Effect of Randomization on the Oxidation of Corn Oil[1]

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ABSTRACT

Randomized corn oil and corn oil methyl esters both oxidized three to four times faster than natural corn oil. The difference in rate could not be attributed to pro- or antioxidants. Thin layer chromatography of the oxidized oils and methyl esters after reduction with hydrogen iodide revealed two bands moving slower than the original esters. One was shown to be a mixture of scission products; the other was monohydroxy-triglyceride. There was three times more scission products from randomized than natural corn oil. Glyceride structure seems not to affect the rate of oxidation of triglycerides by altering substrate availability. The difference in yield of scission products suggests that glyceride structure may affect the rate of initiation.

INTRODUCTION

Oils oxidize more rapidly after randomization of their glycerides, but the reason for this is unclear. Sahasradbudhe and Farn suggested that the unsymmetrical distribution of the unsaturated fatty acids in natural triglycerides might add to their stability (1). Raghuveer and Hammond (2) reported that the rate of oxidation of mixtures of 1.5–2% trilinolein or trilinolenin in tridecanoin decreased after randomization. They attributed this to more complete dispersal of the unsaturated fatty acids in the inert tridecanoin. They noted that most fats were less stable after randomization and proposed a theory based on the hexagonal packing of glyceride acyl chains in the molten state to account for this. They suggested that the acyl groups on the *sn*-1 and *sn*-3-positions of glyceryl should oxidize faster than those at *sn*-2, and the preferential placement of unsaturated acyl groups on *sn*-2 in many natural fats should increase their stability.

Hoffmann et al. (3) studied the oxidative stability of synthetic triglycerides containing palmitic, stearic, oleic and linoleic acids. They concluded that stability was not determined solely by total unsaturation. Triglycerides with the same acyl groups on the α-positions and a different acyl group on the β generally were more stable than the corresponding isomers with the same acyl groups on the β- and one of the α-positions. Catalino et al. (4) arrived at similar conclusions based on studies of natural disaturated olein fractions.

Fatemi and Hammond (5) measured the amounts of oleic, linoleic and linolenic hydroperoxides formed in the oxidation of natural and randomized olive and soybean oils. Randomized caused no detectable difference in the proportion of the hydroperoxides that were formed. They calculated from the extent of asymmetry in acyl group distribution in the natural oils that, if glyceride structure limited contact between acyl groups as Raghuveer and Hammond supposed, the effect on oxidation should be small.

In this study, oxidation rates of natural and randomized corn oil were compared, and the products of oxidation were analyzed to try to find out why randomization affects oxidation rate.

METHODS

Corn oil was randomized by stirring with 0.5% sodium methoxide at 60 C for 5 hr at 1 Torr. Methyl esters of corn oil fatty acids were prepared with 0.5% sodium methoxide (6-hr reflux) or 2% sulfuric acid (18-hr reflux) as catalysts in methanol. The triglycerides and methyl esters were purified by passage through alumina (6) to remove antioxidants and impurities which interfered with subsequent analysis. Tocopherol analyses were performed according to Meijboom and Jongenotter (7). Gas chromatography (GC) was done on a Varian (Palo Alto, CA) 3700 instrument with a flame detector and a 1 m × 3.3 mm glass column packed with 3% JXR. Temperature was programmed from 190 to 230 C at 10 C/min. Unoxidized methyl esters were analyzed on a Beckman (Fullerton, CA) GC 5 instrument fitted with a flame detector and using a 2 m × 3.3 column packed with 15% EGSSX. Column temperature was 110 C. The peak areas were integrated electronically.

All oxidations were in 5-g amounts of oil in 125-mL Erlenmeyer flasks at 28 C without stirring. Peroxide values were determined periodicially by the Stamm method (8). Tetrachloroethane for the Stamm test was purified by treatment at 100 C for 1 hr with laroyl peroxide, distillation at 11 Torr, and redistillation over 1,5-diphenylcarbohydrazide at 11 Torr.

Rac-1-oleyl-2,3-distearin and 2-oleyl-1,3-distearin were synthesized according to Quinn et al. (9). Triacetin was "randomized" by treatment identical to that of corn oil. Distilled methyl esters were prepared with a 48-cm Widmer column at 0.5 Torr.

