The Oxidation of Methyl Oleate. II. A Reaction Between Methyl Hydroperoxido Oleate and Oleic Acid

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ABSTRACT

Oleic acid is intermolecularly oxidized by methyl hydroperoxido oleate at 90°C. through the addition of oxygen at the olefinic bond with the formation of epoxy and dihydroxy compounds. Only the low-melting isomeric form of dihydroxystearic acid could be isolated from the reaction mixture. The oxidation of olefinic linkages by hydroperoxides appears to account, at least in part, for the observed reduction of unsaturation in autoxidizing fats.

IT has been generally observed that autoxidation results in a reduction of the unsaturation of fats. The results of Farmer (1) and others have shown that the products initially formed during oxidation of unsaturated fatty acids are unsaturated hydroperoxides of the same degree of unsaturation as the original unoxidized product. Relatively little is known concerning the reactions by which unsaturation is reduced during the secondary stages of autoxidation, but various theories have been proposed to explain the formation of saturated substances. One theory proposed by Farmer (2) assumes that hydroperoxides react with olefinic linkages to produce epoxides. For example, Farmer reported that a reaction of this kind occurred between the hydroperoxide of cyclohexene and cyclohexene with the formation of a product from which cyclohexene-1,2-diol was isolated after hydrolysis (3).

In the present work the possibility that a reaction occurs between a fatty acid hydroperoxide and an olefinic fatty acid was investigated. Advantage was taken of the fact that the separation of products could be facilitated by using the ester of the hydroperoxide as one reactant and a free acid as the other. The results indicate that, at least under the conditions obtaining in these experiments, methyl hydroperoxido oleate and oleic acid do react in the manner postulated by Farmer, and it may be presumed that reactions between hydroperoxides and olefinic linkages may account, at least in part, for the oft-observed reduction of unsaturation (iodine value) which occurs during the oxidation of fats.

Experimental

Oleic acid, iodine value, 89.4, was prepared by the method of Wheeler and Riemenschneider (5). Methyl hydroperoxido oleate was prepared by the low temperature crystallization technique previously described by Swift, Dollear, and O'Connor (4).

Methyl hydroperoxido oleate (11.7 g.) and oleic acid (11.7 g.) were mixed and stored at 90°C. under an atmosphere of nitrogen for three days. The reading on a manometer which was attached to the flask containing the reactants indicated that no change in the pressure occurred during the three-day interval. At the end of the storage period the reaction mixture had a peroxide number of 190 and contained 50.4% of free fatty acid, calculated as oleic acid. Based on the method of Nicolet (6), approximately 16% of the acids present were found to be epoxy acids.

The reaction product was separated into an ester and an acid fraction by the following method: The product (23.2 g.) was dissolved in ethyl ether and the acid fraction was removed by extracting the ethereal solution three times with 100-ml. portions of 1% potassium hydroxide. The methyl esters produced by decomposition of the hydroperoxide remained in the ethereal solution and were recovered after washing the solution with water, drying it with anhydrous sodium sulfate, and removing the solvent by distillation. The iodine value of the ester fraction was 66.6, thus indicating that it had changed relatively little compared with that of the original methyl hydroperoxido oleate, 69.4.

The aqueous alkaline extract was acidified with hydrochloric acid and extracted with ethyl ether. The ethereal solution was washed with water and the solvent removed by evaporation, whereupon an oil (11.2 g., iodine value, 60.1) was obtained. The oil was dissolved in *ca.* 200 ml. of petroleum naphtha (b.p. 30-75°C.) and allowed to stand overnight, whereupon 0.76 g. of white, slightly oily crystals separated. The crystals were washed with small portions of petroleum naphtha (total volume 40 ml.) which dissolved 0.53 g. of the product and left an acidic residue (0.23 g.) melting at 89-91°C. This fraction, on recrystallization from ethanol, consisted of crystals, m.p. 94-95°C., which when mixed with an authentic sample of 9,10-dihydroxystearic acid, gave no depression of the melting point (95°C.). The petroleum naphtha was removed from the solution of soluble acids (0.53 g.) and the residue repeatedly crystallized from 95% ethanol, whereupon there was obtained a small quantity of an acid, m.p. 59°C. Analysis of the product gave carbon, 72.8%; hydrogen, 11.8%; calculated for epoxy-oleic acid, carbon 72.5%; hydrogen, 11.9%. The epoxy-oleic acid described by Ellis (7) melted at 59.5°C.

The petroleum naphtha solution containing the remainder of the acidic products of reaction was heated to remove the solvent, and the residue was subjected to hydrolysis in 10% aqueous potassium hydroxide for 4 hours at 100°C. The aqueous soap solution was cooled, acidified, and the hydrolyzed acids were removed by extracting with ethyl ether. The ethereal solution was washed with water, dried over anhydrous sodium sulfate, and warmed to remove the solvent. The acids obtained on evaporation of the solvent were shaken with 250 ml. of petroleum naphtha (b.p. 30-75°C.) which resulted in separation, after standing overnight, of soluble and insoluble fractions. On filtration, the insoluble fraction, consisting of slightly oily crystals (0.86 g.), was obtained. Occluded oil was removed by washing with several portions (3-5 ml. each) of petroleum naphtha. The crude acids,

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m.p. 91-92° C., after two crystallizations from 95% ethanol, yielded a fraction melting at 94.5-95°C. and having a neutralization equivalent of 314.5. On analysis the product gave carbon, 68.0%; hydrogen, 11.3%; calculated for dihydroxystearic acid, carbon, 68.3%; hydrogen 11.4%; neutralization equivalent, 316.5. No depression of the melting point was observed when the product was mixed with 9,10-dihydroxystearic acid, m.p. 95°C,

For comparison with the results of the above-described experiment, methyl hydroperoxido oleate (10 g.) was stored at 90°C. for three days under an atmosphere of nitrogen. Using the same procedure, including the method of hydrolysis described above, no epoxy- or dihydroxystearic acids could be isolated from the decomposition products of methyl hydroperoxido oleate.

Discussion

The above results indicate that a reaction occurs between methyl hydroperoxido oleate and oleic acid when a mixture of the two is allowed to stand at 90° C. under an atmosphere of nitrogen and that, under these conditions, oleic acid is intermolecularly oxidized to form 9,10-epoxy-oleic acid and 9,10-dihydroxystearic acids. The low-melting form of 9,10-dihydroxystearic acid has been isolated from oxidized oleic acid or its derived esters by Ellis (7), Swern *et al.*, (8), and Banks and Hilditch (9). The high-melting isomeric 9,10-dihydroxystearic acid, m.p. 132°C., has been isolated from oxidized oleic acid or its derived esters by Skellon (10) as well as by the above-mentioned investigators, generally in larger yields than were obtained in the case of the low-melting isomer. In contrast, the reaction between methyl hydroperoxido oleate and oleic acid produced no detectable quantity of the high-melting isomer which would have been readily isolated if present. Apparently the two isomeric, 9,10-dihydroxystearic acids are produced by different oxidative processes.

Summary

Oleic acid is intermolecularly oxidized by methyl hydroperoxido oleate at 90°C. through the addition of oxygen at the olefinic bond with the formation of epoxy and dihydroxy compounds. Only the low-melting isomeric form of 9,10-dihydroxystearic acid could be isolated from the reaction mixture. The oxidation of olefinic linkages by hydroperoxides appears to account, at least in part, for the observed reduction of unsaturation in autoxidizing fats.

Acknowledgment

The authors wish to acknowledge the assistance of Lawrence E. Brown, Analytical, Physical Chemical, and Physical Division of this laboratory, in supplying the carbon and hydrogen analyses reported here.

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