Reactions of Fatty Materials with Oxygen. XVIII.[1] Catalytic Hydrogenation of Autoxidized Methyl Oleate and Oleic Acid. Preparation of Monohydroxystearic Acids[2]

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THE AUTOXIDATION of methyl oleate and oleic acid is admittedly a complex reaction, and numerous papers have been published which show that many products are formed. Since no single compound predominates, the separation procedure is a tedious one. For this reason there are no commercial procedures for the production of useful chemicals by the autoxidation of methyl oleate or oleic acid.

Many products form during autoxidation because oxidative attack takes place at several positions in the reactive allylic portion of the alkyl chain (13, 21, 28), and double bond shifts (11, 25) and *cis-trans* isomerization (15) occur. The major types of products formed during the autoxidation of methyl oleate and oleic acid are α-methylenic hydroperoxide, α,β-unsaturated carbonyls, oxiranes, and unsaturated hydroxy compounds. These form either by a) direct α-methylenic attack (formation of hydroperoxide), b) decomposition of hydroperoxide (formation of α,β-unsaturated carbonyl and hydroxy), or c) homolytic decomposition of hydroperoxide followed by shifting and coupling of electrons (formation of oxirane) (16). These products, which would be anticipated from predominant α-methylenic attack, have been determined quantitatively in autoxidized methyl oleate (5, 14,26) and have also been isolated (6, 7, 8,-9, 10, 29).

Minor products which may also be formed are dihydroperoxide, α,β-unsaturated dicarbonyl, cyclic peroxide, and polymer.

As we reported in the preceding two papers in this series (5, 26), from the onset of autoxidation of methyl oleate to a peroxide content of about 15% the autoxidation mixture consists almost entirely of peroxides and methyl oleate, and these are readily separated. From about 15% to the peak peroxide content (35-40%) the reaction mixture consists of the products of Table I plus residual methyl oleate (estimated to be about 25% maximum). Between the point at which the peroxide content begins to fall and about 20% peroxide, virtually all the methyl oleate is consumed and the autoxidation mixture consists largely of the products of Table I, that is, singly attacked methyl oleate. At more advanced stages of oxidation however multiple attack on the chain becomes more frequent, polymer formation occurs, and the autoxidation mixture really becomes complicated.

TABLE I
Partial Hydrogenation[a] of Methyl Oleate Peroxide Concentrate (70% peroxide)

	Hydrogenation Time	
	2½ hrs.	48 hrs.
Peroxide oxygen	0	0
Oxirane oxygen	0.3%	0.3
Hydroxyl oxygen	5.1%	5.0
Carbonyl oxygen	2.0%	1.5
Iodine number	41	17

[a] 2% by weight of a 5% palladium on carbon catalyst was used at room temperature; hydrogen pressure, 20-40 lbs.

It should be noted that the peroxide value of autoxidizing methyl oleate does not rise rapidly to a peak value and immediately start to fall. Over a considerable period of time (about 500 hrs. at 35° and 25 hrs. at 70°) as plots of the data clearly show (14), the peroxide content of autoxidized methyl oleate near the peak value rises gradually to its maximum and then falls slowly. During this period peroxide formation and decomposition most nearly approach "steady state" conditions. Inevitably the peroxide content must decrease since, as we demonstrated in an earlier work, the content of methyl oleate has become low and peroxide formation cannot keep up with peroxide decomposition. Oleic acid behaves in essentially the same manner as does methyl oleate except that the peak value for peroxide content is only about 10-15%. Also the time required to autoxidize beyond the peak value to complete autoxidation (single attack) requires only about 45 hrs. at 80° whereas methyl oleate requires about 90 hrs.

It occurred to us that if methyl oleate were autoxidized beyond the peak value to the point (30-20% peroxide) where all of it was singly attacked, the system would consist almost exclusively of compounds which could be hydrogenated to monohydroxystearic acids. This process, if successful, would not only simplify the mixture but might also lead to a feasible commercial process for making monohydroxystearic acids from plentiful domestic fats. It is the purpose of this paper to describe conditions for the conversion in high yield of methyl oleate (and oleic acid) to monohydroxystearic acids simply by autoxidation, catalytic hydrogenation, and saponification. We have recently begun to determine the composition of these mixed hydroxystearic acids, and we hope to report on this at a later date. During the course of the present work several model compounds, hydrogenation catalysts, and partial reduction techniques were studied. The results of these experiments are also described in this paper.