When samples reached peroxide values of 30–40, portions were reduced by the iodometric method of the AOCS (10). The samples were extracted with chloroform, washed with water and 5% sodium bicarbonate solution and dried over sodium sulfate. The chloroform was evaporated at reduced pressure while keeping the temperature below 40 C. Silica Gel G plates, 0.75 mm thick, were used for fractionation of 100-mg portions of the reduced triglycerides. The plates were developed in hexane/ether (60:40), and the bands were visualized by spraying with 0.2% 2′,7′-dichlorofluorescein in ethanol and viewing under ultraviolet light. Castor oil with part of its hydroxy groups converted to trimethylsilyl (TMS) ethers was prepared for a thin layer chromatography (TLC) standard by reacting 10 g of castor oil with 1.06 g pyridine and 1.55 g trimethylchlorosilane. For further analysis, the triglyceride bands were converted to methyl esters by reaction in methanol with 0.5% sodium methoxide or 15% boron trifluoride. Oxidized methyl esters were fractionated under the same conditions used for triglycerides except that methyl ricinoleate was used as a TLC standard.

TMS-ethers of hydroxy fatty acids were prepared according to Fatemi and Hammond (5) except the reaction time was extended to overnight. The material recovered from the TLC plates and their TMS-derivatives were analyzed on a 2 m × 3.3 mm column of 10% OV 225 in a Varian 3700 instrument. Column temperature was 195 C for the TMS-derivatives, and for the other materials, temperature was programmed from 50 to 230 C at 10 C/min. Peak areas were integrated mechanically. Methyl heptadecanoate was used as an internal standard.

[1] Journal Paper no. J-10497 of the Iowa Agriculture and Home Economics Experiment Station, Ames. Project no. 2143.

TABLE I

Rate of Oxidation of Natural and Randomized Corn Oil and Corn Oil Methyl Esters

	Slope[a] ($days^{-1}$)	r^2
Corn oil	0.06	1.00
	0.06	1.00
	0.08	0.92
	0.08	1.00
Randomized corn oil	0.18	1.00
	0.19	0.98
	0.21	1.00
	0.25	0.96
	0.29	0.94
Corn oil methyl esters	0.25	0.99
	0.26	0.97
	0.37	0.89
Corn oil + 3% *rac*-1,2-distearoylolein	0.05	0.95
Randomized corn oil + 3% 1,3-distearo-2-olein	0.25	1.00
Corn oil + "randomized triacetin"	0.06	0.81
Corn oil + triacetin	0.06	0.96
Corn oil methyl esters—before distillation	0.27	0.97
Distillate	0.35	1.00

[a]Rate constant of oxidation.

Infrared (IR) spectra were obtained with a Beckman IR-12 instrument with a beam condenser. Mass spectra were obtained with a Finnegan (Sunnyvale, CA) 400 gas chromatograph-mass spectrometer fitted with an OV 1 capillary column. Lipase hydrolysis was according to Luddy et al. (11). Methyl azelaic semialdehyde was prepared by ozonolysis of methyl oleate (12).

RESULTS AND DISCUSSION

Rate Studies

The logarithm of the peroxide values of the oil samples vs times was fit by linear regression. The slopes and r^2 are given in Table I. The slope is the oxidation rate constant (13). Randomized corn oil oxidized three to four times faster than natural corn oil, and the methyl esters of corn oil oxidized at about the same rate as randomized corn oil. Rate studies such as these are subject to variation because of trace impurities, but the effect of randomization is clear. Analysis showed that the alumina treatment of the esters and oils removed any detectable tocopherol.

Hoffmann et al. (3) have suggested that α,α'-disaturated-β-unsaturated triglycerides are more stable than α,β-disaturated-α'-unsaturated triglycerides of the same fatty acid composition. There is not much disaturated triglyceride in corn oil, but it was possible that these triglycerides exerted some stabilizing or destabilizing influence. 1,3-Distearoylolein was added to randomized corn oil, and *rac*-1,2-distearoylolein was added to corn oil. At the 3% level at which disaturated triglycerides might be expected in corn oil, these triglycerides had no effect on the oxidation rate.

It seems possible that randomization produced some prooxidant or destroyed some antioxidant in the natural oil other than tocopherol. Such a pro- or antioxidant would have to pass through the alumina treatment with the oil an and be produced equally well by sodium methoxide or sulfuric acid catalysis. This seems improbable. One possibility, however, is that the ester groups of the triglycerides engage in some side reaction to produce a prooxidant. To test this, triacetin was treated with sodium methoxide as if to randomize it, added to corn oil so that the amount of glycerol exposed to sodium methoxide was the same as that in corn oil, and the mixture was oxidized. The "randomized" triacetin had no effect on the oxidation rate. If a prooxidant were produced, it might be separated from the methyl esters by distillation; however, distillation of the esters did not reduce the oxidation rate.

