TABLE III

Total Dietary *trans* Acids Found in Tissue

Group No.	Feces	Heart	Liver	Intestinal	Carcass
	%	%	%	%	%
II Glyceryl tri(*trans*)-8-octadecenoate	0.9	0.009	0.03	0.45	11.5
III Trielaidin	0.7	0.012	0.13	0.65	10.8
IV Margarine-base stock	0.8	....	....	0.47	9.1

tween 0.01 and 0.06 g. (0.03 to 0.13%) and the hearts between 0.003 g. and 0.007 g. (0.009 to 0.012%) of *trans* per group. The fate of the *trans* acids is summarized in Table IV, from which it can be seen that the rats being fed *trans* acids were capable of metabolizing them quite efficiently. The position of the *trans* double bond, that is, whether it was in the "natural" 9 position or in the 8 position, appears not to affect the efficiency of metabolism. The effect of the level of dietary fat on the deposition and metabolism of *trans* acids was considered in further studies and will be published elsewhere (16).

TABLE IV

Fate of *trans* Acids

Group	Percentage deposited in tissues	Percentage excreted	Percentage metabolized
II Glyceryl tri(*trans*)-8-octadecenoate	11.9	0.9	87.2
III Trielaidin	11.6	0.7	87.7
IV Margarine-base stock	9.7	0.8	89.5

Summary

Weanling rats were fed diets containing triglycerides composed of both *cis* and *trans* fatty acids for 16 days. The animals were sacrificed, and the lipides were extracted quantitatively from the heart, liver, feces, and the rest of the carcass. Infrared analyses were carried out to determine the fate of the *trans* acids. *Trans* acids with the double bond either in the 8 or 9 position are metabolized efficiently by the rat organism.

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Hydroxylation of Methyl Oleate. A New, Direct Method[1]

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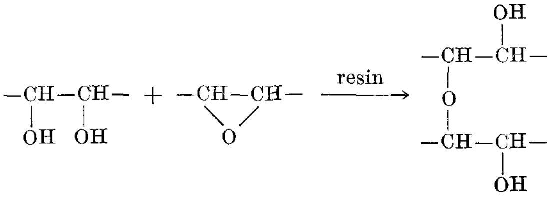
Some time ago (4) our laboratory began to develop a procedure to eliminate undesirable by-products in the epoxidation of fatty oils with hydrogen peroxide. An aim of this program was to investigate solids which might catalyze the reaction of hydrogen peroxide and acetic acid to form peracetic acid. Solid catalysts were expected to provide special surface effects in epoxidation for high yields not readily obtained with mineral acids. In the course of this investigation, polystyrene sulfonic-acid exchange resins of medium or low porosity were found to catalyze epoxidation with virtual exclusion of by-products under certain conditions (2). Additional work on these catalysts led to the discovery of a promising system for hydroxylation of methyl oleate.

Thus methyl oleate was converted directly to methyl 9,10-dihydroxystearate with hydrogen peroxide and acetic acid, catalyzed by polystyrene sulfonic-acid exchange resins of high porosity. Unlike other hydroxylation procedures (6, 7) resin catalysis allowed the ester linkage to remain substantially intact. The dihydroxy derivative was obtained in yields up to 74%. By-products of the reaction consisted of small amounts of epoxide and a polymeric hydroxy ether. The polyether (8) appears to be the product of the reaction of the glycol and epoxide formed transiently.



$$\underset{\mathrm{OH}\quad\mathrm{OH}}{-\mathrm{CH}-\mathrm{CH}-} + \underset{\diagdown\ \mathrm{O}\ \diagup}{-\mathrm{CH}-\mathrm{CH}-} \xrightarrow{\text{resin}} \begin{array}{c} \mathrm{OH} \\ | \\ -\mathrm{CH}-\mathrm{CH}- \\ | \\ \mathrm{O} \\ | \\ -\mathrm{CH}-\mathrm{CH}- \\ | \\ \mathrm{OH} \end{array}$$

Polyether formation is catalyzed by porous exchange resins of the type specified, but not by the less porous resins suitable for epoxidation.