Experimental

Starting Materials. The preparation of pure methyl oleate and oleic acid has been described (17). They contained 97-99% oleic, less than 0.2% polyunsaturates; and they were free of *trans* isomers.

Autoxidation-Hydrogenation Procedure. A typical autoxidation-hydrogenation of methyl oleate is described in detail. Five hundred grams of methyl oleate were autoxidized in the dark at 80° by means of a finely dispersed stream of oxygen until analysis (18) showed that the peroxide oxygen content had passed its peak value (1.86% peroxide oxygen, based on one active oxygen per mole of autoxidized methyl oleate;

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this maximum corresponds to a peroxide content of 38%) and had fallen to about 1.6% peroxide oxygen (peroxide content of 33%).[4] This required about 90 hrs. The autoxidation mixture was a pale yellow oil with a slightly unpleasant odor.

Hydrogenation was usually conducted in two stages although this is not essential, as will be described later. Two hundred and seventy-one grams of the autoxidation mixture, 8 g. of activated Raney nickel catalyst, and 2 g. of 10% palladium on carbon were placed in a hydrogenation apparatus and stirred for 2 hrs. under a hydrogen pressure of 150 lbs. p.s.i. The temperature rose spontaneously from room temperature to about 50° during the reduction of the peroxides.

Since the reduction of peroxides produces sufficient water to reduce markedly the activity of the nickel catalyst (this point will be discussed later), the apparatus was vented and the contents were filtered and dried. The peroxide-free material, which contained substantial amounts of carbonyl and oxirane compounds and had an iodine number of 33, was returned to the hydrogenation apparatus. Twenty grams of Raney nickel catalyst and 5 g. of 10% palladium on carbon were added, and hydrogenation was completed in 5 hrs. at 150° and 150 lbs. p.s.i.

The autoclave was allowed to cool to room temperature and vented. The contents were filtered, and the reduced material was saponified by boiling with 4 N aqueous sodium hydroxide for several hours, followed by acidification with 4 N sulfuric acid. The oil which separated from the hot solution was washed several times with hot water to remove salt and acid. On cooling, a hard, off-white material was obtained which had the following characteristics: m.p. 54-62°; hydroxyl oxygen, 4.92% (calculated for monohydroxystearic acid, 5.32%); neutralization equivalent, 295 (calculated, 300); iodine number, 7 (calculated, 0); and oxirane plus carbonyl oxygen, 0.3% (calculated, 0). From 271 g. of autoxidized methyl oleate, 255 g. of mixed monohydroxystearic acids were obtained.

A similar product was obtained from oleic acid by the autoxidation-hydrogenation-saponification technique. Autoxidation beyond the peak value required only about 45 hrs. at 80°.

The intermediate step of removing the contents of the bomb for drying after peroxides are reduced can be eliminated by continuously blowing off water as it is formed by means of a small hydrogen leak at 150°. Since we have no facilities for collecting hydrogen, we prefer to conduct the hydrogenation in two stages in the interests of safety.

Hydrogenation Catalysts. Initially, 5 and 10% palladium on carbon were freshly prepared before each use (22), but in later studies a commercial material was found to be satisfactory. Raney nickel catalysts were prepared from commercial Raney nickel-aluminum alloy (2, 23). Copper-chromium oxide was prepared by the procedure described by Adkins (1). Palladium-lead on calcium carbonate was prepared by Lindlar's method (19).

Discussion

Before we attempted to reduce autoxidation mixtures, a brief investigation was conducted on the reducibility of model compounds containing the peroxide, oxirane, and carbonyl group. The objects of this preliminary study were to determine a) the mildest conditions which would reduce these functional groups to hydroxy and b) the yield of hydroxy compound and by-products, if any. It is known that if hydrogenation conditions are too severe, carbonyl and hydroxy compounds are reduced to the corresponding hydrocarbon. This, of course, would be undesirable. Also we had qualitative information that when peroxides are reduced by chemical means, they are not converted exclusively to hydroxy compounds but that substantial amounts of carbonyl compounds are formed as well. It was of interest to determine whether catalytic reduction also yielded carbonyls as by-products. Furthermore it was known that, under certain conditions, oxiranes are reduced to a mixture of hydroxy and keto compounds, the former predominating (20).

