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Action of Lead Tetraacetate upon Hydroxylated Fat Acids and Related Compounds. I. Hydroxylated Oleic Acid, Ethyl Oleate and Oleyl Alcohol[1]

BY JOHN T. SCANLAN AND DANIEL SWERN[2]

The hydroxylation of unsaturated fat acids and related compounds and the application of the Criegee reaction to the hydroxylated products offer a means for the utilization of these materials for the production of more valuable products. The Criegee reaction[3] is based on the specific action of lead tetraacetate upon the α-glycol group. In the reaction the bond between the two carbon atoms is broken and, depending upon the other groups attached to these carbon atoms, aldehydes or ketones are obtained. In the reactions dealt with in this investigation, two aldehydes were obtained. The reaction with 9,10-dihydroxystearic acid is typical.

$$CH_3(CH_2)_7\text{—}CHOH\text{—}CHOH\text{—}(CH_2)_7\text{—}COOH \xrightarrow{Pb(OCOCH_3)_4}$$

$$\underset{\text{Pelargonic aldehyde}}{CH_3(CH_2)_7CHO} + \underset{\text{Azelaic half-aldehyde}}{CHO\text{—}(CH_2)_7\text{—}COOH}$$

Oxidation with lead tetraacetate has had very wide application in determining the structures of sugars and it has also been applied to the demonstration of the positions of the hydroxyl groups in di- and tetrahydroxystearic acids and in certain cork acids.[4]

Compounds suitable for the application of this reaction were prepared by hydroxylation of commercial oleic acid, ethyl oleate, and oleyl alcohol, and by the esterification of 9,10-dihydroxystearic acid. A very satisfactory method of hydroxylation with hydrogen peroxide in glacial acetic acid solution has been developed. It was suggested by a method described by Hilditch,[5] but includes numerous improvements. In the Hilditch method all the reactants were mixed together and allowed to react, without application of heat, for about four to nine days, or heated on the steam-bath for several hours. The fact that the reaction is exothermic apparently escaped notice. In batches of the size used in this investigation it was found that if such a mixture is heated to about 85° and then removed from the source of heat the temperature continues to rise until the boiling point of the mixture is reached and remains there for some time. This makes temperature control difficult and high temperatures are undesirable because hydrogen peroxide is lost by decomposition and more acetylation of the product occurs. The alternative procedure at room temperature is much too slow. It was found that, if the hydrogen peroxide solution and the glacial acetic acid were mixed and heated at 85° for an hour, and then cooled to about 25° before the addition of the unsaturated compound to be hydroxylated, the hydroxylation reaction proceeded rapidly without any application of heat and was completed in about four or five hours. The temperature of the reaction mixture never exceeded 75°. The method was further improved by greatly reducing the proportions of acetic acid and hydrogen peroxide to unsaturated compound. The method of recovering the hydroxylated product was simplified and the yields were increased.

The original Criegee method involved isolation of the lead tetraacetate after its preparation by the interaction of red lead (Pb_3O_4) and glacial acetic acid. There is considerable advantage, however, in avoiding the separation of this unstable compound. This can be accomplished by adding red lead to a solution of the hydroxylated compound in glacial acetic acid. This variation has previously been applied in an unsuccessful attempt to prepare ketones from cholesterol[6] and in the preparation of acetylated alcohol from terpenes,[7] but has not been previously applied to the preparation of aldehydes from α-glycols. The method is particularly advantageous when applied to the hydroxylation products prepared by

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(1) Presented at the Boston meeting of the American Chemical Society on September 12, 1939. Not subject to copyright.

(2) Taken in part from a thesis submitted by Daniel Swern to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **495**, 211 (1932); Criegee, Kraft and Rank, *ibid.*, **507**, 159 (1933).

(4) Nunn and Smedley-MacLean, *Biochem. J.*, **29**, 2742 (1935); Zetzsche and Weber, *J. prakt. Chem.*, **150**, 140 (1938). After our work had been completed and while the manuscript was being prepared the following publications appeared: Hsing and Chang, THIS JOURNAL, **61**, 3589 (1939); Isikowa and Miyata, *Science Repts. Tokyo Bunrika Daigaku*, **A3**, 257–263 (1939); *C. A.*, **34**, 981 (1940).

(5) Hilditch, *J. Chem. Soc.*, 1828 (1926).

(6) Montignie, *Bull. soc. chim.*, [5] **1**, 1280 (1934).

