CVIII. AUTOXIDATION OF THE FATTY ACIDS.

II. OXIDO-ELAIDIC ACID AND SOME CLEAVAGE PRODUCTS.

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IN Part I [Ellis, 1932] a method for studying the oxygen uptake of the fatty acids was described. Elaidic acid showed an uptake of over 20 % of its weight in about 36 hours. This rate depended upon high dispersion of the acid at temperatures above its melting point, upon its thorough admixture with cobaltous elaidate as a catalyst and upon a circulation of oxygen with the accompanying removal of the carbon dioxide formed. In subsequent experiments this degree of autoxidation (which marks the end of an even rate of oxygen uptake) has been attained in less than 7 hours; partly by increasing the rate of the circulation of oxygen to 2 ml. per sec. as compared with 0.4 ml. per sec. previously employed. A probable explanation of this effect is that the carbon dioxide formed causes a lowering of the partial pressure of oxygen and may even become adsorbed by the dispersed liquid and its products, so retarding the autoxidation unless removed by a rapid passage of oxygen. An increased proportion of the catalyst from 0.05 % of the metal to 0.5 % has also increased the velocity of the reaction, but no further increase by greater concentration has been noted.

The biochemical significance of this work is not lessened by devoting most of the study to pure elaidic acid instead of to oleic acid, which is so difficult to purify. In Part I it was shown that both acids autoxidise at comparable rates, and since examining the products in the two cases, there is little doubt that their differences may be attributed to stereoisomerism. Nor does the employment of a dry film and of dry oxygen gas detract from this significance, for it will be shown that there are close similarities both in the rate and in the products of dry autoxidation as compared with those observed for autoxidation in oxygen saturated with aqueous vapour at the temperatures of autoxidation. The latter observation has been made with a slight modification of the apparatus shown in Fig. 1, Part I. The cylinder A, containing the dispersed acid, was provided at its base with two perforated porcelain discs between which cotton wool soaked in water was placed. The upcoming oxygen was therefore saturated at the temperature of the reaction. It should be noted that water is an immediate product of autoxidation so that working under actual dry conditions is impracticable. The conditions adopted, therefore, may be compared with the autoxidation of an oil emulsion. Olive oil becomes rancid rapidly when in the form of a very fine emulsion and when a metallic catalyst is present, but it is doubtful whether such a process could lead to satisfactory results: the emulsion would have to be very bulky and autoxidation would lead probably to demulsification and so to practical stoppage of the reaction.

The products are numerous and in some cases complex. Reduction in the time of autoxidation does not appear to have simplified the process or to have produced a main, initial autoxidation product. It has been necessary for practical

results to work at temperatures above 55°. The results obtained in recent work are set out in Table I. This Table is a continuation of Table I, Part I. The elaidic acid has been allowed to autoxidise in lots not exceeding 23 g. A single experiment will not yield fractions which suffice to give some of the quantitative results to be described. Over 70 autoxidations have been carried out and similar fractions have been combined for a number of the actual estimations. The various products obtained will be described under different headings below and in further communications. They are given in the order in which they may be isolated.

Carbon dioxide and water.

These are absorbed from the circulating oxygen system as described in Part I, where the results of various estimations were tabulated. A few additional results have been obtained. In Exps. 4, 16, 15 and 10 of Table I the oxygen uptakes are 16.7, 18.2, 21.6 and 21.1 % respectively (col. 8). The oxygen evolved as carbon dioxide was estimated as 4.4, 4.6, 4.9 and 5.2 % respectively, accounting for 25 % of the oxygen absorbed. These results are in agreement with those obtained in Part I. The water evolved was estimated in Exps. 15 and 16 and amounted to 7.0 and 7.5 % as oxygen. The results of water determinations may be too high, owing to the presence in the absorption tubes of volatile acids. A total water and carbon estimation may be obtained from the difference of the total products calculated from the oxygen uptake and those other than water and carbon dioxide actually isolated. Exp. 74 gave 11.3 % by this method. Exp. 15 gave 11.9 % as oxygen by absorption of both products in dry caustic soda. Both results are probably high, but there is little doubt that when elaidic acid shows an oxygen uptake of about 20 %, nearly half this oxygen is evolved as these two products. These results will be referred to again.