Data obtained in developing this new technique tend to support the interpretation that resin catalysis in hydroxylation involves absorption of the fatty oil. Successful epoxidation probably requires that sorption of fatty oils be limited to adsorption on the surface of the resin.

Experimental

Hydroxylation of Methyl Oleate. A mixture of 29.2 g. (0.10 mole) of technical methyl oleate (iodine number 87.1), 7.5 g. of resin (4% cross-linkage) containing 1.33 g. acetic acid, and 1.97 g. of glacial acetic

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(0.055 mole total acetic acid) was prepared in a 100-ml. vessel equipped with a mechanical stirrer, thermometer, and dropping funnel. While the mixture was being stirred vigorously, 7.45 g. (0.11 mole) of 50% hydrogen peroxide was added so that the temperature reached 60°C. in 15 min. The temperature was maintained at 60°C. for 2–3 hrs., first with intermittent cooling by ice water until the exothermic reaction subsided and then by warming in a water bath. At the end of this time the mixture was kept warm, and the resin was removed by vacuum filtration. The filtrate containing the product was collected in 100 ml. of warm 1% NaCl solution. The oily product layer was separated and then washed with 100-ml. portions of hot water. After drying in a vacuum at 100°C. for 1 hr., followed by cooling, a light-colored solid with an iodine value of 4.8 and a hydroxyl value of 6.44% was obtained.

Recrystallization of the hydroxylated product three times from hot cyclohexane yielded a white powder, m.p. 67°–67.7°C. (3, 5).

Analysis for methyl 9,10-dihydroxystearate. Calc'd: C, 69.04%; H, 11.59%. Found: C, 69.04%; H, 11.40%.

Infrared analysis of this material indicated hydroxyl (2.9 microns) and carbonyl (5.85 microns) absorption but did not show olefinic unsaturation (6.1 microns).

Preparation of Polyether. A polyether similar to the product obtained as a by-product in the hydroxylation reaction was synthesized as follows. Methyl 9,10-dihydroxystearate (20 g.) was mixed with methyl 9,10-epoxystearate (20 g.) and 10 g. of dry "Dowex" 50-X-4 exchange resin. After being heated for 3 hrs. at 90°C. and filtered through a hot vacuum funnel, the reaction mixture yielded a viscous, clear brown liquid. This product was dissolved in cyclohexane, cooled to 10°C., and filtered to remove unreacted materials. Cyclohexane was distilled off to deposit a material which eventually solidified to a pasty mass (hydroxyl value, 3.7%; epoxy oxygen, 0%). The infrared spectrum indicated the presence of an ether linkage (9.1 microns).

Discussion of Results

Resin-catalyzed hydroxylation of methyl oleate is carried out in a one-step procedure, in which a minimum of acetic or formic acid (0.5 mole to 1.0 mole of hydrogen peroxide) is employed. The conditions employed are essentially those used in resin-catalyzed epoxidation. Porous cationic resins (Table I) are necessary for hydroxylation however, whereas less porous resin catalysts are useful in epoxidation.

Present data do not fully explain why porous resins catalyze hydroxylation while less porous resins effect epoxidation. A reasonable and useful interpretation is that porous resins allow uniform penetration of oxidizable fatty oil and that the action of nonporous resins on the oil is restricted mainly to surface effects. Data given here show clearly that porosity (with respect to oxidizable substance) induces conversion to glycol of a considerable quantity of epoxide existing at the beginning of the reaction. That the reaction of methyl oleate and hydrogen peroxide can occur in the absence of organic acids (as shown below) indicates also that the resin's function may be more than a matter of catalyzing peracid formation.

TABLE I

Effect[a] of Resin Porosity on Hydroxyl Value

Resin cross-linking (%)	Hydroxyl value[b] (%)	Epoxy-O (%)	Iodine value
1	3.9	0.33	20.0
2	5.7	0.18	13.0
4	6.5	0.53	17.8
4	6.2[c]	0	4.1

[a] Reaction carried out at 60°C. for 2 hrs. at 50% resin proportion (based on oil wt.); acetic acid system employed.

