After 18, 40, and 53 days, samples were withdrawn and submitted to countercurrent distribution in the system 80% aqueous ethanol and pentane-hexane. In Figure 8 is given the results of a 400-transfer stage countercurrent distribution of the 53-day nitrogen storage. Some differences are found in compounds formed under nitrogen as compared to oxygen. A peak occurs at tube 133 on the oxygen storage curve (Figure 5) but not on the nitrogen. Tube 60 shows a peak on the nitrogen curve but not on the oxygen. The peak at tube 60 is a little more than half the peroxide value of pure MLHP but contains proportionately little diene conjugation. It is the lack of diene conjugation that clearly differentiates this peak from the more polar peak at tube 10 in Figure 8.

Also shown on Figure 8 are some molecular weights on the combined fractions. This pattern is also similar to the molecular weight data for oxygen storage (Figure 5). Again lower molecular weight toward the more polar area of the curve is explained by shorter chain-length scission acids and is confirmed by increased titratable acidity. Less acidity per unit of weight was observed in nitrogen storage than in oxygen and can be explained by the effect of limited oxygen supply on the production of oxidative scission products.

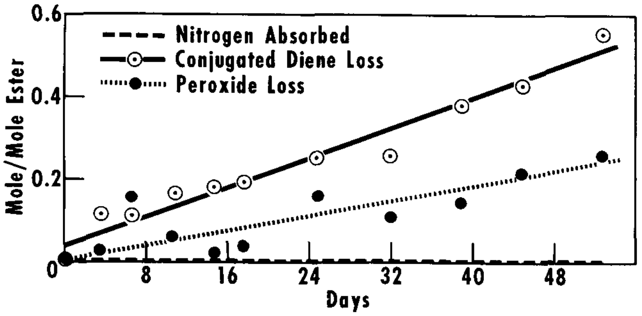

FIG. 7. Storage of methyl linoleate hydroperoxide in nitrogen.

The average molecular weights obtained for material on this curve are somewhat lower than for oxygen storage, and this difference is accounted for, in part, by the 2 moles of oxygen absorbed per mole of dimer formed during oxygen storage; thus in those dimers where no scission takes place, the added oxygen would increase the molecular weight. There is also the possibility that small amounts of trimer or higher molecular weight polymer are formed.

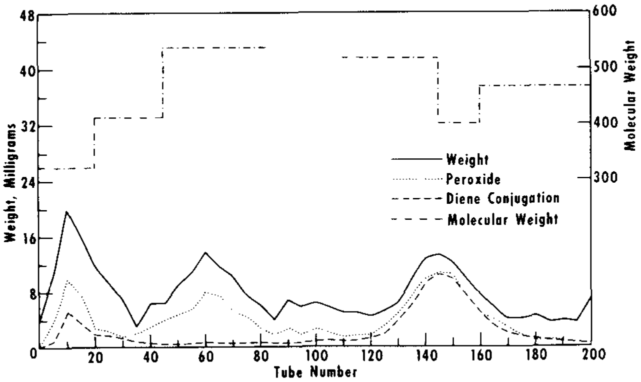

FIG. 8. Countercurrent distribution (400 transfer stages) after 57 days' storage of methyl linoleate hydroperoxide in nitrogen.

Infrared curves run on the nitrogen samples also showed the same pattern of a shift from *cis,trans* to isolated *trans* as the reaction progresses.

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Carbonyls in Oxidizing Fat. V. The Composition of Neutral Volatile Monocarbonyl Compounds from Autoxidized Oleate, Linoleate, Linolenate Esters, and Fats

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The steam volatile monocarbonyl compounds in mildly autoxidized esters of oleic, linoleic, linolenic acids, and animal and vegetable fats were quantitatively estimated. The major aldehydes in oleate and linoleate were those that might be expected from the scission of reported monomeric hydroperoxide isomers. The predominance of hept-2,4-dienal and propanal in linolenate suggested that the major monomeric hydroperoxides were 12- and 16-hydroperoxy conjugated dienoic isomers. The number of minor aldehydes increased with degree of unsaturation of the fatty acid. The amounts of monocarbonyl compounds in the fats examined generally agreed with their average fatty acid composition. Appreciable amounts of heptanal in lamb and beef fat and heptanal and decanal in butterfat, under the conditions of oxidation, could not have come from the three unsaturated acids. Heating at 165°C. in all samples increased the proportions of the most unsaturated major aldehydes.

