BEHAVIOR OF 10,11-UNDECYLENIC ACID ON AIR-OXIDATION AT 80°

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In contrast to naturally occurring acids, 10,11-undecylenic acid represents a relatively simple example of an unsaturated fatty acid. As such it is a nearly ideal subject for oxidation studies since reaction with oxygen would give rise to easily recognizable compounds as contrasted to the complex mixtures resulting, for example, from linoleic and linolenic acids. This investigation was undertaken to explain the changes occurring during thermal oxidation of undecylenic acid and the observed saponifiable component found in stored samples of this compound.

It has been well established that to a large extent oxygen attack during thermal oxidation of fatty material occurs at the double bond. Atherton and Hilditch (1) and Lewis and Quackenbush (2) have obtained evidence that peroxides formed at 20–40° are not identical with those formed at 100–120°. Presumably the peroxides formed at the lower temperatures are α-hydroperoxides as shown by Farmer and Sundrailingham (3). At elevated temperatures, it is possible that peroxide groups are formed directly at the double bond. In addition, ketohydroxy and hydroxy compounds have been observed and isolated from thermally-oxidized fatty materials. The formation of dihydroxystearic acid and epoxystearic acid from the reaction between methyl hydroperoxyoleate and oleic acid has been observed by Swift and Dollear (4). Gillam (5, 6, 7) has found that extensive formation of hydroxyl groups occurs during the auto-oxidation of oils. Furthermore, he found a significant increase in the free carboxyl content resulting from cleavage at the double bond and has reported, from analytical data, the presence of esters resulting from the reaction of these hydroxy and carboxy products.

Although several unsaturated aldehydes have been identified in auto-oxidized cottonseed oil (8), no evidence has been found for aldehyde production in thermally-oxidized fatty materials. This is not surprising since aldehydes would represent an intermediate oxidation state under such conditions.

A mechanism for direct oxygen attack at the double bond has been proposed by Skellon (9).

The results of the analyses for neutral equivalent, saponification equivalent, and iodine number for a group of samples of undecylenic acid which were stored under various conditions are given in Table I. These data indicate that a saponifiable component is present in stored commercial samples and also in those samples of pure or recently obtained commercial undecylenic acid which were exposed to air at elevated temperatures. However, in the presence of nitrogen only a slight indication for such a component was obtained. Furthermore, it is

apparent from Table I that the decrease in the iodine number follows closely the increase in the neutral equivalent.

It was this indication of a saponifiable component in stored samples of undecylenic acid, and the fact that the same changes could be produced on pure acid by exposing it to air for comparatively short periods of time at 80°, that prompted this investigation. The work to be described shows that the reactions between air and undecylenic acid at 80° occur almost exclusively at the site of unsaturation and that formation of peroxides is of little significance within the limits of our observations. Molecular weight growth by esterification between carboxyl and epoxy groups and the formation of free carboxyl groups by oxidative cleavage accounts for most of the observed decrease in unsaturation.

The changes occurring on oxidation of undecylenic acid were induced by subjecting the acid at 80° in a constant-temperature oven to a continuous stream of dry, carbon dioxide-free air and withdrawing samples at periodic intervals for

TABLE I

ANALYSES OF UNDECYLENIC ACID SAMPLES

SAMPLE		NEUTRAL EQUIVALENT	SAPONIFICATION EQUIVALENT	IODINE NUMBER
Stored commercial (1-2 years old)	(A)	203.8	191.4	129.8
	(B)	202.0	188.8	133.0
	(C)	198.0	190.3	132.3
Recent commercial		195.7	192.0	129.8
	a	196.5	190.1	129.5
	b	222.0	180.5	105.9
Pure undecylenic acid		184.0	188.1	134.9
	a	184.8	187.1	136.9
	b	227.2	183.5	88.8

a Maintained for 17.5 days at 80° in a nitrogen atmosphere.
b Maintained for 17.5 days at 80° in air.

analysis. Analyses were made for unsaturation, peroxide, neutral equivalent and for the amount of carboxyl formed by oxidative cleavage. The latter values were determined by measuring the difference between the theoretical neutral equivalent for undecylenic acid and the saponification equivalent for the oxidized sample and were calculated as moles of sebacic acid formed per mole of undecylenic acid. It seemed likely that sebacic acid would account for the majority, if not all, of the carboxyl formed by oxidative cleavage since carbon dioxide was the only gaseous product detected and since sebacic acid was found in appreciable amounts in the oxidized undecylenic acid. The data obtained from these analyses are plotted in Fig. 1 on a mole *per* mole basis (*e.g.*, moles of unsaturation lost per mole of undecylenic acid present). Analyses for epoxide oxygen are not plotted since a maximum of only 1.5% calculated as epoxyhendecanoic acid was found after 44 hours.