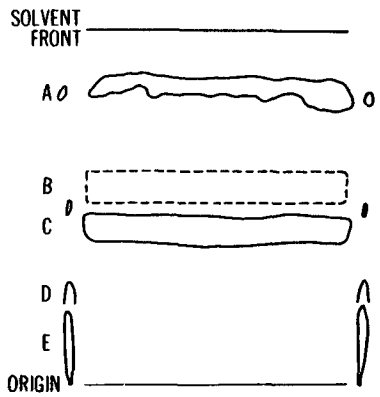

FIG. 1. Preparative thin layer chromatographic separations of oxidized randomized corn oil on Silica gel G. Solvent system: hexane/diethyl ether (70:30, v/v). A, unoxidized triglycerides; B, unknown band; C, monohydroxy-triglycerides; D, dihydroxy-triglycerides; E, trihydroxy-triglycerides.

Analysis of Oxidation Products

A chromatogram of oxidized oil after reduction by hydrogen iodide (HI) is shown in Figure 1. Two bands were produced with R_f values close to those expected for monohydroxytriglycerides. One band, B, traveled slightly ahead and the other, C, slightly behind the second highest spot of the castor oil standard. Two similar bands were obtained when the oxidized methyl esters of corn oil were reduced and fractionated by TLC.

To identify the B-bands from the TLC plates, those obtained from methyl esters were examined directly by GC and GC-MS. Those from oxidized corn oil were examined by GC after transesterification with both sodium methoxide and boron trifluoride in methanol. IR spectra also were obtained. The GC results are given in Figure 2, and the MS data are in Table II. Peak 1 was found only in gas chromatograms of the methyl esters. Its mass spectra matched that of nonanal (14). Peaks 2 and 3 appeared in the chromatograms of the methyl esters and in those of the oxidized triglycerides. The mass spectra of peaks 2 and 3 were identical and were the same regardless of the source. Peaks 1, 2 and 3 all were destroyed by sodium methoxide treatment, suggesting that they all were aldehydes. Peaks 2 and 3 have a mass of 152 and mass spectra similar to that of 2,4-decadienal (14). Peaks 4 and 5 were identified as methyl azelaic semialdehyde and dimethyl azelate by their retention times and mass spectra. Methyl azelaic semialdehyde would be an expected oxidation product of corn oil methyl esters, but dimethyl azelate would not. Moreover, these compounds were definitely present in small amounts in the oxidized triglycerides, where their presence is difficult to explain. They could not be detected in the unoxidized materials. Treatment of the oxidized triglyceride B-band with BF_3-methanol produced considerable amounts of methyl acelaic semialdehyde and its dimethyl acetal (peak 4). Unoxidized fatty acid methyl esters also

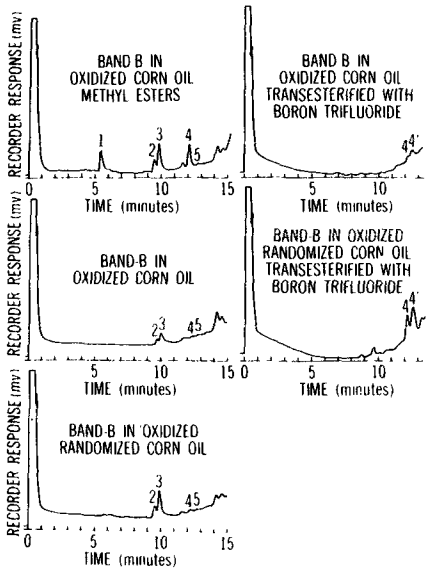

FIG. 2. Gas chromatograms for B-bands in oxidized corn oil methyl esters and oxidized natural and randomized corn oil. GC column was 2 m × 3.3 mm 10% OV 225. Temperature was programmed from 50 to 230 C.