(7) Ward, THIS JOURNAL, **60**, 325 (1938); U. S. Patent 2,080,752 (1937).

the action of hydrogen peroxide in glacial acetic acid upon unsaturated compounds, for it is then possible to carry out the reaction without isolating either the hydroxylated compound or the lead tetraacetate.

The best yields of both the volatile pelargonic aldehyde and the non-volatile azelaic half-aldehyde (as the ethyl ester) were obtained when this modified Criegee reaction was applied to pure ethyl 9,10-dihydroxystearate. With purified 9,10-dihydroxystearic acid the yields of pelargonic aldehyde were almost as good but the yields of azelaic half-aldehyde were much smaller. When the oleic acid hydroxylation product was treated with alkali, to remove the acetyl groups added during the hydroxylation, but was not recrystallized, the impurities present in the oleic acid used did not interfere with the production of good yields of pelargonic aldehyde, but did interfere with the recovery of the non-volatile fraction.

When the reaction was applied to purified 9,10-dihydroxyoctadecanol, obtained by hydroxylation of oleyl alcohol, yields of pelargonic aldehyde comparable to those from 9,10-dihydroxystearic acid were obtained. A good yield of 9-hydroxypelargonic aldehyde was obtained at the same time. Practically the same yields of these two compounds were obtained when the reaction was applied to unrecrystallized 9,10-dihydroxyoctadecanol.

When the reaction was carried out upon the oleic acid and ethyl oleate hydroxylation reaction mixtures without any attempt to separate or purify the hydroxylation products, the presence of acetylated hydroxyl groups slightly reduced the over-all yield of pelargonic aldehyde. The impurities present in the starting materials interfered only with the recovery of the non-volatile fraction. It is doubtful whether the gain in yield of pelargonic aldehyde resulting from the treatment with alkali is sufficient to compensate for the additional expenditure of time and materials. When the starting material is an ester the alkaline hydrolysis to remove acetyl groups cannot be used.

All the compounds obtained by hydroxylation with hydrogen peroxide in glacial acetic acid were the low-melting forms. The high-melting form of 9,10-dihydroxystearic acid (m. p. 130°) was prepared by oxidation of oleic acid with alkaline permanganate.[8] Comparison of the high-melting and low-melting forms of the acid showed that both behaved in exactly the same way in all the reactions tried. The same was found to be true of their esters.

When the character of the starting materials is considered, the yields obtained are better than they appear to be. Commercial, U. S. P. and C. P. oleic acid, commercial ethyl oleate and oleyl alcohol used in these experiments were not pure substances. The iodine number in each case was found to be very close to the theoretical value for the pure compound, but determination of the thiocyanogen values revealed that some of the more highly unsaturated compounds were present and that the increase in the iodine number caused by their presence was compensated for by the presence of an approximately equal quantity of saturated compounds.

Attempts to apply this modified Criegee reaction to hydroxylated olive, peanut and lard oils did not give very satisfactory results. The yields, when compared with those obtained from oleic acid, were much lower than would be expected on the basis of the composition of these glycerides.

Experimental

Character of Materials.—The oleic acid used was a commercial product sold as the U. S. P. grade. The oleyl alcohol and ethyl oleate were of comparable quality. Calculations based upon the iodine numbers and thiocyanogen values gave the following approximate percentage compositions: oleic acid, 75% oleic acid, 13% linoleic acid, 12% saturated fatty acids and unsaponifiable matter; ethyl oleate, 85% ethyl oleate, 6% ethyl linoleate, 9% ethyl esters of saturated fatty acids and unsaponifiable matter; oleyl alcohol, 70% oleyl alcohol, 17% linoleyl alcohol, 13% saturated fatty alcohols.

Preparation of 9,10-Dihydroxystearic Acid.—At room temperature, 567 g. (5 moles) of 30% hydrogen peroxide solution and 1800 cc. of glacial acetic acid were mixed and heated at 80–85° for one hour. After cooling this solution to about 25° it was mixed with 706 g. (2.5 moles) of oleic acid. The ensuing exothermic reaction was allowed to proceed without application of heat but occasional agitation was found to be necessary. When the temperature had reached about 65° the reaction mixture became homogeneous. The temperature continued to rise until it had reached a maximum of about 72° and then slowly declined to room temperature. A small quantity of a waxy solid was removed by filtration at 20–25°. The filtrate was poured into 6000 cc. of hot water, the aqueous layer was siphoned off and rejected, and the oily layer was dissolved in about 4500 cc. of normal sodium hydroxide solution and heated for two hours on the steam-bath. The hot solution was made acid with 6 *N* hydrochloric acid, cooled, and the solidified dihydroxystearic acid separated from the aqueous layer. This crude product was remelted and washed