Inspection of Fig. 1 shows that the three main reactions with oxygen at 80°

are decrease in unsaturation, scission at the double bond, and molecular weight growth. If the sum of the values for the latter two reactions are plotted, a curve is obtained which fits the unsaturation decrease curve reasonably well. From the small amount of peroxide and epoxide formed, it can be assumed that under the conditions of this experiment the contribution to the molecular weight and to unsaturation decrease from these factors is slight. It is interesting to note that the peroxide formed is rapidly destroyed by heating the oxidized acid sample under nitrogen. This behavior parallels that observed by Swift and Dollear (4) for the reaction between methyl hydroperoxyoleate and oleic acid. The relatively large amounts of carboxyl acidity developed appears to be due to direct oxygen attack at the double bond and seems to be rapid since neither peroxide nor epoxide is formed in sufficient quantity to account for it. Some reactions, although
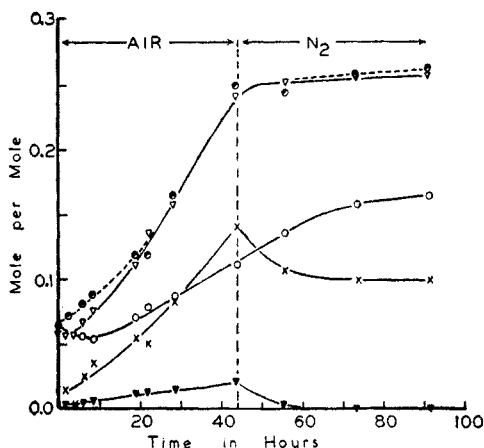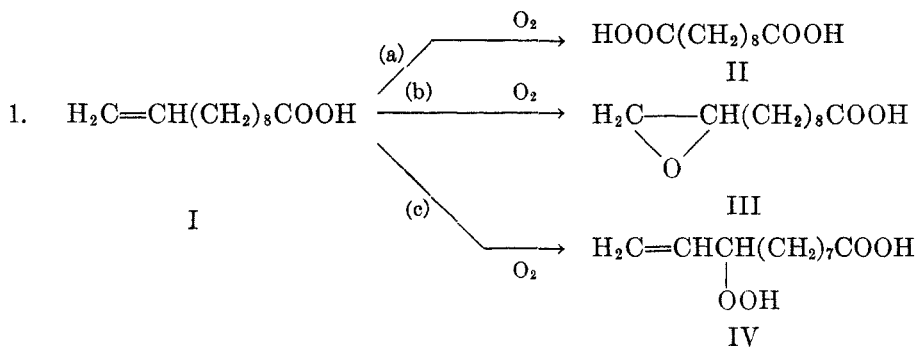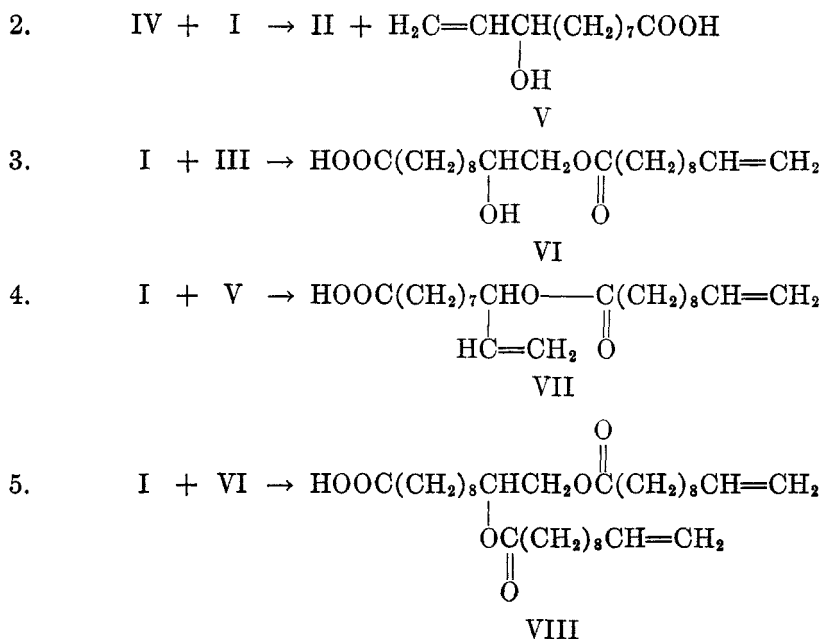