OXIDATIVE RANCIDITY in various fats develops at different peroxide levels. This, regardless of causative factors, is a reflection of the kinds and amounts of carbonyl compounds generated and is of great interest in the study of the nature of rancidity. The qualitative analysis of the volatile monocarbonyl compounds produced by mildly oxidized esters of oleic, linoleic, linolenic acids, and several animal and vegetable fats was recently described (5). This report contains an extension to the quantitative estimation of the separated 2,4-dinitrophenylhydrazone derivatives.

Experimental

Materials (except for butterfat[1]), as well as methods, were the same as described in the preceding publication (5), with thin films of samples oxidized under ultraviolet light at room temperature. Hydrazones of steam volatile monocarbonyls from unheated and heated (165°C. for 15 min. in open vessel) samples (10) were separated by paper chromatographic methods into individual compounds (3,11), and these were identified and estimated by previously reported methods and applications (4,11,12,13). Results are based on contents of 10 g. of oxidized sample, with correction factors applied as indicated by experiments with known mixtures (4).

Results and Discussion

Volatile aldehydes measured in oxidized methyl oleate and triolein are shown in Table I. Over-all there was good agreement between the ester and triglyceride. Oleate has been found to form monomeric hydroperoxide isomers 8, 9, 10, and 11 in equal amounts (19). The expected aldehydes from these hydroperoxides, undec-2-enal, dec-2-enal, n-nonanal, and n-octanal, respectively, were the major compounds, but they were not individually equal. n-Nononal predominated in the unheated and undec-2-enal and dec-2-enal in the heated. Since heating at 165°C. was probably accompanied by some loss of the more volatile compounds and further oxidation, the results were not entirely representative of the effect of heat on the hydroperoxides and carbonyl generation. Nevertheless there appeared to be a considerable difference in the scission of monomeric hydroperoxide isomers if they were present and formed in equal amounts.

Ethanal, n-hexanal, n-undecenal, and non-2-enal were also present in minor amounts. Ethanal and non-2-enal were found in both linoleate and linolenate (Table II). These compounds cannot be due to linolenate impurity since the characteristic major monocarbonyl compounds of that acid were not present. Possibly these compounds arise from mutually-contained impurities. n-Hexanal is strongly characteristic of linoleate (Table II). The relatively high proportions of this compound in aldehydes from both oleates make it difficult to explain on the basis of linoleate impurity. However the effect of linoleate impurity would be marked because of its higher oxidation rate. Both oleate samples contained some linoleate impurity as indicated by the detection of traces of alk-2,4-dienals in more oxidized samples. Fritsch and Deatherage (7) found C_6, C_7, C_8, and C_9 saturated acids in decomposed volatile peroxides isolated from methyl oleate oxidized at 80°C. These volatile peroxides yielded carbonyl compounds on reduction and could be partially converted into carbonyl derivatives. The carbonyl compounds which these interesting compounds might yield were not determined (7). n-Undecanal was found only in the oxidized oleates. The mechanism of formation of this compound is not known since the evidence is that the double bond migrates only between the 11 and 8 carbons.

The carbonyl compounds determined in oxidized ethyl linoleate and methyl linoleate are indicated in Table II. According to existing theories, as reviewed by Badings (1), the formation of three isomeric hydroperoxides is possible in autoxidized linoleate. These are the nonconjugated 11 and conjugated 9 and 13 isomers which would yield oct-2-enal, dec-2,4-dienal, and n-hexanal, respectively. Badings (1) found these carbonyls to be the major monocarbonyl compounds in oxidized ammonium linoleate. In this work n-hexanal and dec-2,4-dienal were the predominant volatile aldehydes found. This agrees with the reports (1) that the greater part of the hydroperoxides formed have conjugated double bonds. Hept-2-enal, oct-2-enal, and non-2-enal were present among the minor carbonyl compounds with hept-2-enal predominating