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(8) Saytzeff, *J. prakt. Chem.*, [2] **33**, 300 (1886); Le Sueur, *J. Chem. Soc.*, **79**, 1313 (1901).

thoroughly with about 3000 cc. of hot water slightly acidulated with hydrochloric acid, cooled, separated from the wash water, and recrystallized from alcohol; yield, 353 g., or 45%; m. p. 89–91°; literature 95°;[5] neutralization equivalent, calcd. for ($C_{18}H_{36}O_4$), 316; found, 316.

Preparation of Ethyl 9,10-Dihydroxystearate.—This compound was prepared by the esterification of 9,10-dihydroxystearic acid prepared as described above, except that the acid was used without recrystallization. The method of esterification was similar to the one described by Clarke and Davis.[9] After the carbon tetrachloride had been removed by distillation, the ester was separated from the residual alcoholic solution by dilution with water and recrystallized from aqueous alcohol; yield 29% (calculated on the basis of the oleic acid used for the preparation of the dihydroxy acid); m. p. 56.5–58.5°; literature 59–60°.[10] Saponification equivalent calcd. for ($C_{20}H_{40}O_4$): 344. Found: 347.

Preparation of 9,10-Dihydroxyoctadecanol.—This trihydroxy alcohol was prepared by the hydroxylation of oleyl alcohol using the same molecular proportions of reactants and following the procedure described for the preparation of 9,10-dihydroxystearic acid up to the point where the product is separated by dilution of the reaction mixture with hot water. After this dilution the aqueous layer was rejected, the residual oil was neutralized with normal alcoholic potassium hydroxide and a sufficient excess of the same reagent was added to supply one mole of potassium hydroxide for each mole of oleyl alcohol.[11] After refluxing for two hours this solution was concentrated by evaporating most of the alcohol and the product was separated as an oil by dilution with hot water, followed by vigorous stirring. After cooling to room temperature the oil had solidified and the aqueous layer was discarded. The solid cake was remelted and then washed thoroughly with about one liter of hot water. After cooling, the solidified oil was separated from the wash water, broken up, and air-dried. When dry, the product was recrystallized from ethyl acetate after decolorization of the solution with charcoal; yield, 46%; m. p. 73–75°; literature 82–82.5°.[11]

Oxidation of Purified 9,10-Dihydroxystearic Acid with Red Lead (Pb_3O_4) and Glacial Acetic Acid.—A solution of 63.2 g. (0.2 mole) of 9,10-dihydroxystearic acid (prepared and recrystallized as previously described) in 500 cc. of glacial acetic acid was heated to 55–65°, and the temperature was maintained within that range while 151 g. (0.22 mole) of red lead was added in 5 to 10 g. portions through a 40-mesh sieve, with continuous stirring. Each portion was added only after the previous portion had been decolorized completely. After the last portion had been added the heating and stirring were continued until a test portion gave no green coloration when placed in contact with a few crystals of leuco-malachite green. Only a few minutes elapsed between the addition of the last portion of red lead and the completion of the reaction. The products were recovered from the reaction mixture by either of the two following methods.

Method 1.—The reaction mixture was diluted with 500 cc. of water and steam distilled until no more oil came over. The distillate was extracted with ether, and the ether solution was washed with water, sodium bicarbonate solution, and again with water until the washings were neutral. The ether solution was dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The residue was a colorless oil, with a sharp but pleasant odor; yield, 20 g. or 71%. It was found to contain 94% pelargonic aldehyde as determined by the hydroxylamine hydrochloride method.[12] It could be further purified by vacuum distillation. The identity of this product was confirmed by preparation of the oxime, m. p. 62–63°; literature, 64°[13]; the 2,4-dinitrophenylhydrazone, m. p. 106–106.5°, literature 106–106.4°.[4] Pelargonic aldehyde is spontaneously converted to the acid on standing in contact with air. It was rapidly converted to pelargonic acid in 94% yield by air-oxidation at room temperature in the aerator described by Senseman and Stubbs.[14] The reaction was exothermic. The acid was purified by vacuum distillation; b. p. 142–150° (13 mm.), m. p. 11–12°; *p*-bromophenacyl ester, m. p. 64–65°, literature, 63.5°.[15]

