7

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

$$CH_3—(CH_2)_5—CHOH—CH_2—CH{=}CH—(CH_2)_7—COOH \xrightarrow{H_2O_2}$$
$$CH_3—(CH_2)_5—CHOH—CH_2—CHOH—CHOH—(CH_2)_7—COOH \xrightarrow{Pb(OCOCH_3)_4}$$
$$CH_3—(CH_2)_5—CH{=}CH—CHO + CHO—(CH_2)_7—COOH$$

semicarbazone and 2,4-dinitrophenylhydrazone were prepared from the aldehyde, and the amide and *p*-bromophenacyl ester from the acid. Melting points of the solids were obtained and all the compounds were carefully analyzed. The analyses checked closely with the theoretical for α-nonenaldehyde and α-nonenoic acid and their derivatives. The melting points of the derivatives also checked with those reported in the literature as derivatives of α-nonenaldehyde and α-nonenoic acid prepared by other methods. One derivative of α-nonenaldehyde, the 2,4-dinitrophenylhydrazone, has been erroneously reported in the literature as a derivative of β-hydroxypelargonic aldehyde.[4]

The loss of the elements of water occurred during the oxidation with red lead and glacial acetic acid. That the starting material was actually 9,10,12-trihydroxystearic acid, and not an unsaturated compound, was demonstrated by the fact that its iodine number was only 0.8. Furthermore, its neutralization equivalent agreed closely with the theoretical value. It seems improbable that the dehydration occurs during the recovery by steam distillation because β-hydroxypelargonic aldehyde has been produced by the action of periodic acid upon 9,10,12-trihydroxystearic acid and recovered by steam distillation without dehydration.[5]

When 9,10,12-trihydroxystearic acid was used the non-volatile residue consisted of impure azelaic half-aldehyde, and when hydroxylated castor oil was used the non-volatile residue consisted of mixed glycerides of azelaic half-aldehyde, saturated fat acids and probably acetylated hydroxy acids. Since no satisfactory method could be developed for the recovery of azelaic half-aldehyde as such, it was oxidized in both cases and recovered as azelaic acid in fairly good yields. Glycerol is also recoverable in these processes.

Experimental

The castor oil used was a colorless oil of U. S. P. grade, having an iodine number of 84.0 and a saponification number of 180.

Preparation of 9,10,12-Trihydroxystearic Acid.—A solution of 225 g. (2.0 moles) of 30% hydrogen peroxide and 820 cc. of glacial acetic acid was heated for one hour at 80–85°. To this solution, cooled to 25°, 311 g. (about 0.33 mole) of castor oil was added. The mixture was stirred occasionally by hand, and the temperature rose rapidly, without the application of heat, until it reached 70°, at which point the solution became homogeneous and the temperature then declined slowly. After the reaction mixture had cooled to room temperature, the acetic acid was removed by steam distillation. The residual white, viscous oil was refluxed for two hours with one liter of 10% sodium hydroxide solution. The hot alkaline solution was then acidified with dilute sulfuric acid. The 9,10,12-trihydroxystearic acid separated as an oil which solidified to a light brown solid on cooling. The lower aqueous layer was discarded and the solid cake was remelted and thoroughly washed with about one liter of boiling water. The mixture was again cooled, the supernatant aqueous layer was discarded and the solid cake was recrystallized from ethyl alcohol after decolorizing the solution with activated carbon; yield, 92 g., or 36% (calculation based on the assumption that ricinoleic acid constituted 80% of the total fatty acids in the castor oil); m. p. 108–109°; literature, 110–111°.[6] Neutralization equivalent: Calcd. for ($C_{18}H_{36}O_5$): 332. Found: 337. Iodine number: 0.8. (Determined to eliminate possibility that product might be an unsaturated compound and not 9,10,12-trihydroxystearic acid.)

Oxidation of Purified 9,10,12-Trihydroxystearic Acid with Red Lead (Pb_3O_4) and Glacial Acetic Acid.—This oxidation was carried out according to the method described for dihydroxystearic acid in the first paper of this series,[3] using 66.4 g. (0.2 mole) of 9,10,12-trihydroxystearic acid, 500 cc. of glacial acetic acid, and 151 g. (0.22 mole) of red lead. The products were recovered by steam distillation (Method 1).

The aldehyde which was isolated from the steam distillate was a pale yellowish-green oil with a sweet but slightly rancid odor; yield, 20 g. or 67%; found to contain 94% α-nonenaldehyde by the hydroxylamine hydrochloride method.[7] This aldehyde could be further purified by vacuum distillation; b. p. 56–58° (0.1 mm.). It is improbable that the dehydration mentioned above took place in this step because of the low temperature and the fact that the chemical properties of the steam distilled product were not changed by the vacuum distillation.

Anal. Calcd. for $C_9H_{16}O$: C, 77.1; H, 11.5. Found: C, 77.0, 76.8; H, 11.4, 11.5. Refractive index, $n^{25}D$ (Abbe) 1.4502. Density, d^{25}_4 0.8418. Molecular refractivity: calcd., 43.3. Found, 44.7.

It will be observed that the experimental value for the molecular refractivity is slightly higher than the calculated one. This is to be expected in a compound containing a conjugated system of double bonds.