TABLE I

Comparison of Volatile Monocarbonyl Composition of Ester and Triglyceride

	Monocarbonyl 2,4-Dinitrophenylhydrazones/10 g.							
	Methyl oleate (peroxide 40.8)				Triolein (peroxide 43.0)			
	Unheated		Heated		Unheated		Heated	
	Micromoles	%	Micromoles	%	Micromoles	%	Micromoles	%
Alkanals	4.44	58.2	10.68	29.9	3.34	67.2	8.25	27.4
C_1	......	......	......	......	......	......	......	......
C_2	......	......	......	......	0.42	8.5	......	......
C_3	......	......	......	......	......	......	......	......
C_4	......	......	......	......	......	......	......	......
C_5	......	......	......	......	......	......	......	......
C_6	1.22	16.0	1.45	4.1	0.84	16.9	1.06	3.5
C_7	......	......	......	......	......	......	......	......
C_8	0.79	10.4	1.88	5.3	0.54	10.9	1.04	3.5
C_9	1.85	24.2	5.45	15.2	1.14	22.9	4.40	14.6
C_{10}	......	......	......	......	......	......	......	......
C_{11}	0.58	7.6	1.90	5.3	0.40	8.0	1.75	5.8
Enals	3.19	41.8	25.04	70.1	1.63	32.8	21.87	72.6
C_3	......	......	......	......	......	......	......	......
C_4	......	......	......	......	......	......	......	......
C_5	......	......	......	......	......	......	......	......
C_6	......	......	......	......	......	......	......	......
C_7	......	......	......	......	......	......	......	......
C_8	......	......	......	......	......	......	......	......
C_9	0.45	5.9	1.45	4.1	0.31	6.2	0.84	2.8
C_{10}	1.36	17.8	10.29	28.8	0.73	14.7	9.42	31.3
C_{11}	1.38	18.1	13.30	37.2	0.59	11.9	11.61	38.5

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[1] Furnished by D.P. Schwartz of our Dairy Products Laboratory.

TABLE II

Volatile Monocarbonyl Content of Oxidized Polyene Esters

	Monocarbonyl 2,4-Dinitrophenylhydrazones/10 g.							
	Ethyl linoleate—pv 200				Methyl linolenate—pv 93			
	Unheated		Heated		Unheated		Heated	
	Micromoles	%	Micromoles	%	Micromoles	%	Micromoles	%
Alkanals	9.84	57.5	12.69	11.6	3.72	45.6	3.70	13.3
C_1	......	......	......	......	......	......	......	......
C_2	1.01	5.9	......	......	0.10	1.2	0.26	0.9
C_3	0.44	2.6	......	......	2.59	31.8	2.65	9.5
C_4	......	......	......	......	1.03	12.6	0.79	2.9
C_5	......	......	......	......	......	......	......	......
C_6	8.39	49.0	9.54	8.7	......	......	......	......
C_7	......	......	......	......	......	......	......	......
C_8	......	......	......	......	......	......	......	......
C_9	......	......	3.15	2.9	......	......	......	......
Enals	3.21	18.7	17.82	16.3	1.94	23.8	4.07	14.6
C_3	......	......	......	......	......	......	......	......
C_4	......	......	......	......	0.27	3.3	0.51	1.8
C_5	......	......	......	......	0.60	7.3	1.49	5.4
C_6	......	......	......	......	0.54	6.6	0.95	3.4
C_7	1.95	11.4	6.96	6.4	0.38	4.7	0.66	2.4
C_8	0.79	4.6	4.00	3.7	......	......	......	......
C_9	0.47	2.7	6.86	6.2	0.15	1.9	0.46	1.6
C_{10}	......	......	......	......	......	......	......	......
C_{11}	......	......	......	......	......	......	......	......
Dienals	4.08	23.8	79.05	72.1	2.50	30.6	20.06	72.1
C_7	......	......	......	......	2.35	28.8	12.56	45.1
C_8	......	......	......	......	......	......	......	27.0
C_9	0.41	2.4	......	......	0.15	1.8	7.50	......
C_{10}	3.67	21.4	79.05	72.1	......	......	......	......
C_{11}	......	......	......	......	......	......	......	......
C_{12}	......	......	......	......	.....	......	......	

in this group. These carbonyl compounds might arise from nonconjugated hydroperoxides, but the lack of supporting evidence for the presence of such hydroperoxides makes this mechanism of formation questionable (1). Patton *et al.* (18) have reported the presence of hept-2-enal, non-2-enal, dec-2-enal, and dec-2,4-dienal in the steam distillate of methyl linoleate. Modest quantities of ethanal, propanal, and non-2,4-dienal found potentially could come from linolenate impurity, but the major monocarbonyl component of linolenate, hept-2,4-dienal, was not detected. In higher oxidized samples of linoleate, small amounts of dodec-2,4-dienal were found. Chang and Kummerow (2) obtained ethanal, pentanal, and hexanal from oxidized polymers of ethyl linoleate, but pentanal was not found in our study. The small amounts of nonanal detected could not have come from oleate impurity as dec-2-enal and undec-2-enal were not present.