Reduction of Peroxide. a) *tert-Butyl hydroperoxide.* This peroxide was selected as the model compound. In the absence of or with 2.5% of copper-chromium oxide as catalyst, no hydrogen was absorbed by this compound dissolved in glacial acetic acid or 95% ethanol at 25° under a hydrogen pressure of 50 lbs. On the other hand, with 2% by weight of 5% or 10% palladium on carbon as catalyst, *tert*-butyl hydroperoxide (15 g. of commercial 60% grade dissolved in 75 ml. of glacial acetic acid) absorbed the calculated quantity of hydrogen (0.12 mole) in about 10 min. at 31° under an initial hydrogen pressure of 27.5 lbs.

b) *Methyl oleate peroxide concentrate (70% peroxide).* This material was prepared from autoxidized methyl oleate by the urea precipitation technique (4). Fifteen grams dissolved in 75 ml. of glacial acetic acid, to which 3 g. of 5% palladium on carbon was added, absorbed 0.062 mole of hydrogen in about 25 min. at 28° under an initial hydrogen pressure of 20-40 lbs., and only an additional 0.003 mole in two more hours. Table I shows the characteristics of the hydrogenated product. Although peroxides were completely reduced, the high iodine number was surprising since, in calibrating our hydrogen absorption apparatus, we had determined that under identical conditions methyl oleate was completely reduced under the above conditions in less than 10 min. Pure methyl

TABLE II

Partial Reduction Studies on Methyl Oleate Peroxide Concentrates and Methyl Oleate

Material reduced	Reduction method	Reduction product [a]	
		Iodine number	Carbonyl oxygen %
75% peroxide concentrate...	$NaHSO_3$ [b]	59	1.8
75% peroxide concentrate...	$KI\text{-}CH_3COOH$ [c]	61	2.8
75% peroxide concentrate...	$Sn\ Cl_2$ [d]	58	2.3
75% peroxide concentrate...	H_2-Pd on C	17–41	1.5–2.8
Methyl oleate [e].....................	H_2-Pd on C	0	0
Methyl oleate [e].....................	H_2-Pb, Pd on $CaCO_3$ [f]	84	0
70% peroxide concentrate...	H_2-Pb, Pd on $CaCO_3$ [f]	62	1.7

[a] All reduced products were free of peroxide.

[b] Details are given in reference 18 under "Procedure for Reduction of Peroxides."

[c] After analysis of the concentrate for peroxides by the modified Wheeler method (18), the reduced sample was isolated.

[d] Details are given in reference 3.

[e] Iodine number, 85.

[f] Thirty grams of material to be reduced were dissolved in 60 ml. of petroleum naptha, boiling range 100-140°; and 3 g. of catalyst (19) were added. Hydrogenation was conducted at room temperature under an initial pressure of 20-30 lbs. Methyl oleate consumed less than 5% of the calculated amount of hydrogen and was isolated substantially unchanged. (This amount of hydrogen might have been consumed by the solvent or lost by leakage.) The peroxide concentrate absorbed the calculated amount (0.07 mole) of hydrogen for the peroxide group within 10 min., and then absorption stopped.

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[4] More recent work has suggested that the autoxidation be continued until the peroxide oxygen value has fallen to about 1.2%. This reduces the amount of methyl oleate to an almost negligible value.

stearate, iodine number 0, was isolated in quantitative yield. The hydrogenation of the peroxide concentrate was then repeated for 48 hrs.; results are listed in the last column of Table I. It is evident that the double bond is quite resistant to hydrogenation although with increased reaction time it is gradually disappearing.

It was concluded that the presence of negative (electron-withdrawing) groups close to the double bond must slow down the reaction with hydrogen. Confirmation of this was obtained by attempting to hydrogenate methyl ricinoleate, which is somewhat related structurally to the partially reduced oxidation product. This model compound absorbed negligible amounts of hydrogen in one-half hour under the above conditions, and its iodine number was unchanged.

c) *Chemical Reduction of Peroxides and Comparison with Catalytic Methods.* In view of the results obtained in b) it was of interest to determine the actual degree of unsaturation of the peroxide concentrate, thereby permitting us to learn how much hydrogenation of the double bond had taken place. Chemical methods were mainly studied because it was expected that they would not affect the degree of unsaturation. At the time this work was being done, a palladium-lead catalyst on calcium carbonate was described (19), which was reported to be unable to reduce double bonds. The effect of this catalyst in reducing peroxides was therefore included in this study. Results of chemical and catalytic reduction are summarized in Table II.