TABLE II

Mass Spectral Data of the Scission Products Present in B-Band

Identification	Fragments m/e (relative abundance)
Peak 1 (nonanal)	71(100), 85(57.7), 70(44.0), 84(23.4), 67(12.0), 99(12.3), 69(10.6), 98(10.7), 142(6.6), 113(5.7)
Peaks 2 and 3 (2,4-decadienal)	81(100), 67(27.9), 65(12.4), 66(12.4), 83(11.2), 79(7.2), 152(2.9), 109(1.4), 123(1.4)
Peak 4 (methyl azelaic semialdehyde)	74(100), 87(49.4), 83(34.8), 111(24.2), 143(15.7), 155(8.4), 98(7.3), 94(5.6), 115(5.6), 158(3.9), 129(1.7)
Peak 5 (dimethyl azelate)	74(100), 152(62.6), 83(61.5), 111(45.3), 185(44.7), 84(33.0), 87(31.3), 143(25.7), 97(19.6), 124(14.2)

were produced by transesterification. They are not visible in the gas chromatograms in Figure 2 but could be observed under isothermal conditions.

IR spectra of the B-bands showed that the B-band from methyl esters was similar to that for methyl azelaic semialdehyde and that from oxidized corn oil was similar to that of corn oil, except the unsaturation bands at 3010 and 3040 cm^{-1} were reduced.

These results all are consistent with the B-bands containing aldehyde scission products of the oxidized fatty acids. In the oxidized triglycerides, an azelaic semialdehyde moiety is attached to the triglyceride. Presumably, products representing scission at the 13-position of linoleate are present as well, but they possessed retention times too great to be detected under the GC conditions that were used. Previous investigations did not report a B-band in oxidized esters (5,15). Probably this is because the B-band is not resolved from the unoxidized methyl esters if the

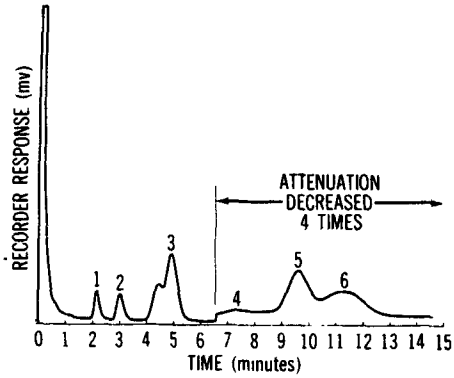

FIG. 3. Typical gas chromatograph of TMS derivatives of methyl hydroxyesters of oxidized corn oil. 1,3: unoxidized fatty acid methyl esters; 2: methyl heptadecanoate; 4: TMS-oleate; 5,6: TMS-linoleate. GC column was 2 m × 3.3 m 10% OV 225. Temperature was 195 C.

TLC plate is heavily loaded. Such heavy loading was used in the earlier investigations to maximize the yield of hydroxyesters.

There was an important difference in the B-bands from corn oil and randomized corn oil. The amount of B-band was much greater in randomized oils. This could be seen on TLC plates in which oils of similar peroxide value were fractionated, and the difference was verified by the GC results on the amounts of oxidation products (Fig. 2) as well as unoxidized fatty acids. The amount of B-band in the randomized oil was about 3 times greater than in the unrandomized corn oil.

To identify the C-bands from the TLC plates, those obtained from corn oil methyl esters were silylated and examined by GC, and those from oxidized triglycerides were converted to methyl esters with sodium methoxide-methanol before silylation. The C-bands from triglycerides gave results such as those in Figure 3, which indicated that they contained a mixture of unoxidized methyl esters and the TMS-ether of methyl hydroxyoctadecadienoate. The corresponding band from corn oil methyl esters contained only the TMS-ether. There was very little TMS-ether of methyl hydroxyoctadecenoate. This was expected from the relative rates of oxidation of oleate and linoleate reported previously (5).

Table III gives the apparent recovery of unoxidized and hydroxy esters based on the GC internal standard and the peroxide value, assuming all the hydroperoxide is recovered as the TMS-ether of methyl hydroxyoctadecadienoate. As previous results have shown, the recoveries are not quantitative. Wong and Hammond (15) reported recoveries of 63 and 40% for methyl oleate and linoleate hydroperoxides, respectively; Fatemi and Hammond (5) reported corresponding values of 62 and 44%. In this study, the recovery of methyl linoleate hydroperoxides in the corn oil methyl esters averaged 55%. This improved yield probably can be attributed to an increased time in the silylation reaction. If the 55% value is used to correct the yields obtained from the corn oil and randomized corn oil C-bands, the recoveries range from 68 to 83%. The low yields must be attributed to losses during transesterification and mechanical losses. The ratio of hydroxy ester (using corrected values) to unoxidized ester ranged from 1:1.5 to 1:2.0. Undoubtedly the C-bands in the oxidized oils represent monohydroxytriglycerides arising from monohydroperoxytriglycerides. Thus, the ratio should be 1:2. The slightly lower recoveries of the unoxidized fatty acids suggest the hydroxyester values have been overcorrected. This must at least partly be because some of the hydroperoxide is con-