The nature of the process of linolenate autoxidation has not been completely established (16). Fugger *et al.* (8) found diene and triene conjugation and only a small amount of monomeric hydroperoxide. As shown in Table II, the major carbonyl compounds were propanal and hept-2,4-dienal. These compounds could come from a single resonating radical form (6), giving diene conjugated hydroperoxides 16 and 12, with unsaturation in 9, 12, 14 and 9, 13, 15 positions, respectively. Heating had the effect of making hept-2,4-dienal and non-2,4-dienal the predominant compounds. In addition to the major carbonyl compounds butanal and but-2-enal, pent-2-enal, and hex-2-enal appeared characteristic of linolenate. However the other minor carbonyl compounds could not be logically traced to linoleate impurity. Kawahara *et al.* (15) found ethanal, propanal, but-2-enal, and pent-2-enal in autoxidized linolenate. Their presence in soybean oil was rationalized by Kawahara and Dutton (14) by the hydroperoxide hypothesis of Farmer *et al.* (6). A small amount of trienal monocarbonyl compound was detected in our work (5), which has not been identified.

Each autoxidized fatty acid produced several major characteristic aldehydes. In the case of oleate and linoleate, these compounds would result from the scission of the monomeric hydroperoxides known to be present. Little is known about the monomeric hydroperoxide isomers of linolenate, but their behavior in carbonyl formation may be similar to the less unsaturated acids. The number of minor monocarbonyl compounds increased with the degree of unsaturation. The mechanism of their formation is not clear. Some may be formed by side reactions involving the volatile

TABLE III

Comparison of Mixtures of Stearic, Palmitic, Oleic, and Linoleic Esters

	Volatile Monocarbonyl 2,4-Dinitrophenylhydrazones/10 g.					
	Pork mixture (Peroxide 28.0)		Lamb mixture (Peroxide 31.0)		Beef mixture (Peroxide 33.0)	
	Unheated	Heated	Unheated	Heated	Unheated	Heated
	% of 4.40 µm	% of 10.63 µm	% of 5.95 µm	% of 12.36 µm	% of 3.93 µm	% of 15.49 µm
Alkanals	67.1	39.0	63.2	51.1	62.3	43.6
C_2	6.2	......	4.7	......	......	......
C_3	3.2	......	......	......	......	......
C_4	......	......	......	......	......	......
C_5	......	......	......	......	......	......
C_6	28.4	16.2	18.7	12.5	18.6	8.0
C_7	......	......	......	......	......	......
C_8	8.2	4.6	11.8	6.4	10.7	6.9
C_9	16.1	14.2	22.5	27.5	29.5	21.5
C_{10}	......	......	......	......	......	......
C_{11}	5.0	4.0	5.5	5.1	3.5	7.2
Enals	23.6	36.7	29.6	38.3	30.3	47.6
C_3	......	......	......	......	......	......
C_4	......	......	......	......	......	......
C_5	......	......	......	......	......	......
C_6	......	......	......	......	......	......
C_7	2.7	9.5	2.9	4.3	2.3	3.5
C_8	3.8	4.1	2.7	2.6	2.0	2.7
C_9	2.5	2.9	3.9	3.7	4.1	4.4
C_{10}	8.0	11.5	9.9	15.9	12.2	20.7
C_{11}	6.6	8.7	10.2	11.8	9.7	16.3
Dienals	9.3	24.3	7.2	10.2	7.4	8.7
C_7	......	......	......	......	......	......
C_8	......	......	......	......	......	......
C_9	1.4	0.9	1.2	1.3	1.3	0.8
C_{10}	7.0	21.3	4.8	7.5	5.1	6.4
C_{11}	......	......	......	......	......	......
C_{12}	0.9	2.1	1.2	1.4	1.0	1.5

peroxides described by Fritsch and Deatherage (7).

The effect of simultaneously oxidizing mixtures of palmitic, stearic, oleic, and linoleic esters is shown in Table III. Mixtures were made up in the proportions usually found in pork, lamb, and beef fat [pork: palmitate 30.1%, stearate 16.2%, oleate 46.6%, and linoleate 7.1%; lamb: 24.4%, 34.5%, 39.1%, and 2.0%, respectively; and beef: 32.0%, 21.0%, 45.9%, and 1.1%, respectively]. Proportions of volatile monocarbonyl compounds found were generally as might be expected from the amounts of oleate and linoleate.