FIG. 1. COURSE OF THERMAL OXIDATION OF 10,11-UNDECYLENIC ACID. Open triangles indicate decrease in unsaturation; open circles, increase in neutral equivalent; crosses, sebacic acid content; closed triangles, peroxide content; half closed circles represent the summation of the sebacic acid content and the increase in neutral equivalent.

others are not excluded, which could be postulated for the observed behavior would be as follows:

1. $H_2C{=}CH(CH_2)_8COOH$

(a) $\xrightarrow{O_2}$ $HOOC(CH_2)_8COOH$

II

(b) $\xrightarrow{O_2}$ $H_2C{-}{-}CH(CH_2)_8COOH$ $\diagdown O \diagup$

III

(c) $\xrightarrow{O_2}$ $H_2C{=}CHCH(CH_2)_7COOH$ $|$ OOH

IV

I

2. $IV + I \rightarrow II + H_2C{=}CHCH(CH_2)_7COOH$

  $\underset{OH}{|}$

  V

3. $I + III \rightarrow HOOC(CH_2)_8\underset{\underset{OH}{|}}{C}HCH_2O\underset{\underset{O}{\|}}{C}(CH_2)_8CH{=}CH_2$

  VI

4. $I + V \rightarrow HOOC(CH_2)_7\underset{\underset{HC{=}CH_2}{|}}{C}HO{-}{-}\underset{\underset{O}{\|}}{C}(CH_2)_8CH{=}CH_2$

  VII

5. $I + VI \rightarrow HOOC(CH_2)_8\underset{\underset{OC(CH_2)_8CH{=}CH_2}{|}}{C}HCH_2O\overset{\overset{O}{\|}}{C}(CH_2)_8CH{=}CH_2$

  $\underset{O}{\|}$

  $VIII$

Although very little of VII and VIII would be anticipated, these reactions represent the most likely routes to the plausible esters, VI, VII and perhaps to some diester, VIII. The esters so produced would account for the increase in molecular weight and some of the decrease in unsaturation. Reaction between epoxide and carboxyl as in reaction 3 has been shown to go readily by Swern, Billen, and Eddy (10) and by Nicolet and Poulter (11) for 9,10-epoxystearic acid to give principally linear polymers. This same reaction was observed by the authors during several attempts to prepare 10,11-epoxyhendecanoic acid. Failure to detect appreciable amounts of epoxide in samples of thermally-oxidized undecylenic acid can be interpreted on the basis that reaction 3 is rapid in comparison to reaction 1 (b) and therefore the latter reaction is the rate-controlling step.

It seemed likely that IV might be an intermediate in the formation of III. Farmer and Sundrailingham (3) have demonstrated that the decomposition of α-hydroperoxide, either at elevated temperatures or by prolonged standing at lower temperatures, gave rise to epoxides. This would indicate that if peroxides were formed during thermal oxidation they would readily react, at elevated temperatures, with unsaturated centers to give secondary products such as ketols, epoxides, α-hydroxy acids, and carboxylic acids by addition to and scission of the double bond. In addition to these recognizable products, oxygenated polymers have also been observed. To obtain confirmatory evidence for the intermediate production of epoxide, a sample of methyl undecylenate was subjected to the same conditions of thermal air-oxidation as were used for the acid. Analyses were made for epoxide, unsaturation, and carboxyl. Results from this experiment are plotted in Fig. 2.

