2356.

(9) *Helvetica Chim. Acta*, **9** (1926), 264.

methyl hydrogen succinate, methyl ester of succinic semi-aldehyde, carbon dioxide, acetic acid and acetaldehyde were found. Three last named compounds are considered to be formed by the secondary decomposition of malonic acid and the corresponding aldehyde which are derived from the $=CH\cdot CH_2\cdot CH=$ group. The presence of malonic acid, though in a small quantity, in the products of ozonolysis was also indicated. In the next place, tetrathiocyano-derivative was prepared from methyl moroctate, and it was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, carbon dioxide, acetic acid, acetaldehyde and an oily thiocyano-compound were recognised. The oily thiocyano-compound yielded, on elimination of thiocyanogen followed by hydrolysis, a decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid). Hence, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid which is expressed by the following formula.

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

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