In Table IV a comparison was made of pork, lamb, beef, and butterfat with palm oil (fruit-coat) and cocoa butter. Pork fat and palm oil, and lamb fat cocoa butter are, in general, similar in composition but different in glyceride structure (5). These fats varied considerably in the effect of heating at 165°C. on the amounts and proportions of monocarbonyl compounds. It is not clear whether this was due to antioxidants, glyceride structure, fatty acid content, or to degree of oxidation, as judged from peroxide determination. Peroxide values are not entirely satisfactory as a means of determining comparable degrees of attack by oxygen.

Fairly abundant amounts of heptanal were found in lamb, beef, and butterfat. Butterfat also contained an appreciable amount of decanal. These two carbonyls did not originate from oleate, linoleate, and linolenate. Undec-2,4-dienal was found in small amounts in butterfat but not in the other fats or esters except for traces in beef fat. This is an elusive compound. In earlier work it was found in small amounts in oxidized pork tissue fat (12). Witting and Schweigert (20) found predominant amounts of this compound in lard oxidized with *gamma* irradiation. On the other

TABLE V

Volatile Monocarbonyl Composition of Highly Unsaturated Vegetable Oils

	Carbonyl 2,4-Dinitrophenylhydrazones/10 g.					
	Peanut oil (Peroxide 26.0)		Soybean oil (Peroxide 33.0)		Linseed oil (Peroxide 33.0)	
	Unheated	Heated	Unheated	Heated	Unheated	Heated
	% of 2.22 μm	% of 5.85 μm	% of 3.51 μm	% of 7.70 μm	% of 10.56 μm	% of 16.19 μm
Alkanals	58.6	46.0	57.0	44.6	48.4	32.0
C_1	......	......	1.7	......	......	......
C_2	3.6	......	3.5	......	4.3	1.6
C_3	......	......	13.7	5.5	14.7	12.1
C_4	......	......	......	......	6.0	4.0
C_5	......	......	......	......	......	......
C_6	35.6	32.5	25.4	21.3	12.3	9.4
C_7	......	......	......	......	......	......
C_8	9.5	......	6.2	7.5	......	......
C_9	9.9	13.5	6.5	10.3	11.1	4.9
C_{10}	......	......	......	......	......	......
C_{11}	......	......	......	......	......	......
Enals	23.0	23.4	19.4	25.6	20.1	21.4
C_3	......	......	......	......	......	......
C_4	......	......	......	......	2.3	1.4
C_5	......	......	2.3	......	5.9	5.9
C_6	......	......	2.6	1.6	5.4	5.7
C_7	6.3	12.0	4.3	7.8	4.4	5.3
C_8	6.8	3.7	3.1	3.5	......	......
C_9	7.2	5.1	4.6	7.3	2.1	3.1
C_{10}	1.8	1.2	1.4	3.2	......	......
C_{11}	0.9	1.4	1.1	2.2	......	......
Dienals	18.5	30.6	23.7	29.9	31.5	46.6
C_7	2.7	2.9	10.9	6.2	26.3	27.2
C_8	......	......	......	......	......	......
C_9	3.2	2.1	3.4	2.5	3.2	11.2
C_{10}	12.6	22.4	9.4	20.9	2.0	8.2
C_{11}	......	......	......	......	......	......
C_{12}	......	3.3	......	0.3	......	......