As expected for methyl undecylenate, epoxide oxygen was formed to a significant extent accompanied by cleavage and reduced unsaturation. With the exception of epoxide formation, the curves of Fig. 2 for methyl undecylenate resemble those for undecylenic acid in Fig. 1. As in the experiments with undecylenic acid, relatively small amounts of peroxide were found again showing a minor contribution to molecular weight increase and unsaturation decrease from this source. A high epoxide level would be expected in a low carboxyl environment, since reaction between these two groups would not occur. Appreciable cleavage is indicated by the curve for free methyl hydrogen sebacate. The presence of such carboxyl groups means that the amounts of epoxide and carboxyl found analytically are significantly lower than actually formed during oxidation. This is due
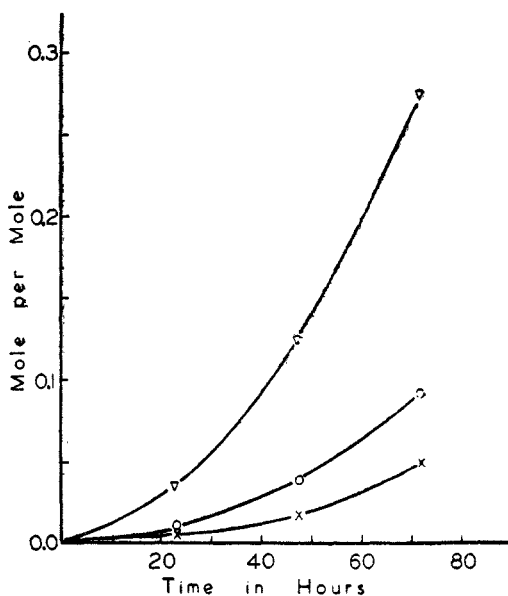

FIG. 2. COURSE OF THERMAL OXIDATION OF 10,11-METHYL UNDECYLENATE. Triangles indicate decrease in unsaturation; crosses, methyl hydrogen sebacate content; circles, epoxide content.

to the reaction of these groups with each other to give hydroxyl esters as in reaction 3 above. In agreement with this, the values for the methyl hydrogen sebacate curve in Fig. 2, when added to those for the epoxide curve, do not coincide with the unsaturation decrease curve.

As in the case of undecylenic acid, carbon dioxide was the only volatile oxidation product detected in the oxidation of methyl undecylenate. This also suggests that methyl hydrogen sebacate is one of the products of this oxidation. Additional proof that this half ester was the main product of oxidative cleavage was obtained in another experiment in which methyl undecylenate was thermally oxidized in the same way for 100 hours. After this time, the acidity as determined by titration with standard alkali and calculated as methyl hydrogen sebacate

amounted to 9.6%. This acid fraction was then extracted from the mixture with dilute aqueous alkali, which gave 8.9% of an oil having a neutral equivalent of 246 (theory for methyl hydrogen sebacate is 216). Saponification of this half ester gave sebacic acid. The data from this experiment and the results shown in Fig. 2 indicate that the reactions 1 (b) and 3 are highly probable. It cannot be established under these temperature conditions whether these are the actual routes taken, or whether as Farmer (3) suggests, peroxides are necessary to the formation of epoxides and scission at the double bond.

In order to establish further that the mechanism of the thermal oxidation of undecylenic acid involves reactions 1(b) and 3, the high-molecular weight com-
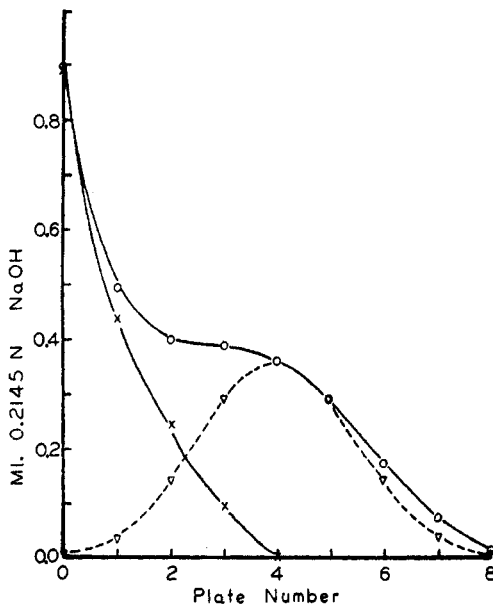