The main autoxidation products.

The fine, purified sand, used as dispersing agent, is extracted in a Soxhlet apparatus with ether. From 20 g. of the acid nearly 23 g. of an oily extract are obtained. This mixture is yellow to light brown and will darken slightly on a water-bath. Otherwise it appears fairly stable. Kept for some hours it will deposit crystalline matter, which cannot be separated advantageously at this stage. It is completely soluble in sodium carbonate and titrates to an equiv. wt. about 250. It gives i.v. up to 50, which is partly accounted for by the presence of unchanged elaidic acid. It possesses a pungent odour resembling "drying" linseed oil. This odour is also obtained in the autoxidation of stearic acid (Part I). It liberates iodine from an acetic acid solution of potassium iodide in amounts corresponding to 1–2 % of a peroxide of elaidic acid. When boiled with water or dilute acids, the aqueous portion gives a faint colour with titanous acid, but not more than can be accounted for by the peroxides in the ether used in the extraction. It is miscible with small proportions of most solvents, but is only partly soluble in large proportions of light petroleum, carbon disulphide and cold methyl alcohol. It forms a slightly gelatinous solution in benzene. Many attempted fractionations of the salts of lead, zinc, magnesium, calcium and copper have not proved satisfactory. Of the various methods tried, that which has proved the most successful for the separation of the various constituents will be detailed under the different headings below. It has been found advisable to express their yields as the amounts obtained from the autoxidation of 100 g. of elaidic acid. For this purpose, when necessary, any unchanged acid has been estimated and this amount deducted from the weight experimented upon.

Table I. *Products of the autoxidation of elaidic acid.*

Percentages relate to 100 g. of elaidic acid autoxidised.

No. of exp.	Weights		Temp. °C.	Catalyst		Oxygen % by total wt. as at N.T.P.	Azelaic and suberic acids %†	Nonanoic and octanoic acids %‡	Oxido-elaidic acid %	Oils sol. in light petroleum %	Other oily products %¶	Remarks
	g.	g.*		wt. %	ml.							
1	5.24	5.24	67	0.4	1088	29.7	(11.0)	—	—	10.4	40.0	—
2	4.60	4.60	55	0.2	553	16.6	—	—	—	—	—	Oxygen saturated with aqueous vapour
3	20.00	17.52	43	Nil	2357	19.2	8.5	(3.8)	—	—	—	—
4	7.00	6.55	48	Nil	765	16.7	(10.0)	(5.3)	—	28.2	37.2	Oxygen saturated with aqueous vapour
5	20.18	18.52	19	0.1	2194	17.2	(10.8)	—	14.4	26.8	—	—
6	20.18	16.35	19	0.1	2240	19.6	—	—	16.3	25.4	46.1	—
7	20.91	17.29	48	0.4	1614	13.4	—	—	—	77.9	—	—
8	20.91	13.88	30	0.4	2313	23.8	(6.3)	5.0	5.4	32.3	43.8	—
9	22.98	18.15	10	1.3	2700	21.3	(15.3)	—	16.8	32.7	35.4	—
10	20.91	20.64	7	0.4	3054	21.1	(10.0)	6.7	11.7	27.1	38.7	—
11	20.00	17.72	48	Nil	2368	19.1	9.1	—	1.6	23.5	39.6	—
12	21.81	21.80	17	0.9	3279	21.0	9.3	8.1	15.1	30.5	36.7	—
13	21.37	16.09	23	0.9	1741	15.6	—	(9.2)	0.4	17.2	44.4	Oxygen contained aqueous and hydrochloric acid vapours
14	21.81	18.32	10	0.9	2550	19.9	(11.0)	—	14.8	—	30.8	—
15	7.45	6.74	12	0.7	1017	21.6	(11.4)	(4.9)	17.4	26.7	35.8	—
16	5.00	3.06	22	Nil	390	18.2	(6.5)	(3.1)	2.7	19.9	51.5	—
17	7.45	6.00	6	0.7	798	19.0	(9.4)	(3.1)	12.2	22.8	48.9	Oxygen saturated with aqueous vapour. Duration continued 21 hrs. at 50°
18	4.91	3.91	7	1.8	706	25.8	(11.0)	—	10.1	34.4	30.9	—
19	4.91	4.26	29	1.8	868	28.5	(6.5)	—	15.1	28.6	34.8	—

* *I.e.* col. 2 less acid recovered unchanged.