From the results of chemical reduction, confirmed by hydrogenation in the presence of palladium-lead on calcium carbonate, it can be concluded that the iodine number of the original peroxide concentrates was about 60. Hydrogenation with palladium-lead on calcium carbonate completely eliminated peroxides and did not affect double bonds. This latter conclusion was confirmed with methyl oleate. Hydrogenation with palladium on carbon, on the other hand, resulted in a 30-70% reduction in unsaturation up to 48 hrs. of hydrogenation (Tables I and II). Palladium-lead on calcium carbonate should prove to be a useful catalyst for certain types of partial hydrogenation.

The partial reduction of the fraction isolated as a filtrate from the urea complex separation (non-complex-forming fraction) yields a material which is fairly high in carbonyl oxygen and corresponds to as much as 55% of monocarbonyl compound (calculated carbonyl oxygen for methyl ketooleate, 5.12%) and as little as 30%. As we showed in our previous paper (5), the content of carbonyl compounds in the peroxide concentrate (non-complex-forming fraction) must be quite low since the bulk of such compounds precipitate as urea complexes. It must be concluded therefore that about 40-75% of the peroxide is converted to carbonyl on reduction, rather than completely to the anticipated hydroxy compound.

Independent confirmation of this conclusion was obtained by studying the partial reduction of unfractionated autoxidation mixtures rather than of peroxide concentrates. In a typical methyl oleate autoxidation mixture, autoxidized to the peak peroxide value and beyond it, analysis showed the following composition (5): peroxide, 33%; hydroxy compounds, 26%; oxirane compounds, 24%; and α,β-unsaturated carbonyl compounds, 15%. If peroxides were reduced to hydroxy compounds only, the reduced product should contain about 60% hydroxy compounds and 15% of carbonyls. Actually it contained only 47% hydroxy and 37% carbonyl compounds. In this case, in which palladium on carbon was the catalyst, about 67% of the peroxides were converted to carbonyls. In a duplicate experiment with sodium bisulfite as the reducing agent, about 50% of the peroxide was converted to carbonyl. In general, sodium bisulfite reduction of peroxides results in less carbonyl formation than does catalytic reduction, with the exception of palladium-lead on calcium carbonate as the catalyst.

Reduction of oxirane. *cis*-9,10-Epoxystearic acid, m.p. 59.5° (12), was selected as the model compound. This was hydrogenated in glacial acetic acid with palladium on carbon as catalyst (20). The resulting product contained only 72% hydroxy compound and 16% carbonyl compound; the remainder was largely unreduced oxirane. It is reported (20) that the use of ethanol as the solvent does not appear to lead to the formation of keto compounds.

Since Raney nickel is also reported to reduce oxirane to hydroxy (carbonyl byproduct?) (25) and we were planning to use Raney nickel in our study of the reduction of carbonyl to hydroxy, no further work was done on oxirane compounds.

Reduction of Carbonyl. 12-Ketostearic acid and stearone were selected as the model compounds. 12-Ketostearic acid (30 g.) dissolved in 95% ethanol (100 ml.) was not reduced with hydrogen at 50 lbs. in the presence of 3 g. of Raney nickel W-6 (2).

Attempted reduction with aluminum isopropoxide in isopropanol solution (30) yielded no acetone and the 12-ketostearic acid was unchanged. With toluene as the solvent and a 4-hr. reaction period a product was obtained which contained, surprisingly, 7% hydroxyl oxygen and 1.2% carbonyl oxygen although the original 12-ketostearic acid contained only 5.1% carbonyl oxygen and no hydroxyl oxygen. This line of investigation was not pursued further.

Similar high oxygen values on reduced materials were also obtained on refluxing 10 g. of 12-ketostearic acid or stearone with 150 ml. of 95% ethanol containing 10 g. of Raney nickel W-6 while a vigorous stream of hydrogen was passed through the solution. With glacial acetic acid as the solvent at 100° and either Raney nickel or palladium on carbon as catalyst, no reduction was experienced. Palladium on carbon gave no reduction even in refluxing ethanol.