TABLE III

GLC Analyses on the Recovery of TMS-Derivatives of Methyl Hydroxyesters of Oxidized Natural and Randomized Corn Oil and Methyl Esters of Corn Oil Based on PV

Oil	PV	Fatty acid % recovery		
		Oxidized	Unoxidized	Ratio oxidized: unoxidized
Corn oil[a]	30.5	70.2	61.0	1:1.7
	36.7	71.3	66.6	1:1.9
	43.4	68.2	53.6	1:1.6
Randomized corn oil[a]	23.9	68.9	57.9	1:1.7
	30.9	69.4	71.0	1:2.0
	31.1	82.6	57.4	1:1.4
	37.1	82.3	62.1	1:1.5
Methyl esters corn oil	26.7	52.6		
	34.0	58.6		
	45.7	56.1		
	45.8	57.2		
	48.7	51.4		

[a]Correction factors of 0.62 for methyl hydroxyoleate (5) and 0.55 for methyl hydroxylinoleate were applied in the calculation.

TABLE IV

Fatty Acid Composition of Unoxidized Methyl Esters Recovered from Monohydroxy-Triglycerides by Percent

Corn oil	Fatty acids				
	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Natural					
Triglycerides	10.71	1.35	24.62	62.55	0.77
Monohydroxy-triglycerides	12.22	1.63	23.56	61.74	0.84
Randomized					
Triglycerides	11.19	1.48	25.82	60.96	0.55
Monohydroxy-triglycerides	12.00	1.82	26.89	58.55	0.80

verted to B-band material. This loss is compensated in the correction factor for hydroxyesters but not for the unoxidized methyl esters.

The unoxidized fatty acids recovered from the C-band were analyzed and their compositions are given in Table IV. Attempts to determine the distribution of the unoxidized and hydroxy fatty acids on the glycerol positions with pancreatic lipase were unsuccessful because of the limited amount of material.

Theoretical Implication

The kinetic studies make it seem probable that glyceride structure affects the rate of oxidation, but it is unclear how this is accomplished. Raghuveer and Hammond (2) suggested that glyceride structure affected the rate of oxidation by altering the effective concentration of substrate, thus affecting the propagation rate. They suggested that, because of the hexagonal packing of the acyl chains in liquid fat, acyl groups attached to the *sn*-1- and 3-positions of the same glycerol molecule could readily interact with each other, and if one became oxidized, the other was likely to be oxidized. They also suggested that acyl groups attached to *sn*-2 were surrounded by acyl groups attached to the *sn*-1- and 3-positions of other glycerol molecules. It follows that, in an oil such as corn oil in which the more rapidly oxidizing linoleyl groups are concentrated at *sn*-2 and the saturated and slower oxidizing oleyl groups are concentrated at *sn*-1 and 3 (16), this should result in a slower rate of oxidation. But it was never clear that the asymmetry of this distribution was rigorous enough to result in much increased stability. Fatemi and Hammond (5), could find no difference in the proportions of oleate, linoleate and linolenate hydroperoxides in oxidized oils before and after randomization. If the asymmetry of the distribution changed the availability of substrate fatty acids significantly, there should have been a difference.

Clearly our results do not support the theory of Raghuveer and Hammond, because if the oxidation of an acyl group attached to the *sn*-1 position of a glycerol molecule is likely to result in the oxidation of an acyl group on *sn*-3, and vice versa, then there ought to be a substantial amount of dihydroperoxy-triglycerides in oxidized fats, and the proportion should increase with randomization. We could find no evidence for a detectable amount of dihydroperoxy-triglycerides at the oxidation levels we studied. Presumably, if such a compound existed, there would have been an additional, slower-moving band on the TLC plates.

The unoxidized methyl esters recovered from the C-band were not significantly different from those of unoxidized corn oil. Thus, the oxidation attack seems random, and there is no evidence that particular glycerides are singled out for oxidation.