FIG. 3. DISTRIBUTION CURVE FOR FRACTION CONTAINING 10,11-DIHYDROXYHENDECANOIC ACID. Circles indicate the experimental distribution curve; triangles, a theoretical curve for a constant of unity; crosses, calculated curve for impurity present with dihydroxy-hendecanoic acid.

ponent from an oxidized sample of this acid was isolated and analyzed. A sample of undecylenic acid which had been aerated at 80° for 7 days was extracted with petroleum ether. This operation, which is similar to that used by Szent-Györgyi (12) and Gillam (6), separated the oxidized undecylenic acid into soluble and in-soluble fractions. The ether-insoluble fraction, amounting to 36% of the weight of oxidized sample taken, was found to be homogeneous to further extraction with petroleum ether and had a neutralization equivalent of 310 and an iodine number of 66. This petroleum ether extraction affected only a qualitative separation of the oxygenated material, since the neutral equivalent of the ether-soluble fraction was 264 (theory for undecylenic acid is 184).

The ether-insoluble fraction (neutral equivalent, 310) was saponified with

caustic, reacidified, and again extracted with petroleum ether. The ether-soluble fraction amounted to 33% of the sample and consisted almost entirely of undecylenic acid. The petroleum ether-insoluble fraction from the saponification was subjected to a nine-plate countercurrent distribution using the system ethyl ether/40% methanol-water. The results of this distribution are shown in Fig. 3. The material in plates 4 to 8 was shown from its neutralization equivalent, melting point, and mixed melting point to consist of nearly pure 10,11-dihydroxy-hendecanoic acid. From the experimental curve in Fig. 3, the distribution coefficient of this compound in plates 4 to 8 was calculated and was found to be close to that observed for the pure dihydroxy acid. From the theoretical distribution curve, also shown in Fig. 3, it was deduced that dihydroxyhendecanoic acid would account for nearly 46% of the petroleum ether-insoluble fraction from the saponified material.

The remainder of the ether-insoluble fraction of the saponified material, which was in plates zero to three, was isolated as a viscous oil, and had the neutral equivalent 172 and iodine number 39. Negative tests for both epoxide and carbonyl groups were obtained and uncrystallizable oils were produced in several attempts to prepare ester derivatives. However, oxidation with alkaline potassium permanganate gave a mixture of dibasic acids which was shown to consist principally of azelaic and sebacic acids. These observations together with the solubility of the sample and the color change observed during the saponification step suggested that this fraction consisted of an aldol type condensation product which was produced from ketonic oxidation products during the saponification. This would require the formation of ketonic oxidation products from undecylenic acid, possibly through a heat-induced rearrangement of epoxide, as observed by Nicolet and Poulter for epoxystearic acid (11). Although the presence of carbonyl groups in the various fractions of oxidized undecylenic acid could not be detected by any of the standard reagents, it is possible that comparatively unreactive ketonic groups similar to those found in ketols were present. A similar anomaly has been noted by Gunstone and Hilditch (13). The behavior of this material closely resembles the polymeric residue from the catalytic air oxidation of methyl oleate encountered by Swern, *et al.* (14).

EXPERIMENTAL

PREPARATION OF MATERIALS

Undecylenic acid. Commerical acid was distilled and the fraction of b.p. 152–154° at 7.5 mm. was fractionally crystallized from petroleum ether. (All petroleum ether used was the 60–70° fraction.) The material melting at 24–25° was used as pure 10,11-undecylenic acid. Iodine number, 135; neutral equivalent, 184. (Theoretical values 138 and 184, respectively.) Commerical acid was used where indicated.

Methyl undecylenate. Commercial undecylenic acid was esterified by refluxing 100 g. of the acid with 500 ml. of methanol containing 2% of sulfuric acid for 6 hours. The fraction that distilled at 121.5–123° at 11.5 mm. was obtained in 81% yield and had the iodine number 125 and saponification equivalent 200. Theoretical values, 128 and 198, respectively.