† Present as cobaltous elaidate.

‡ Calculated as azelaic. Results in brackets are approximate.

§ Results in brackets are approximate.

|| Results include those of col. 10.

¶ To be described with previous column in another communication.

The product oxido-elaidic acid with notes on its isomeride oxido-oleic acid.

The main autoxidation products from elaidic acid, obtained as described above, were dissolved in seven times their bulk of alcohol. The solution was cooled in ice and diluted with water until a cloudiness appeared. Salt was then added to the ice and the solution of the products stirred from time to time during several hours. The deposit of crystals was filtered rapidly on a cooled Büchner funnel and washed with a little cold 70 % alcohol. A further small crop of crystals has sometimes been obtained by cooling the mother-liquor by means of carbon dioxide snow. The dried crystals were fractionated in light petroleum. The solution must not be cooled below 15° until most of the oxido-elaidic acid has been separated; otherwise unchanged elaidic acid is deposited and little fractionation is effected. The oxido-elaidic acid separated in this way was recrystallised from dilute alcohol or acetone. It is readily soluble in most solvents in the cold, with the exception of light petroleum. It crystallises from alcohol, acetone or light petroleum in minute but perfectly formed rhombic plates of m.p. 55.5°. (Found: equiv. wt. 299; mol. wt. cryoscopic in benzene 333; in acetic acid 285; by Rast's method 304. C, 72.48; H, 11.35 %. $\text{C}_{18}\text{H}_{34}\text{O}_3$ requires mol. wt. 298; C, 72.42; H, 11.49 %.) It gave i.v. 1.0 and 0.0. When boiled with 40 % NaOH it was nearly completely converted into dihydroxystearic acid, m.p. 133°. An identical oxido-elaidic acid was synthesised. Elaidic acid was dissolved in dilute NaOH and $1\frac{1}{2}$ mol. proportions of dilute NaOCl added. Carbon dioxide was passed in and the mixture left for 12 hours. The solid chlorohydrin was separated, dried and added to excess of sodium ethoxide in alcohol. The mixture was shaken frequently for 2 hours at about 40°. The acidified, diluted solution gave a good yield of crystals, which on purifying with light petroleum gave the same minute rhombic plates melting at 55.5°, unchanged on admixture with the autoxidation product.

The percentage yields of oxido-elaidic acid are shown in Table I, col. 11. These are for the purified product and are therefore low, but it is not thought that more than 20 % of this product is formed. It results from catalytic autoxidation, for Exps. 11 and 16 gave very low results and these are the only two conducted in the absence of the catalyst. The results of Exps. 8 and 13 are the only others giving low figures. The former was conducted at a temperature below the melting point of elaidic acid and was therefore considerably prolonged, whilst the latter represented an autoxidation in the presence of hydrochloric acid vapour. In both these cases hydrolysis of the oxido-derivative must have taken place, but hydrolysis by aqueous vapour for the shorter periods corresponding to those of the majority of the autoxidations is very slight. Exp. 17 gave a fair result although the oxygen employed was saturated by aqueous vapour at the temperature of autoxidation. Further evidence regarding hydrolysis was obtained as a result of Exp. 9, not recorded in detail in Table I. The usual drying tubes were employed with the circulating oxygen, but the contents of the autoxidation cylinder were removed in three parts and examined separately for their oxido-content. These parts comprised a lower portion into which the dry oxygen entered, a middle portion receiving in addition the water vapour formed in the lower portion, and an upper portion under additional humid conditions. These fractions contained 15.6, 13.0 and 9.4 % respectively, of oxido-elaidic acid. There is evidence of slight hydrolysis. On the other hand when 1.005 g. of the pure