The striking difference in the amount of scission product found in corn oil and randomized corn oil oxidized to the same extent probably plays some role in the difference in oxidation rates. It is unclear how much of this increase in scission occurred during oxidation and how much during the reduction of the hydroperoxides. In any event, the

hydroperoxides produced in randomized oil must somehow be more subject to scission. This might lead to an increased rate of the initiation reaction. There is considerable evidence that the hydroperoxides in oxidized fats associate (13). Possibly the glyceride structure of fats alters the associations that occur or the stress placed on the associated molecules so that the rate of decomposition of the hydroperoxides and their tendency to scission is altered.

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[Received December 28, 1981]

Derivatization of Keto Fatty Acids: I. Synthesis and Mass Spectrometry of Thiazolidinones[1]

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ABSTRACT

The synthesis of alkyl chain-substituted thiazolidinones from oxo acids is described. Reactions of mercaptoacetic acid with three oxo-esters, methyl 10-oxoundecanoate, methyl 12-oxooctadecanoate and methyl 9,10-dioxooctadecanoate gives excellent yields of the corresponding thazolidinones. Mass spectral fragmentation patterns of these long-chain thiazolidinone derivatives are discussed.

INTRODUCTION

Fatty acid derivatives that are chain-substituted by nitrogen or sulfur are, with few exceptions, rather obscure laboratory curiosities and are not found naturally except in the antibiotic actithiazic acid (1-3). Compared to the acyclic sulfur/nitrogen-containing fatty acid derivatives, scant literature is available for heterocycles such as thiazolidinones (4-6) and oxathiolane (7). Thiazolidinone derivatives are known to possess fungicidal, insecticidal, pesticidal and bactericidal properties. A number of pharmacological activities such as anesthetic, narcotic, sedative, anticonvulsant, anti-inflammatory and antithroidal effects have been found to be associated with these compounds (4-8). This paper reports the synthesis of chain-substituted sulfur/nitrogen heterocyclics from oxo-esters. Thiazolidinone derivatives have been identified spectroscopically. Only a few literature reports deal with the mass spectra (MS) of these compounds. MS of chain-substituted thiazolidinones have not been reported previously. Thus, MS of chain-substituted thiazolidinone derivatives was studied to obtain the basic fragmentation and to establish the position of the heterocyclic ring in the fatty acid chain.

[1]Presented at the ISF/AOCS World Congress, 1980, New York.

EXPERIMENTAL PROCEDURES

Infrared (IR) spectra were obtained with a Perkin-Elmer 621 spectrophotometer, using a 1% solution in carbon tetrachloride. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ with a Varian A60 spectrometer. Chemical shifts were measured in ppm downfield from internal tetramethylsilane ($\delta = 0$). MS were measured with an AEI MS 902 mass spectrometer.

Analytical thin layer chromatography (TLC) was done on glass plates (20 × 5 cm) with a layer of Silica Gel G (0.25 mm thickness). Mixtures of diethyl ether and petroleum were used as developing solvents. Components on TLC plates were made visible by spraying with an aqueous solution (20%) of perchloric acid and heating at 120 C.

Methyl esters were preapred by refluxing the acids with absolute methanol containing catalytic amounts of sulfuric acid.

Preparation of Oxo-Fatty Acids

10-Oxoundecanoic acid (I). Solvomercuration-demercuration of 10-undecenoic acid yielded 10-hydroxyundecanoic acid (9), mp 49 C. (All melting points are uncorrected.) The pure 10-hydroxyundecanoic acid, upon Jones' oxidation (10), afforded 10-oxoundecanoic acid, mp 58-59 C. IR (CCl_4) 1710, 1720 cm^{-1}. NMR ($CDCl_3$), δ 2.36 (4 protons), 1.9 (3 protons, singlet).

12-Oxooctadecanoic acid (II). Pure 12-hydroxy-*cis*-9-octadecenoic acid was isolated from castor (*Ricinus communis*) seed oil by Gunstone's partitioning procedure (11). This hydroxyolefinic acid, upon hydrogenation with palladium on charcoal in ethyl acetate, yielded 12-hydroxyoctadecanoic acid, mp 79 C. Jones' oxidation of saturated 12-hydroxy acid gave 12-oxooctadecanoic acid, mp 82-82.5 C IR (CCl_4) 1710, 1720 cm^{-1}.