TABLE IV

Comparison of Animal and Vegetable Fats

	Volatile Monocarbonyl 2,4-Dinitrophenylhydrazones 10 g.											
	Pork fat (rendered) (Peroxide 30.8)		Palm oil (Peroxide 27.0)		Lamb fat (rendered) (Peroxide 30.0)		Cocoa butter (Peroxide 33.0)		Beef fat (rendered) (Peroxide 31.5)		Butterfat (Peroxide 30.1)	
	Unheated	Heated	Unheated	Heated	Unheated	Heated	Unheated	Heated	Unheated	Heated	Unheated	Heated
	% of 3.51 μm	% of 9.70 μm	% of 2.64 μm	% of 5.86 μm	% of 4.79 μm	% of 10.35 μm	% of 3.02 μm	% of 5.52 μm	% of 4.75 μm	% of 7.38 μm	% of 5.61 μm	% of 14.03 μm
Alkanals	65.0	37.9	73.5	58.4	55.5	54.1	66.6	56.2	63.2	49.5	66.3	39.1
C_1	......	......	......	......	......	......	......	......	......	......	1.0	......
C_2	1.7	2.8	4.6	......	2.1	3.2	3.0	......	1.3	......	3.4	......
C_3	11.7	2.4	3.4	......	6.4	7.7	4.6	......	3.4	......	13.0[a]	......
C_4	......	......	......	......	......	......	......	......	......	......	......	......
C_5	......	......	......	......	......	......	......	......	......	......	8.0	4.6
C_6	27.3	13.9	37.1	31.2	9.8	9.5	24.5	24.1	16.2	10.6	11.1	8.7
C_7	......	......	......	......	11.9	11.0	......	......	7.4	6.4	8.9	8.1
C_8	8.0	4.7	6.1	4.6	6.7	5.7	8.3	6.5	9.1	7.7	5.9	4.4
C_9	12.0	10.7	17.8	18.3	14.4	12.8	23.2	22.3	19.8	18.6	11.1	9.5
C_{10}	......	......	......	......	......	......	......	......	......	......	3.9	3.8
C_{11}	4.3	3.4	4.5	4.3	4.2	4.2	3.0	3.3	6.1	6.2	......	......
Enals	22.5	25.5	15.5	27.7	39.7	37.1	21.9	33.0	29.1	41.6	23.5	30.1
C_3	......	......	......	......	......	......	......	......	......	......	......	......
C_4	......	......	......	......	......	......	......	......	......	......	1.8	......
C_5	2.3	......	1.1	......	2.7	3.6	......	......	1.7	......	2.3	1.7
C_6	......	......	1.5	......	......	......	......	......	......	......	2.5	2.3
C_7	5.4	5.4	3.8	11.8	3.6	4.1	4.7	10.1	3.0	4.5	2.6	3.9
C_8	4.6	3.5	2.7	4.5	4.4	3.8	3.6	4.0	3.6	4.9	2.6	3.2
C_9	3.4	3.8	3.0	3.9	18.6	12.4	3.0	2.9	8.6	8.2	6.1	9.3
C_{10}	4.0	6.5	2.3	4.8	5.6	7.2	7.0	10.0	6.5	12.6	2.7	4.9
C_{11}	2.8	6.3	1.1	2.7	4.8	6.0	3.6	6.0	5.7	11.4	2.9	4.8
Dienals	12.5	36.6	11.0	14.0	4.8	8.8	11.6	10.9	7.8	8.9	10.2	13.0
C_7	4.3	2.8	1.9	2.4	1.7	2.4	2.7	1.8	1.5	1.2	3.4	4.6
C_8	......	......	......	......	......	......	......	......	......	......	......	......
C_9	2.0	1.7	2.7	2.1	1.0	1.3	2.7	1.6	1.7	1.1	2.1	1.6
C_{10}	6.2	29.6	6.4	8.5	2.1	4.1	6.2	6.2	3.6	5.3	2.5	5.5
C_{11}	......	......	......	......	......	......	......	......	Tr.	Tr.	2.2	1.3
C_{12}	......	2.5	......	1.0	......	1.0	......	1.3	1.0	1.3	......	......
2-Alkanone												17.9
C_5	......	......	......	......	......	......	......	......	......	......	......	2.9
C_7	......	......	......	......	......	......	......	......	......	......	......	4.6
C_9	......	......	......	......	......	......	......	......	......	......	......	3.2
C_{11}	......	......	......	......	......	......	......	......	......	......	......	3.4
C_{13}	......	......	......	......	......	......	......	......	......	......	......	2.3
C_{15}	......	......	......	......	......	......	......	......	......	......	......	1.5

[a] Mixture of 2-alkanone C_3 and alkanal C_3.

hand, dodec-2,4-dienal in the current work has been consistently found in linoleate and in most of the fats. The possibility has been considered that undec-2,4-dienal and dodec-2,4-dienal might be mistaken for one another, but this is not believed to be the case (4). It may be that both compounds are present but approach trace amounts in proportion to the other aldehydes (12). Heating the oxidized butterfat produced over 17% 2-alkanone class consisting of C_5, C_7, C_9, C_{11}, C_{13}, and C_{15} ketones. These compounds are not due to oxidation as their formation in heated fresh butterfat has been described by Patton and Tharp (17).