product were dispersed on sand and maintained at 65° while oxygen saturated by aqueous vapour at this temperature was circulated for 12½ hours, 0.9781 g. of pure oxido-elaidic acid and 0.0136 g. of the nearly pure acid were recovered. There was little or no hydrolysis. Interest in this question was partly due to the possibility of this derivative being a precursor of dihydroxystearic acid. This latter compound is not present in the free state in any appreciable amount as an autoxidation product, but, as will be shown in a further communication, in combination it represents a large proportion of the oily products.

Some interesting comparative work on the autoxidation of oleic acid has been undertaken. This will be described in more detail in a further communication, but mention may be made here of the possible formation of an isomeric oxido-oleic acid. Pure oleic acid was not employed, but the commercial samples were nearly freed from the saturated fatty acids by crystallising these out from dilute acetone at -30°. The crystalline portion of the autoxidation products was very soluble and could only be separated from dilute alcohol by cooling well below 0° for some hours. Recrystallised from light petroleum, a fraction only slightly soluble in this cold solvent yielded the thin, minute, rhombic crystals of oxido-elaidic acid. The melting point of this and of its mixture with the elaidic acid derivative was 55.5°. The mother-liquors yielded a crystalline mass of M.P. 52° and this was thought to be the oxido-oleic acid obtained by Bauer and Bahr [1929] by the oxidation of oleic acid with perbenzoic acid and having this melting point. The microscopic appearance of the autoxidation product did not point to its being a pure substance. On repeated recrystallisation from light petroleum followed by dilute acetone a very soluble mass crystallising in long thin plates was obtained. It melted at about 58° but could not be freed from a trace of impurity. It approximately agreed with a perbenzoic acid oxidation product of oleic acid obtained by Pigulevski and Petrova [1926] who gave the M.P. as 57.5-58°. A product synthesised by Nicolet and Poulter [1930] through the chlorohydrin was described as melting at 53.8°, and a similar product from elaidic acid likewise melted at 53.8°. These latter results cannot be accepted. Previously Nach and Saytzeff [1892] had obtained by the action of silver oxide on the dibromide of oleic acid a "glycidic acid" of M.P. 57-60°, while Albitzki [1900] describes a chlorohydrin synthesis of the oxido-derivative of oleic acid leading to an oil, the product from elaidic acid having M.P. 57-60°. In view of the uncertainty existing it was decided to repeat the above described successful synthesis of oxido-elaidic acid substituting oleic acid of fair commercial purity. The yield was poor, nor could the mixture of the small amount of oxido-oleic acid be separated from the saturated fats originally present in the oleic acid. The experiment was repeated with 5 g. of free acid suspended in 500 ml. of water containing a little gum arabic. To the emulsion was added dilute NaOCl (1.5 mols.) and carbon dioxide was passed in until the mixture was saturated. After 12 hours the liquid or mucilaginous chlorohydrin was extracted with ether from the acidified solution. The evaporated solution was dissolved in alcohol and cooled in ice. Water was then added until a slight opacity was observed. The solution was cooled by carbon dioxide snow with constant stirring, and the separated fatty acids were filtered off, advantage being taken of the highly soluble, liquid chlorohydrin for the removal of these impurities. The alcohol solution was dried by anhydrous sodium sulphate and left for 3 hours with excess of sodium ethoxide in alcohol. The diluted, acidified mixture was extracted with ether. A white crystalline mass (25%) was obtained. A comparative treatment of 20 g. of oleic acid yielded 20%. Pure oxido-oleic acid is difficult to isolate. Its solubility may be compared with that of palmitic