However, in refluxing butyl acetate or even anhydrous isopropanol, partial reduction was obtained and, of more importance, the sum of hydroxyl oxygen and residual carbonyl oxygen equalled the original carbonyl oxygen content of the starting material. It was concluded that a higher temperature or perhaps a higher pressure (25) was required to reduce carbonyl to hydroxy, and solvent should be avoided so as to keep the concentration of reducible material as high as possible and to minimize side reactions. This last conclusion was found to be correct.

In various experiments, of which the one described in detail in the experimental part of this paper is typical, carbonyl oxygen was substantially completely reduced to hydroxyl with Raney nickel catalyst at 150° under 150 lbs. pressure in the absence of solvent. Oxirane was also reduced to hydroxyl. We have used a mixture of two catalysts in our work because we have found that the presence of palladium results in a lower final iodine number. With Raney nickel alone at 125-150° we have not been able to reduce the iodine number of autoxidized methyl oleate below about 27. Even castor oil, in which the hydroxyl group is in the β-position to the double bond, behaved similarly. With the mixed catalysts iodine numbers of 5-7 (but not lower) are consistently obtained. Undoubtedly, a detailed study of hydrogenation conditions and catalysts would reveal the optimum technique, but we are presently studying the composition of the mixed hydroxy acids and do not intend to explore the hydrogenation reaction further.

To obtain hydroxyl oxygen contents of about 5% (calculated for monohydroxystearic acids, 5.3%) it is necessary to saponify the hydrogenation product. Some esters form during autoxidation and hydrogenation largely because of reaction between oxirane and carboxyl groups. The saponified product therefore should contain dihydroxystearic acid with contiguous hydroxyl groups. Analysis (24) of the final product indicates about 10% of α-glycols. Whether this arises exclusively from the oxirane ring-opening reaction or also from cyclic peroxide by reduction is not known. Earlier evidence suggests that the α-glycol is formed, at least in part, from cyclic peroxide (27).

Summary

Autoxidation of methyl oleate and oleic acid beyond the peak peroxide values followed by catalytic hydrogenation gave mixed monohydroxystearic acids in high yield. The complicated autoxidation mixture which contains peroxides, hydroxy, carbonyl, and oxirane compounds was simplified considerably in composition by this procedure.

For complete reduction of the double bond, and the carbonyl and oxirane groups, hydrogenation was conducted at about 150° and 150 lbs.. Peroxides were reduced at room temperature. Catalysts used were palladium on carbon and Raney nickel.

The selective reduction of peroxides in autoxidation mixtures has been studied by chemical and catalytic means. Peroxides were converted largely to carbonyl compounds rather than to the anticipated hydroxy compounds. Palladium-lead on calcium carbonate is an excellent catalyst for reducing peroxides with hydrogen.

tert-Butyl hydroperoxide, 12- ketostearic acid, stearone, *cis*-9,10-epoxystearic acid and methyl oleate peroxide concentrate were employed as model substances in determining hydrogenation conditions.

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Urea Adducts of Mono- and Diesters of Fatty Acids

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Some of the uses for monoglycerides indicate that they should be free of di- and triglycerides and preferably contain unsaturated fatty acid esters (1, 2). The wide difference in molecular weights of mono- and diesters suggests a distillation process, but low vapor pressure and thermal instability make molecular distillation the only possible distillation method effective (1). The molecular distillation method reduces the amount of undesirable di- and triglycerides and produces a monoglyceride that contains 90-95% monoester. However the molecular distillation process has been of little value in fractionating soybean glycerides with respect to unsaturation. A spread of 12 units in iodine number (127-139) is the maximum reported (3). Kuhrt *et al.* (1) have obtained a 30% cut taken between 142-168°C. at .04 mm. pressure from a reaction product of a partially hydrogenated vegetable oil and glycerine that contained 94% monoesters. This cut represented 75% of the monoglycerides present. Although no commercial solvent extraction process is available at present to refine technical monoglycerides, Feuge and Gros (4) have purified a technical monoglyceride by distributing it between hexane and aqueous methanol or ethanol. They obtained a product from the ethyl alcohol layer that contained 70% of the monoglycerides in 80% purity. No evidence was given to show any degree of separation based on unsaturation.

It was the purpose of this work to determine what kind and degree of separation could be obtained by reacting crystalline solid urea with the fatty acid mono- and di-esters of glycerol. The 18 carbon nor-