THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XIV. OXIDATION OF POTASSIUM CLUPANODONATE WITH POTASSIUM PERMANGANATE IN AQUEOUS SOLUTION.

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As described in the preceding report⁽¹⁾ of this series, the oxidation of methyl clupanodonate with potassium permanganate in acetone solution yielded propionic acid, acetic acid, succinic acid and methyl hydrogen succinate. Since acetic acid is believed to be formed by the secondary decomposition of malonic acid, the above results indicated that the respective groups jointed by the ethylenic linkings in clupanodonic acid consisted of $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$, and they agreed fully with the results derived from the ozonolysis of amyl clupanodonate in the 8th report⁽²⁾ of this series. The present paper deals with the results of the oxidation of potassium clupanodonate with potassium permanganate in aqueous solution. In the present experiment propionic acid, acetic acid and succinic acid were separated and identified from the oxidation products, and also the presence of malonic acid was indicated. Of these compounds acetic acid is considered to be formed by a further degradation of malonic acid which was formed primarily from the group $=CH \cdot CH_2 \cdot CH=$. Accordingly the respective groups jointed by the ethylenic linkings in clupanodonic acid consist of $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, three of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$ assuming that the terminal group containing carboxyl group is $=CH \cdot (CH_2)_2 \cdot COOH$. These results also agree fully with those derived from the ozonolysis of amyl clupanodonate and the permanganate oxidation of methyl clupanodonate in acetone.

Experimental.

1. **Oxidation of Potassium Clupanodonate with Potassium Permanganate in Alkaline Aqueous Solution.** Clupanodonic acid used in the present experiment is the same as that used in the previous experiment of ozonolysis, and had the following characteristics: d_4^{15} 0.9390, n_D^{15} 1.5035, neutr. value 170.4 (calc. 169.8), iodine value (Wijs) 383.2 (calc. 384.2).

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(1) This Bulletin, **11** (1936), 745.

(2) This Bulletin, **10** (1935), 441.

Five grams of clupanodonic acid was mixed with 2 g. of potassium hydroxide and 500 c.c. of water giving a dilute alkaline solution of potassium clupanodonate. The solution was ice-cooled, and solutions of potassium permanganate were added gradually with constant stirring. Solutions of potassium permanganate consisted of 500 c.c. of a 2% solution, 400 c.c. of a 3% solution, 450 c.c. of a 4% solution and 400 c.c. of a 5% solution which were added successively in the course of 3 hours. After addition of the entire quantity of potassium permanganate, the solution was allowed to stand in an ice box for 17 hours, and then sulphur dioxide was passed through the solution in order to reduce the excess of potassium permanganate. The solution was then filtered with suction, and the precipitate of brown oxides of manganese was washed several times with hot water, using 300 c.c. each time. The filtrate and the washings were united, and after making the solution slightly alkaline, it was evaporated to dryness, and then acidulated with dilute sulphuric acid. The total volume of the solution was made up to about 100 c.c., and it was extracted with 5 l. of ether. The ether (a) was removed from ethereal solution by distillation, and there was obtained 7.3 g. of residue which was then extracted three times with petroleum ether using 100 c.c. each time. The petroleum ether solution and the insoluble portion (b) were separated. On distilling the petroleum ether solution, the distillate (c) boiling below 100° which consisted mainly of petroleum ether containing only a small proportion of other volatile substances was separated, and there remained 1.1 g. of residue (d).

2. **Oxidation Products Carried over with Solvents.** The ether (a) and the distillate (c) consisting largely of petroleum ether showed acidic reaction. These were shaken with potassium hydroxide solution, and the acidic substances were separated as the potassium salt solution. On acidification with sulphuric acid, the acidic substances were liberated, and after addition of a small amount of potassium permanganate, which oxidised sulphurous acid dissolved in the solution, it was distilled. The distillate amounted to 29 g. and had acid value 12.2, from which the acidic substances contained in the distillate is calculated to be 0.38 g. as acetic acid. The distillate was neutralised with alcoholic potash and refluxed with calculated amount of *p*-bromophenacyl bromide. The *p*-bromophenacyl ester formed was separated and recrystallised from 60% alcohol, giving crystals which melted at 84.5–85°, both alone and after admixture with a pure specimen of *p*-bromophenacyl ester of acetic acid.

3. **The Portion Soluble in Petroleum Ether.** The residue (d) obtained by removing the solvent from petroleum ether solution formed an orange yellow liquid. On distilling this portion the following two fractions were separated: (1) below 130°, 0.11 g.; (2) 130–140°, 0.22 g. The fraction (2) was converted into the *p*-bromophenacyl ester which on recrystallisation from 70% alcohol melted at 61.5–62°. The melting point was not lowered when the substance was admixed with *p*-bromophenacyl ester of propionic acid, m.p. 62.5–63°, in various proportions. The final residue from distillation was a dark brownish viscous liquid and appeared to contain intermediate oxidation products which escaped a complete oxidation. It was subjected to a further oxidation with an alkaline solution of potassium permanganate, and after acidification the product was taken up with ether. Removal of ether from ethereal solution left behind a mixture of crystalline solid and viscous liquid. The latter was removed by washing with a little cold ether, and there was obtained a crystalline solid which consisted of impure succinic acid melting at 178–179°.

4. **The Portion Insoluble in Petroleum Ether.** This portion (b) amounted to 5.8 g. It was washed with cold ether, and there remained 2.9 g. of crystalline solid (i). On removal of ether from the ethereal washing there remained a reddish orange liquid which was contaminated with a small proportion of crystalline solid and contained possibly substances of relatively high molecular weight which escaped a complete oxidation. For a further oxidation, it was oxidised by using 130 c.c. of an alkaline solution (5%) of potassium permanganate, and after treatment with sulphur dioxide, the product was taken up with ether. On removal of ether from ethereal solution there was obtained 2.6 g. of crystalline solid (ii) which was still contaminated with a small proportion of liquid substances. The crystalline solids (i) and (ii) were united and recrystallised from ethyl acetate, yielding succinic acid of neutr. value 950.1 (calc. 950.6) and m.p. 180–181°. On removal of ethyl acetate from the mother liquor from recrystallisation there remained a mixture of crystalline solid and viscous liquid, which was then extracted with a little water in which viscous liquid remained insoluble. The aqueous extract was saturated with sodium chloride and shaken with a large amount of ether. A crystalline substance was obtained after removal of ether from the ethereal solution. It had neutr. value 988.4 and decomposed when heated at 135°. On passing the volatile substances formed by the decomposition into a solution of barium hydroxide, it became turbid.

Summary.

Potassium clupanodonate has been oxidised with potassium permanganate in alkaline solution under cooling. Among the oxidation products, propionic, acetic and succinic acids have been separated. Also the presence of malonic acid is indicated. Of these compounds acetic acid is believed to be formed by a further degradation of malonic acid, and consequently the above results show that the respective groups jointed by the ethylenic linkings in clupanodonic acid are $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot CH_2\cdot CH=$, three of $=CH\cdot(CH_2)_2\cdot CH=$, and $=CH\cdot(CH_2)_2\cdot COOH$, provided the terminal group containing the carboxyl group is assumed to be $=CH\cdot(CH_2)_2\cdot COOH$. The results of the present experiment agree fully with those obtained in the previous experiments of the ozonolysis of amyl clupanodonate and the permanganate oxidation of methyl clupanodonate in acetone solution.

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