acid, with which it was probably mixed. The mixture was fractionated many times with ice-cold light petroleum (40–60°) with the occasional use of activated charcoal in small quantities. The melting point was gradually raised from below 53 to 57°. Finally, the product was recrystallised slowly from about 80 % acetone, until it had M.P. 59.5°. The pure product is highly characteristic. It is very soluble in all the common organic solvents including the various chloro-derivatives in use. It crystallises in long plates, so thin as to be almost invisible under the microscope and when suspended in dilute acetone. (Equiv. wt. 296.5; C, 72.50; H, 11.50 %.) Boiled with 20 % aqueous NaOH it yielded over 90 % of dihydroxystearic acid, M.P. 94°; confirmed by a mixed melting point with a known permanganate oxidation product of elaidic acid. Although melting higher than the product obtained by Pigulevski and Petrova [1926] the comparison is only a question of relative purity, for these authors noted hydrolysis to the dihydroxystearic acid of M.P. 94°. It was somewhat unexpected to find the oleic acid product of higher melting point than that obtained from elaidic acid. The readjustment of this reversion on hydrolysis of the oxido-compounds to their dihydroxystearic acids is also of interest.

The total solid acids of the main autoxidation products from 20 g. of oleic acid yielded 3.9 g., composed largely of the oxido-elaidic acid. Its isomeride could not be freed from traces of fatty acids, so that the melting point was not raised to that of the chlorohydrin synthetic product. The characteristic long, thin plates readily soluble in warm light petroleum were obtained. The extreme difficulty of its separation from the mixed fatty acids originally present in the oleic acid accounts for the various failures on the part of previous workers, as mentioned above, to isolate this compound in a pure state. It may be concluded that autoxidation of both elaidic and oleic acids yields the same oxido-elaidic acid, to the extent of about 20%. Oxido-oleic acid does not appear to be formed in any appreciable amounts.

The water-soluble cleavage products: suberic, azelaic and oxalic acids.

The alcoholic filtrate from the crystalline fraction described above is diluted with water until oil is no longer precipitated. The emulsified oil is partly removed by filtration through a fine paper. The filtrate contains for the most part suberic and azelaic acids, which are highly soluble in the diluted alcohol, and which are therefore almost entirely removed in this process from the remaining oily products. This removal is of importance in order to facilitate examination of the oils to be described later. To isolate the dibasic acids the dilute alcohol is evaporated. The residue is taken up in hot water and some oil is removed by absorption on cotton wool. This oil is extracted with hot water until it is clear when cold. The aqueous extracts are concentrated and cooled in ice. The mixed acids are filtered off, dried and treated with chloroform. Most of the suberic acid remains undissolved. The use of this solvent for the separation of suberic and azelaic acids is more efficacious than other methods which have been proposed from time to time. The suberic acid is purified from chloroform containing a little alcohol. Very pure products have been obtained, possessing the characteristic crystalline appearance and solubilities. One preparation gave: M.P. 140°, equiv. wt. 88.4, 88.8. A mixed melting point established its identity. Azelaic acid has been isolated in the pure condition with difficulty. The mother-liquors were evaporated, and the crude acid crystallised from concentrated, warm aqueous solution. Traces of suberic acid in the chloroform mother-liquors accumulate with the azelaic acid at this stage, so that further treatment with chloroform becomes necessary. The azelaic acid is then crystallised from benzene and

finally again from water. This acid has been obtained in a pure form from a number of experiments. It possessed the highly characteristic crystalline appearance, forming shining, rectangular platelets. It gave M.P. 106° , equiv. wt. 94.0, 94.5, and a mixed M.P. confirmed its identity.