[b] Determined by lead tetraacetate; theoretical hydroxyl value, 10.29%.

[c] Reaction carried out at 60°C. for 3 hrs. at 25% resin proportion (based on oil wt.).

In hydroxylation, as in epoxidation, the sulfonic-acid groups of the resin act upon hydrogen peroxide and the aliphatic acid to form peracid. Formation of peracid occurs in the resin bead wherever sulfonic acid groups are located. In hydroxylation, according to the above interpretation, the fatty oil is absorbed into the interstices of the resin catalyst bead. The slow absorption process allows sufficient time for the epoxide formed initially to be cleaved to glycol by the acid components of the bead. Epoxidation, on the other hand, probably involves a rapid adsorption of the oil on the surface of the bead to preserve the epoxide by minimizing the effect of the acidity of the resin.

Peracid existing in the reaction medium separated from the catalyst does not depend upon the resin to initiate its attack on the unsaturated centers of the fatty oil. Hydroxylation or epoxidation of methyl oleate under resin catalysis does not require however that peracid be formed by interaction of organic acid and hydrogen peroxide. Preliminary trials indicated a 15% yield of methyl 9,10-dihydroxystearate in the absence of organic acid. This yield was obtained by reacting 50% hydrogen peroxide, methyl oleate, and dry "Dowex" 50-X-4 exchange resin (4% cross-linking). Similarly a 33% yield of methyl 9,10-epoxystearate was obtained by reacting 50% hydrogen peroxide, methyl oleate, and dry "Amberlite" IR-120 resin (8% cross-linking). These trials suggest that at least part of these resin-catalyzed reactions is confined to the environment of the resin bead, especially when a large proportion of resin to oil is used.

The use of formic acid (1) in resin-catalyzed hydroxylation of methyl oleate produces a slightly higher hydroxy value than that obtained by use of acetic acid. A comparison of Tables II and III

TABLE II

Effect of Temperature[a] Hydroxylation of Methyl Oleate[b] in an Formic Acid System

Temperature (°C.)	Hydroxyl value[b] (%)	Epoxy-O (%)	Iodine value
40	3.8	2.45	7.0
60	7.6	0.44	1.2
70	5.7	0	7.8

[a] "Dowex" 50-X-4 or "Amberlite" IR-112; reaction time, 3 hrs.

[b] Determined by acetic anhydride in pyridine; theoretical hydroxyl value, 10.29%.

TABLE III

Effect of Temperature[a] Hydroxylation of Methyl Oleate[b] in an Acetic Acid System

Temperature (°C.)	Hydroxyl value[c] (%)	Epoxy-O (%)	Iodine value
40	4.97	1.0	2.8
60	6.4	0	4.1
85	6.44	0	4.8

[a] Reaction time 2–3 hrs.

[b] Iodine value, 87.1.

[c] Determined by acetic anhydride in pyridine; theoretical hydroxyl value, 10.29%.

shows the relative efficiency of each system. Mixtures of formic acid and hydrogen peroxide however tend to degrade the resin catalyst to a greater extent.

Earlier procedures (6, 7) for hydroxylation of methyl oleate would require saponification of an intermediate hydroxy acyloxy derivative. The separate saponification treatment destroys the original ester. Use of resin catalysts containing no less than 4% cross-linkage in the new technique allows maximum hydroxylation (Table I, Figure 1) with minimum hydrolysis of ester. Table IV shows the effect of resins of various porosities on ester hydrolysis. Polystyrene sulfonic acid resins of 8% cross-linkage or greater used in epoxidation produce essentially no ester hydrolysis.