10,11-Dihydroxyhendecanoic acid. The procedure of Findley, *et al.* (15) was followed using glacial acetic acid instead of 98–100% formic acid. An improvement over that used by Findley, *et al.* was found for recrystallizing this compound. The crude reaction product

was dissolved with vigorous stirring in the minimum amount of acetone and then filtered. Petroleum ether was added slowly to the appearance of permanent cloudiness. The solution was cooled to 0° and centrifuged. A fine powder was obtained which dried easily with little or no caking. After this crystallization, the product melted at 83–85° and had the neutral equivalent 214 (Theoretical, 218).

<div align="center">THERMAL OXIDATION OF UNDECYLENIC ACID</div>

Commercial acid (25 g.) was placed in an 8″ Beckman tube which was fitted with a sintered-glass inlet tube and an outlet tube. This apparatus was held at 80° in a constant-temperature oven and dry, carbon dioxide-free air was passed through the sample at the rate of approximately 1.5 liters per hour. After 44 hours the air stream was exchanged for nitrogen for an additional 48 hours. Samples were withdrawn at intervals for analysis. The peroxide content was determined by the method of Wheeler (16). Iodine numbers were obtained by the Hanus method (17) and the epoxide content was determined as described by Swern, et al. (18). Neutral equivalents were obtained by titrating 200-mg. samples in 95% ethanol with standardized 0.2 N sodium hydroxide. Saponification equivalents were measured by refluxing weighed samples for 30 minutes with excess 0.5 N potassium hydroxide and back-titrating with standardized 0.2 N sulfuric acid.

The air, emerging from the sample, was passed through dilute aqueous barium hydroxide solution. A precipitate formed showing carbon dioxide present. Aliquots of the solution were acidified and titrated hot with standard permanganate. This test for formic acid was negative. An additional aliquot gave a negative test for formaldehyde when tested with chromotropic acid in concentrated sulfuric acid.

Another 100-g. sample of commercial undecylenic acid was subjected to the same oxidation treatment for a total of 7 days. This material (80 g.) was distilled rapidly at 1.5 mm. pressure and gave 14 g. which was shown to be pure undecylenic acid.

Petroleum ether-insoluble fraction. The residue of 65 g. from the above distillation was extracted in a separatory-funnel with three 100-ml. portions of petroleum ether. Forty-four grams of soluble material, neutral equivalent 264, and 21 g. of a yellow insoluble fraction, neutral equivalent 310 and iodine number 66, were obtained. An additional 7.5 g. of petroleum ether-insoluble material, neutral equivalent 307, was obtained by re-extracting the soluble fraction with three more 100-ml. portions of the solvent. The total insoluble fraction amounted to 36% of the original oxidized material, and was completely soluble in dilute sodium hydroxide, indicating the absence of any appreciable amount of neutral material in this fraction. Repeated solvent fractionation of this insoluble material with petroleum ether-ethyl ether mixtures did not appreciably change the neutral equivalent.

Undecylenic acid from petroleum ether-insoluble fraction. A 0.496-g. sample of the insoluble fraction was saponified with 5 ml. of 1 N alcoholic potassium hydroxide for one hour. This treatment caused the reaction mixture to turn orange-brown in color. After acidification with dilute hydrochloric acid, the mixture was extracted with three 30-ml. portions of petroleum ether. Removal of the solvent to constant weight gave 0.159 g. or 33% of an oil which solidified at 20°, had the neutral equivalent 187, and iodine number 118; the p-bromophenacyl derivative had m.p. 58–60°. Found for authenic p-bromophenacyl undecylenate, 59–60.5°.

10,11-Dihydroxyhendecanoic acid from petroleum ether-insoluble fraction. The material remaining after the extraction of the undecylenic acid in the previous step was taken up in three 30-ml. portions of ethyl ether. After drying to constant weight, the material weighed 0.328 g. and had the neutral equivalent 179 and iodine number 20.4. This material was submitted to a nine-plate countercurrent distribution employing the solvent system 40% methanol-water/ethyl ether. The transfers were made in 50-ml. separatory-funnels with the lower phase moving and 10 ml. of each solvent phase was used for each plate; 0.1231 g. of the ether-soluble fraction was distributed. The total plate contents after distribution were titrated with standardized 0.2 N sodium hydroxide. In this system the distribution

coefficient for pure 10,11-dihydroxyhendecanoic acid is 0.95 and the experimentally determined value from Fig. 3 is 1.0 as calculated by the method of Williamson and Craig (19). From the experimental curve it was calculated that the sample contained 46% 10,11-dihydroxyhendecanoic acid.