The residue after the removal of the pelargonic aldehyde by steam distillation was cooled and extracted with ether. The ether solution was washed free of lead salts and acetic acid, dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The residue, a pale yellow, viscous oil which solidified on cooling, was mainly azelaic half-aldehyde (8-formyl-1-octanoic acid); yield 22 g. or 64%. Some difficulty was experienced in the recovery and purification of this product because of polymerization. It was best purified by vacuum distillation; b. p. 195–197° (15 mm.). The purified azelaic half-aldehyde was a white solid, m. p. 40–42°; literature 38°.[16] Neutralization equivalent: Calcd. for ($C_9H_{16}O_3$): 172. Found: 177. The semicarbazone, m. p. 161–162°; literature, 162°.[17] A sample of the crude azelaic half-aldehyde was oxidized to azelaic acid with alkaline potassium permanganate. The azelaic acid was purified by recrystallization from water; yield 25% calculated on the basis of the dihydroxystearic acid used in the first step; m. p. (and mixed melting point) 104–106°.

Method 2.—The reaction mixture was diluted with 500 cc. of water and extracted with two 500-cc. portions of ether. The combined ether extracts were washed with water until free from lead salts and acetic acid, dried over calcium sulfate, and the ether was removed by evaporation under reduced pressure. The pale yellow, limpid residue was chilled to about −10° and the precipitated azelaic acid (4 g.) was removed by filtration. The filtered oil was fractionated under reduced pressure with the following results: fraction (1) b. p. 35–90° (15 mm.), 4 g. (discarded); (2) b. p. 90–100° (15 mm.), 16 g., 99–100% pelargonic aldehyde, yield 57%; (3) b. p. 145–155° (15 mm.), 8 g., pelargonic acid, m. p. 11–12°; (4) b. p.

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[9] Clarke and Davis, "Organic Syntheses," Collective Vol. I, 1932, p. 258.

[10] Smit, *Rec. trav. chim.*, **49**, 675 (1930).

[11] Collin and Hilditch, *J. Chem. Soc.*, 246 (1933).

[12] Reclaire and Frank, *Perfumery Essent. Oil Record*, **29**, 212 (1938).

[13] Bagard, *Bull. soc. chim.*, [4] **1**, 319, 352 (1907).

[14] Senseman and Stubbs, *Ind. Eng. Chem.*, **24**, 1184 (1932).

[15] Powell, THIS JOURNAL, **53**, 1171 (1931).

[16] King, *J. Chem. Soc.*, 1826 (1938).

[17] Haller and Brochet, *Compt. rend.*, **150**, 496 (1910).

195–197° (15 mm.), 14 g., azelaic half-aldehyde, yield 41%, m. p. 40–42°.

Oxidation of Unrecrystallized 9,10-Dihydroxystearic Acid.—The dihydroxystearic acid used in this experiment was prepared by the method previously described for the hydroxylation of oleic acid, but was not recrystallized. The hydroxylation of 282 g. (1.0 mole) of oleic acid yielded 288 g. of the crude product in the form of a solid cake which was broken up, air-dried, dissolved in 2200 cc. of glacial acetic acid, and treated with 754 g. (1.1 moles) of red lead as previously described. The products were separated according to Method 1. Volatile fraction, 95% pelargonic aldehyde; yield 51 g. or 36% calculated on the basis of oleic acid used. Since no satisfactory method was found for recovering the azelaic half-aldehyde from the non-volatile residue when unrecrystallized dihydroxystearic acid was used, this residue was oxidized with alkaline potassium permanganate, thus converting the available azelaic half-aldehyde to azelaic acid; yield 11 g. or 6% calculated on the basis of oleic acid used; m. p. (and mixed melting point) 104–106°.

Hydroxylation of Oleic Acid and Oxidation without Isolation of Dihydroxystearic Acid.—The hydroxylation was carried out as previously described using 282 g. (1.0 mole) of oleic acid, 225 g. (2.0 moles) of 30% hydrogen peroxide solution, and 720 cc. of glacial acetic acid. When the exothermic reaction was completed and the reaction mixture had cooled to room temperature, it was diluted with 1480 cc. of glacial acetic acid, heated to 55–65°, and the oxidation carried out as previously described using 754 g. (1.1 moles) of red lead. The initial portions of red lead are consumed in the decomposition of excess peroxides present in the solution. Some effervescence occurs at this point. The products were recovered by Method 1: volatile fraction, 94% pelargonic aldehyde, yield 33 g. or 23%, calculated on the basis of the oleic acid, as compared with a yield of 36% when the unrecrystallized dihydroxystearic acid was oxidized, and 33% when the dihydroxystearic acid was recrystallized before oxidation. No azelaic half-aldehyde could be isolated from the non-volatile fraction. Potassium permanganate oxidation yielded only 4 g. of azelaic acid.