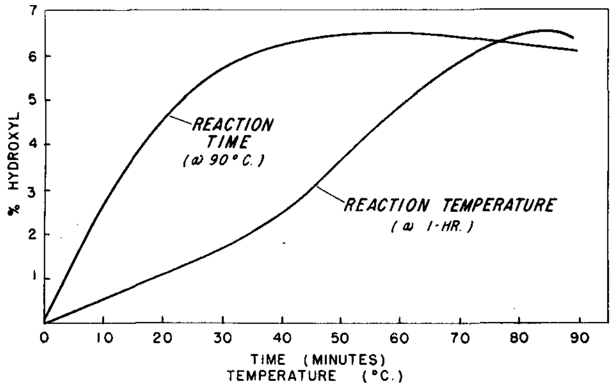

Fig. 1. Effect of reaction variables.

TABLE IV

Effect of Resin Porosity in the Hydrolysis of Methyl Oleate During Hydroxylation[a]

Resin cross-linking (%)	Neutral equivalent (N. E.)[b]	Carboxylic acid (%, approx.)
1[c]	742	42.5
2[c]	2,690	11.6
4[d]	3,970	8.0

[a] In an acetic acid system.
[b] Grams of product containing one mole of carboxyl group.
[c] "Dowex" 50-X-1 and "Dowex" 50-X-2. Percentage cross-linking is an expression of the proportion of divinyl benzene used in manufacture of the resin.
[d] "Amberlite" IR-112 or "Dowex" 50-X-4.

The by-product formation of hydroxy polyether prevents the complete conversion of methyl oleate to the 9,10-glycol. As indicated by Figure 2, glycol and epoxide are produced in the early stages (one hour or less) of the reaction of methyl oleate and hydrogen peroxide-acetic acid catalyzed by 4% resin. Essentially no polyether is formed in this period. The extension of reaction time in an effort to increase yields of glycols results in the formation of 16%–20% of hydroxy polyether. As reaction proceeds, the epoxide is virtually eliminated while dihydroxy formation levels off. The net effect is that unsaturation available after the first hour of reaction is converted to polyether.

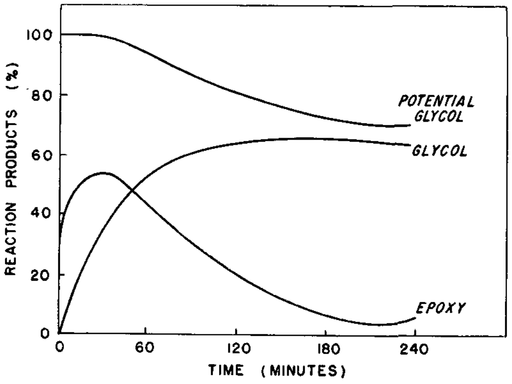

Fig. 2. Hydroxylation of methyl oleate.

The obtaining of higher yields of glycol requires minimizing of the effect of the polyether side reaction. The proportion of resin catalyst used is not critical (Table I) and should have little effect in reducing side reactions if other factors are equal. Of considerable importance however is the porosity of the catalyst. The use of more porous resins induces greater polyether formation. Statistical analyses by these laboratories on the reaction of hydrogen peroxide and methyl oleate have indicated that the increasing of the molar ratio of acetic acid to hydrogen peroxide (from 0.4:1 to 0.5:1) has three times the effect of increasing resin proportion (from 40% to 50% of the weight of oil). Increasing temperature (from 40°C. to 50°C.) or increasing hydrogen peroxide (from equimolar to 10% excess) has four times the effect. These factors should have a similar relative effect in inducing polyether formation after the first hour of reaction.

The polyether has been synthesized by reacting methyl 9,10-epoxystearate and methyl 9,10-dihydroxystearate under catalysis by resin (4% cross-linking). Additional work on the suppression of this reaction is contemplated.

Summary

A new, direct method for hydroxylation of methyl oleate and related fatty materials is described. Yields of 74% methyl 9,10-dihydroxystearate have been obtained directly by use of hydrogen peroxide catalyzed by 4% cross-linked cationic exchange resins. An interfering side-reaction is the formation of an hydroxy polyether. No effort has been made to characterize the polyether which probably exists as a mixture of several polyethers.

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