After titration the contents of plates 4 to 7 were combined and the ether, methanol, and most of the water was removed under a vacuum until a volume of 15 ml. remained. After acidification to litmus the solution was extracted with five 10-ml. portions of ethyl ether. After evaporating the ether extracts to dryness, 34 mg. of a white solid (m.p. 72–78°, neutral equivalent, 222) was obtained. A large scale countercurrent distribution was carried out in the same manner on 3.5 g. of the saponified fraction of the petroleum ether-insoluble material. In this case 100-ml. volumes of the solvent phases were used. Plates 4 to 7 gave after three crystallizations 0.55 g. of the same white material, m.p. 84–85°, mixed melting point with pure 10,11-dihydroxyhendecanoic acid gave no depression; the p-bromophenacyl ester had m.p. 103–105°. (Found for authenic 10,11-dihydroxyhendecanoic acid ester, m.p. 104–106°.)

Material in plates 0 and 1. The isolation method used for the material in Plates 4 to 7 was repeated on Plates 0 and 1. From the large scale distribution, 1.2 g. of material having the neutral equivalent 172 and iodine number 39 was obtained. No reaction was observed with periodic acid, sodium bisulfite, or 2,4-dinitrophenylhydrazine which indicated the absence of adjacent hydroxy, epoxy, and carbonyl groups. Oxidation of 1.0 g. of this fraction with alkaline potassium permanganate according to the directions given in Shriner and Fuson (20) gave a solid having the neutral equivalent 97. This solid was twice crystallized from water and yielded 0.2 g. of a crystalline material, m.p. 129–131°, mixed m.p. with sebacic acid gave no depression. An ether extraction of the mother liquor gave 0.48 g. of a solid which after three crystallizations from water had m.p. 93–99° and neutral equivalent, 90. Further recrystallization was impractical so the material was converted to the *p-bromophenacyl ester* (m.p. 130–132°); a mixed m.p. with authenic *p-bromophenacyl azelate* showed no depression.

THERMAL OXIDATION OF METHYL UNDECYLENATE

The ester (21 g.) was oxidized in the same way as was undecylenic acid. No nitrogen was used in this experiment. In addition to analyses for epoxide and unsaturation, the acidity developed during oxidation was determined by titration by standard alkali and calculated as methyl hydrogen sebacate.

A second sample of 10.5 g. was oxidized for 100 hours with air. After this time, an acidity which amounted to 9.6% when calculated as methyl hydrogen sebacate was developed. The oxidized ester was dissolved in 50 ml. of ethyl ether and extracted three times with 10-ml. portions of 5% sodium hydroxide. The alkaline extracts were combined, washed twice with ether, and acidified with dilute sulfuric acid. The insoluble oil formed was extracted with ethyl ether and when the ether was evaporated, 0.87 g. of an oil having the neutral equivalent 247 was obtained. (Theoretical neutral equivalent for methyl hydrogen sebacate is 216.) Saponification of 0.35 g. of this oil with excess potassium hydroxide gave 0.27 g. of a solid (m.p. 95–111°, neutral equivalent 111, p-bromophenacyl ester m.p. 144–146°, mixed m.p. with authenic *p-bromophenacyl sebacate* gave no depression).

SUMMARY

Samples of 10,11-undecylenic acid which were oxidized at 80° in the presence of air showed a decrease in unsaturation, the presence of saponifiable material, an increase in carboxyl content, and small amounts of epoxides and peroxides.

Products resulting from this attack have been identified as sebacic acid, 10,11-dihydroxyhendecanoic acid, and some polymeric material.

The sebacic acid arises from oxidative cleavage at the double bond.

The 10,11-dihydroxyhendecanoic acid, present in the oxidized undecylenic acid as high-molecular weight ester, apparently resulted from the reaction of epoxide and carboxyl groups.

The polymeric material was isolated after saponification of the high-molecular weight ester fraction. This material may have arisen from aldol type condensations of keto oxidation products.

The presence of very little peroxide in oxidized undecylenic acid suggests that this type of compound is either not formed or if produced, it must react readily to give other oxidation products.

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