Oxidation of Ethyl 9,10-Dihydroxystearate.—This oxidation was carried out in exactly the same way as the oxidation of pure 9,10-dihydroxystearic acid, using 69 g. (0.2 mole) of the ester, 500 cc. of glacial acetic acid, and 151 g. (0.22 mole) of red lead. The products were recovered by Method 1. Yields were, pelargonic aldehyde, 25 g. or 88%; ethyl ester of azelaic half-aldehyde, 36 g. or 90%. As initially isolated from the steam distillation residue, this ester had a saponification equivalent of 192.0, calculated ($C_{11}H_{20}O_3$), 200.1. It was vacuum distilled more satisfactorily than the free acid. The purified ester was a colorless oil with a pleasant odor; b. p. 158–160° (14 mm.) and 100–102° (1 mm.); saponification equivalent, 198.5–201.5.

Anal. Calculated for $C_{11}H_{20}O_3$: C, 66.0; H, 10.1. Found: C, 65.9, 65.8; H, 10.2, 10.1. Refractive index, n^{25}_D (Abbe) 1.4348. Density, d^{25}_4 0.9380. Molecular refractivity: Calcd., 54.5. Found, 55.7.

This ester formed, in quantitative yields, a 2,4-dinitrophenylhydrazone which crystallized from 95% ethyl alcohol as glistening, yellow needles, m. p. 63–64°.

Anal. Calculated for $C_{17}H_{24}O_6N_4$: C, 53.7: H, 6.36. Found: C, 53.6, 53.5; H, 6.35, 6.34.

All attempts to prepare the semicarbazone of this ester yielded oils which could not be induced to crystallize.

Hydroxylation of Ethyl Oleate and Oxidation without Isolation of the Ethyl 9,10-Dihydroxystearate.—The hydroxylation was carried out as described for oleic acid, using 310 g. (1.0 mole) of ethyl oleate, 225 g. (2.0 moles) of 30% hydrogen peroxide, and 1120 cc. of glacial acetic acid. When the exothermic reaction was completed and the reaction mixture had cooled to room temperature, it was diluted with 1080 cc. of glacial acetic acid, heated to 55–65°, and the oxidation carried out as previously described using 754 g. (1.1 moles) of red lead. The products were recovered by Method 1. Volatile fraction, 93% pelargonic aldehyde, yield 47 g. or 33% on the basis of ethyl oleate used. The non-volatile residue was a dark brown oil and weighed 263 g. It was vacuum-distilled and the fraction boiling from 95–115° (1 mm.) was the ethyl ester of azelaic half-aldehyde; yield, 25 g. or 12% on the basis of ethyl oleate used; aldehyde content, 97%. Saponification equivalent: Calculated, 200.1. Found, 201.5. 2,4-Dinitrophenylhydrazone, m. p. (and mixed m. p.) 63–64°.

Oxidation of Purified 9,10-Dihydroxyoctadecanol.—The oxidation was carried out as described for purified 9,10-dihydroxystearic acid using 151 g. (0.5 mole) of 9,10-dihydroxyoctadecanol, 1230 cc. of glacial acetic acid, and 377 g. (0.55 mole) of red lead. The products were recovered by Method 2—yields: pelargonic aldehyde, 50 g. or 70%, b. p. 49–52 (1 mm.); 9-hydroxypelargonic aldehyde, 40 g. or 51%, b. p. 119–125° (1 mm.). This hydroxy aldehyde is a white crystalline solid with a very pleasant odor, m. p. (constant after two recrystallizations from xylene), 55–56°; literature, m. p. 58°; b. p. 155–157° (14 mm.).[18]

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.3; H, 11.5. Found: C, 68.2, 68.2; H, 11.6, 11.5.

All attempts to prepare the benzoate and 3,5-dinitrobenzoate of this hydroxy aldehyde yielded uncrystallizable oils.