The aldehyde, when dissolved in carbon tetrachloride and treated with a 5% solution of bromine in carbon tetrachloride, absorbed bromine very rapidly without evolution of hydrobromic acid.

It formed, in about 70% yield, a semicarbazone which

crystallized from methyl alcohol as small white needles, m. p. 165–165.5°; literature 163°.[8]

Anal. Calcd. for $C_{10}H_{19}ON_3$: C, 60.8; H, 9.71. Found: C, 60.8, 60.7; H, 9.85, 9.76.

The 2,4-dinitrophenylhydrazone crystallized as small, orange-red needles from ethyl alcohol in 90% yield, m. p. 126°; literature,[4] 124° (reported as a derivative of β-hydroxypelargonic aldehyde).

Anal. Calcd. for $C_{15}H_{20}O_4N_4$: C, 56.2; H, 6.29. Found: C, 56.3, 56.3; H, 6.23, 6.26.

All attempts to prepare the oxime of this aldehyde yielded uncrystallizable oils.

By passing air through samples of this aldehyde for twenty-seven hours at room temperature in the aerator of Senseman and Stubbs,[9] the corresponding acid, α-nonenoic acid was prepared in 87% yield. The acid was readily purified by vacuum distillation, but for the purpose of preparing derivatives the aeration mixture served equally well; b. p. 135–138° (5 mm.); m. p. 0–1°; literature, 0.3°.[10]

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 69.2, 69.1; H, 10.3, 10.4. Neutralization equivalent: calcd. for ($C_9H_{16}O_2$): 156.2. Found: 156.5. Refractive index, $n^{25}D$ (Abbe) 1.4561. Density, d^{25}_4 0.9286. Molecular refractivity:[10] calcd.: 44.8. Found: 45.7.

The pure acid was practically colorless, had a sharp, slightly rancid odor, and in carbon tetrachloride absorbed bromine very rapidly without evolution of hydrobromic acid. The *p*-bromophenacyl ester of this acid was prepared. It crystallized from ethyl alcohol as glistening, pearly flakes with m. p. 77.5–78°.

Anal. Calcd. for $C_{17}H_{21}O_3Br$: C, 57.8; H, 5.99; Br, 22.6. Found: C, 57.8, 57.7; H, 5.85, 5.92; Br, 22.6.

The amide of the acid crystallized from aqueous methanol as glistening plates, m. p. 130–130.5°; literature, 126–127°.[11]

No azelaic half-aldehyde could be isolated from the steam distillation residue. It was, therefore, oxidized directly to azelaic acid by means of alkaline potassium permanganate solution. The azelaic acid was purified by recrystallization from water; yield, 14 g. of azelaic acid, or 37% (calcd. on the basis of the trihydroxystearic acid); m. p. (and mixed m. p.) 104–106°.

Hydroxylation of Castor Oil and Oxidation without Isolation of the Hydroxylated Material.—The hydroxylation was carried out as described for the preparation of trihydroxystearic acid using 225 g. (2.0 moles) of 30% hydrogen peroxide solution, 311 g. of castor oil and 820 cc. of glacial acetic acid. When the exothermic reaction was completed and the reaction mixture had cooled to room temperature, it was diluted with 1380 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 separated by the steam distillation method described in a previous publication.[3] The aldehyde which was isolated from the steam distillate was α-nonenaldehyde, yield 50 g. This material was found to contain 94% α-nonenaldehyde.[7]

The steam distillation residue was cooled and extracted with ether. The ether solution was washed free of lead salts and the ether was removed by evaporation under reduced pressure. The brown, viscous oil which was thus obtained was dissolved in one liter of glacial acetic acid and 225 g. of 30% hydrogen peroxide solution was added. The solution was allowed to stand at room temperature for about twenty-four hours, then heated on the steam-bath until the maximum temperature was reached. At this time it was removed and allowed to cool to room temperature. The acetic acid was then removed by steam distillation and the residual pale-yellow oil was refluxed for two hours with one liter of 10% sodium hydroxide solution. The alkaline solution was acidified while hot and as much as possible of the supernatant oil was removed by filtration of the hot solution. To remove the small amount of oil which passed through the filter paper, the filtrate was boiled with a small amount of "Darco" and refiltered. This filtrate was allowed to cool slowly. The azelaic acid which precipitated was filtered off, washed free of acid and air-dried; yield, 27 g.; m. p. (and mixed m. p.) 104–106°. The oil which was filtered off solidified to a dark brown, waxy solid, weighing about 220 g., from which no definite products could be isolated.

Acknowledgment.—The writers wish to acknowledge the advice and coöperation of Mr. P. H. Groggins of the Bureau of Agricultural Chemistry and Engineering and of Professor Nathan L. Drake of the University of Maryland.

Summary

1. An improved method of hydroxylating castor oil with hydrogen peroxide in glacial acetic acid solution is described.

2. The hydroxylated product, 9,10,12-trihydroxystearic acid has been oxidized by means of the Criegee reaction, so modified that it was not necessary to isolate the lead tetraacetate. The products obtained were α-nonenaldehyde and azelaic half-aldehyde. The latter was oxidized and recovered as azelaic acid.

3. It has been found that the application of the modified Criegee reaction directly to the castor oil hydroxylation reaction mixture gives better results than the alternative method in which the trihydroxystearic acid is isolated and purified before the oxidation.