Quantitative work involved in the separation of these acids must be approximate only, but it was noticed in one separation that whilst about 0.57 g. of fairly pure suberic acid was isolated, only 0.45 g. of azelaic acid was obtained. The latter would suffer greater loss owing to its more difficult isolation, but the large proportion of the 8-carbon dibasic acid indicated a cleavage of some interest, particularly as no other dibasic acid could be isolated. For this reason a further product comprising these mixed acids was thoroughly investigated. Many fractionations on the lines indicated above were conducted which need not be recorded. Adipic, pimelic and sebacic acids were carefully looked for. It is doubtful whether they are present even in traces. The results obtained were as follows: pure suberic acid 1.27 g.; pure azelaic acid 0.74 g.; impure azelaic acid (M.P. $86-104^{\circ}$, equiv. wt. 111) 0.06 g., residue (impure, white solid) 0.23 g., equiv. wt. 106. Further separation could not be effected. These results show almost certainly that the cleavage of this form of oxidation is almost entirely such as gives rise to azelaic acid and to suberic acid. The isolation of the latter led to a search for oxalic acid. This could not be found with these acids. Its low solubility in ether, together with its probable combination with the cobalt used as catalyst, tends to prevent its removal in the extract of the sand described above. In several cases this sand was subsequently extracted with dilute HCl. This, on evaporation to small bulk, neutralisation and precipitation of the cobalt as sulphide, yielded a calcium salt insoluble in acetic acid. Permanganate titrations of these salts treated with sulphuric acid gave amounts varying from a trace to 0.15 %.

The percentage yields of the mixture of azelaic and suberic acids are set out in Table I, col. 9. These figures are too high in most cases because the diluted, alcoholic solution yields on evaporation some oil which is not redissolved in pure water. The figures in brackets are obtained by titration of the solution of the crude acids before the oil is removed, and the titration value has been expressed as azelaic acid. In the several cases in which the crude acids have been analysed for azelaic and suberic acids as described above, the yield of oil has approximated to 20 or even to 30 %. On the average, deducting 20 % of oil, about 8 % of these acids has been obtained, and this, as shown, represents about 4 % of each of the two acids. Azelaic acid is of almost common occurrence amongst the products of any oxidation of oleic or elaidic acid. The appearance of suberic acid, with traces of oxalic acid, will be referred to below.

The volatile cleavage products: nonanoic and octanoic acids.

The oily products precipitated from the diluted alcohol as described above are taken up in light petroleum ($40-60^{\circ}$). They are miscible with small proportions of this solvent but continue to be precipitated almost indefinitely on dilution. In practice these products, when from 20 g. of elaidic acid, have been extracted with about 400 ml. of the ice-cold solvent. On evaporation a clear, straw-coloured or almost colourless oil remains. Some of the yields of this fraction are shown in Table I, col. 12. The variations (20-30 %) are partly due to the imperfect separation of this fraction from that of the insoluble fractions shown in col. 13. Nonanoic and octanoic acids have been obtained from the light petroleum fraction by steam-distillation and also by distillation *in vacuo*. These acids have also been obtained by steam-distillation of the whole autoxidation

products, in which case they may be accompanied by nonaldehyde due to a decomposition to be dealt with in a further communication. The two volatile acids have been isolated and identified in the course of several different experiments. In one case the zinc salts were obtained from a steam-distillation product. Crystallisation from alcohol yielded fairly pure zinc nonanoate, M.P. 129°. The acid recovered was of the highly characteristic odour; it readily crystallised in ice and had equiv. wt. 159. When the mixed volatile acids from several experiments were fractionally distilled *in vacuo* the first fraction had equiv. wt. 149. This is a little high for octanoic acid (144), probably owing to the presence of a little nonanoic acid. Moreover the not unpleasant odour of nonanoic acid is markedly different from the sweat-like odour of octanoic acid as obtained in the first distilled fraction. This product likewise crystallised readily on cooling. It would not be possible to separate quantitatively these two acids. Their presence was to be expected when it was realised that azelaic and suberic acids were amongst the products of autoxidation. Since the dibasic acids appear to be formed in about equal amounts the two volatile acids should be formed to the extent of 83 % of these, assuming mol. proportions of azelaic and nonanoic and of suberic and octanoic acids. Actually as will be seen by reference to Table I, col. 10, the yields obtained are considerably less, but the volatile acids are more difficult to determine quantitatively. They are slightly soluble in the diluted alcohol which is employed to remove the dibasic acids. Further, their vapour pressures at the temperatures of autoxidation are sufficient to cause their appearance in the absorption tubes of the oxygen circulating system employed. The latter cause for low results particularly accounts for those of Exps. 10 and 17, when small quantities of elaidic acid were experimented upon, and where the error becomes more apparent. Generally the results shown in cols. 9 and 10 are confirmatory and point to a total of 16–20 % of these cleavage products from the elaidic acid autoxidised.