Composition of volatile monocarbonyl compounds found in the more highly unsaturated peanut, soybean, and linseed oils is shown in Table V. Amounts of the major characteristic aldehydes reflect the larger proportions of linoleic and linolenic acids in these oils.

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Ozonization of Soybean Oil. The Preparation and Some Properties of Aldehyde Oils[1]

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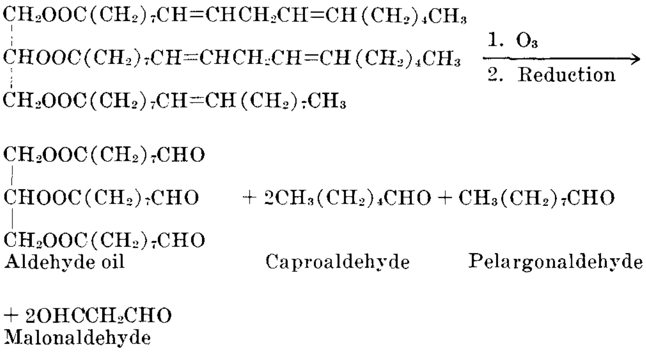
A polyaldehydic product called aldehyde oil was prepared by the ozonization of soybean oil, followed by reductive decomposition of the ozonolysis products. Reductive decomposition by chemical means gave 85–90% yields of carbonyl in the aldehyde oil. Catalytic reduction gave 75–80% yields. Partially-hydrogenated soybean oil gave more efficient results than did unhydrogenated oil. The polyfunctional aldehyde oil was found to undergo condensation reactions with phenolic compounds, urea, amines, and polyols to give cross-linked polymers.

OZONE IS ONE of the most attractive reagents for carrying out oxidative cleavage of unsaturated fatty materials because of its relatively low cost, its availability, and the quantitative nature of the reaction. Either carboxylic acids or aldehydes may be obtained, depending upon whether oxidative or reductive decomposition of the ozonolysis products is carried out. Oxidative cleavage has been successfully applied on a commercial scale to the production of pelargonic and azelaic acids from oleic acid (1). Reductive cleavage for the production of fatty aldehydes possibly would be of equal commercial interest because of the versatility of the aldehyde group in chemical reactions. An attractive aldehydic product is the glyceride of azelaic semi-aldehyde, obtained by the ozonization of an unsaturated oil. The polyfunctionality of this compound makes it useful in a variety of cross-linking and resin-forming reactions. The one mention in the literature (2) describes it only as a brown, viscous oil. It was obtained *en route* to the preparation of azelaic acid from castor oil by hydroxylation with hydrogen peroxide, cleavage with lead tetra-acetate, followed by oxidation with hydrogen peroxide, then by saponification.

This paper describes a relatively simple method of preparing an aldehyde oil in good yield from soybean oil and also describes some of its properties. The effects of solvent and the method of reduction were studied in some detail in order to obtain high yields.

The course of the reaction may be illustrated with an idealized triglyceride structure for soybean oil:



$$\begin{array}{l} CH_2OOC(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CHOOC(CH_2)_7CH{=}CHCH_2CH{=}CH(CH_2)_4CH_3 \\ | \\ CH_2OOC(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array} \xrightarrow[\text{2. Reduction}]{\text{1. } O_3}$$

$$\underset{\text{Aldehyde oil}}{\begin{array}{l} CH_2OOC(CH_2)_7CHO \\ | \\ CHOOC(CH_2)_7CHO \\ | \\ CH_2OOC(CH_2)_7CHO \end{array}} + \underset{\text{Caproaldehyde}}{2CH_3(CH_2)_4CHO} + \underset{\text{Pelargonaldehyde}}{CH_3(CH_2)_7CHO}$$

$$+ \underset{\text{Malonaldehyde}}{2OHCCH_2CHO}$$

In addition to the linoleic and oleic acids indicated in the formula, palmitic, stearic, and linolenic acids are also present but to a lesser extent. From 100 lbs. of the soybean oil used in these experiments, there would be obtained theoretically 31.8 lbs. of volatile aldehydes, 16.0 lbs. of malonaldehyde, and 67.5 lbs. of aldehyde oil.

The production of aldehydes (Table I) was measured by reaction with hydroxylamine hydrochloride.

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