Oxidation of Unrecrystallized 9,10-Dihydroxyoctadecanol.—The dihydroxyoctadecanol used was prepared by the hydroxylation of 268.5 g. (1.0 mole) of oleyl alcohol according to the method already described, except that the product was not recrystallized. The 278 g. of crude product was in the form of a solid cake which was broken up, air-dried, dissolved in 2200 cc. of glacial acetic acid, and treated with 754 g. of red lead as previously described. The products were recovered by Method 2—yield, pelargonic aldehyde, b. p. 40–42° (0.1 mm.), 38 g. or 27% on the basis of the oleyl alcohol used. This compares with a yield of 33%, calculated on the same basis, when the purified 9,10-dihydroxyoctadecanol was used. The yield of 9-hydroxypelargonic aldehyde of b. p. 99–120° (0.1 mm.) was 36 g. or 23% on the basis of the oleyl alcohol used, which is practically the same as the yield obtained from the purified dihydroxyoctadecanol; m. p., after two recrystallizations from xylene, 52–54°.

Attempts to oxidize hydroxylated oleyl alcohol without isolating the hydroxylated product were not successful.

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[18] Helferich and Schaefer, *Ber.*, **57**, 1911 (1924).

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Summary

1. An improved method of hydroxylating commercial oleic acid and oleyl alcohol with hydrogen peroxide in glacial acetic acid solution is described.

2. The hydroxylated products, 9,10-dihydroxystearic acid, ethyl 9,10-dihydroxystearate, and 9,10-dihydroxyoctadecanol, have been oxidized by means of the Criegee reaction, so modified that it was not necessary to isolate the lead tetraacetate. The products obtained were pelargonic aldehyde, azelaic half-aldehyde and its ethyl ester and 9-hydroxypelargonic aldehyde.

3. It has been found that the modified Criegee reaction could be applied in some cases to the hydroxylation reaction mixture without isolating the hydroxylated products. This method was quite satisfactory for the preparation of pelargonic aldehyde from oleic acid and ethyl oleate.

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Action of Lead Tetraacetate upon Hydroxylated Fat Acids and Related Compounds. II. Hydroxylated Ricinoleic Acid and Castor Oil[1]

BY JOHN T. SCANLAN AND DANIEL SWERN[2]

In the first paper of this series[3] an improved method for the hydroxylation of commercial oleic acid and the preparation of aldehydes from the hydroxylated product by the application of a modified Criegee reaction (oxidation with lead tetraacetate) has been described. It was reported that these reactions could not be applied successfully to olive, peanut or lard oils, although they contain large proportions of oleic acid. In this investigation the same series of reactions has been applied to ricinoleic acid and it was found that although commercial ricinoleic acid could not be used, castor oil, of which ricinoleic acid is a major constituent, could be used quite successfully. It is probable that freshly prepared ricinoleic acid would be satisfactory, but since castor oil can be used directly the extra steps necessary for the isolation of the acid are superfluous.

Two procedures were found to be applicable. In one, the castor oil was hydroxylated, the hydroxylated product was saponified, and the trihydroxy acid thus obtained was oxidized with red lead and glacial acetic acid. In the other method the castor oil was hydroxylated and the subsequent oxidation was carried out without isolating the intermediate product from the hydroxylation reaction mixture. The latter method was superior in every way. There were fewer steps and the yields of both fractions were appreciably larger.

Another possible procedure was investigated. In this method castor oil was hydroxylated, the hydroxylation product was separated from the reaction mixture and an attempt was made to develop a method of preferential hydrolysis by which acetyl groups added during the hydroxylation could be removed from the hydroxyls without hydrolyzing the glyceride linkage. This result was sought because it would facilitate conversion of the azelaic half-aldehyde to azelaic acid and would also result in an increased yield of aldehydes. Since no satisfactory method could be developed for the selective hydrolysis of the acetyl groups, this procedure could not be used.

On the basis of the structure of ricinoleic acid one would expect the products of this series of reactions to be azelaic half-aldehyde and β-hydroxypelargonic aldehyde. Instead of the latter, however, an unsaturated compound, α-nonenaldehyde, is produced.

The identity of this unsaturated aldehyde was established by the following procedures. The molecular refractivities of both the aldehyde and the corresponding acid were determined and found to check closely with the theoretical values. The

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[1] Presented at the Boston meeting of the American Chemical Society on September 12, 1939. Not subject to copyright.

[2] Taken in part from a thesis submitted by Daniel Swern to the Faculty of the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Scanlan and Swern, THIS JOURNAL, **62**, 2305 (1940).