The smallness of the amount of oxalic acid obtained is due, with little doubt, to its suffering further autoxidation, for Jorissen [1899] has shown that solutions of this acid autoxidise in the presence of magnesium sulphate, a catalyst closely comparable in its effect with the salts of cobalt. Curiously, Jorissen observed that the absence of light was a necessary factor, which, however, was a condition of the present experiments. This cleavage is comparable with the oxidation of oleic acid by potassium permanganate in slightly alkaline solutions. Lapworth and Mottram [1925] showed that suberic, oxalic and octanoic acids are obtained in nearly theoretical yields when dihydroxystearic acid M.P. 133° is so oxidised. The latter is formed from oleic acid by the same reagents under more carefully controlled conditions. It may be a precursor of the three cleavage products. Mention has been made that this dihydroxystearic acid occurs in combination amongst the oily products to be described. Saytzeff [1885], however, showed that a similar permanganate oxidation of elaidic acid gave the dihydroxystearic acid M.P. 94°, which has not been found as an autoxidation product. Although selective oxidation may tend to produce only one of the two dihydroxystearic acids, either may suffer cleavage of the nature found in this autoxidation.

The disappearance of most of the oxalic acid accounts for about half of the carbon dioxide obtained during these autoxidations, but only for a small proportion of the water formed.

SUMMARY.

The rate of autoxidation of elaidic acid has been increased from that described in Part I to an oxygen uptake of 20 % in less than 7 hours. Carbon dioxide must be removed by rapid circulation of oxygen over the dispersed acid, and as much as 0.2 % of cobalt, as the salt of elaidic acid, must be added. The presence of aqueous vapour does not appreciably affect the rate of autoxidation.

When a 20 % oxygen uptake is recorded, a large proportion of this oxygen is evolved as carbon dioxide and water. The former may account for 25 % of this oxygen and the latter for even more.

Oxido-elaidic acid,

is formed during catalytic autoxidation of elaidic acid to the extent of 16 or perhaps 20 % of the acid autoxidised. It is only formed in small amounts in the absence of a catalyst and can be obtained in nearly similar amounts whether autoxidation occurs in oxygen dried by calcium chloride or saturated with aqueous vapour. It melts at 55.5° and crystallises in minute, perfectly formed rhombic plates. It is fairly stable and requires strong alkali for hydrolysis to dihydroxystearic acid m.p. 133°. It is not readily further acted upon by oxygen in the presence of cobalt.

An identical oxido-elaidic acid has been synthesised. Similar autoxidation of oleic acid of fair purity yields about 20 % of the same oxido-elaidic acid but in addition a small percentage of an oxido-oleic acid of m.p. 59.5° which crystallises in very thin elongated plates, and which has been synthesised from the chlorohydrin of oleic acid. Both of these isomerides, obtained by autoxidation and by syntheses, have been purified with great care with a view to clearing up some doubts which had arisen regarding various syntheses of these compounds previously described by different workers.

Certain cleavage products obtained amount to 16–20 % of the elaidic acid autoxidised. Of these the dibasic acids consist almost entirely of azelaic and suberic acids in about equal amounts and of a trace of oxalic acid. Of the volatile acids nonanoic and octanoic acids predominate. In addition to the very usual cleavage of elaidic acid into azelaic and nonanoic acids, there appears to be one causing a simultaneous double fission into suberic, oxalic and suberic acids. This latter seems to approximate in amount to the former.

With an oxygen uptake of 20 % the 120 % products obtained from 100 parts of elaidic acid include: carbon dioxide about 6.5 %; oxido-elaidic acid 16–20 %; cleavage products azelaic, suberic, oxalic, nonanoic and octanoic acids totalling 16–20 %. These account for 42–54 %. The remaining 68–76 % are the oils which will be described in a further communication.

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