

below 210°F. At lower temperatures the spread of boiling pressures over the whole range of composition is small compared to the spread at the higher temperatures.

At a given pressure there is a small change in the boiling point for miscellas having the low oil content. However above 30% oil by weight there is a more pronounced temperature rise, and after 80% oil by weight there is a rapid rise in the boiling temperature

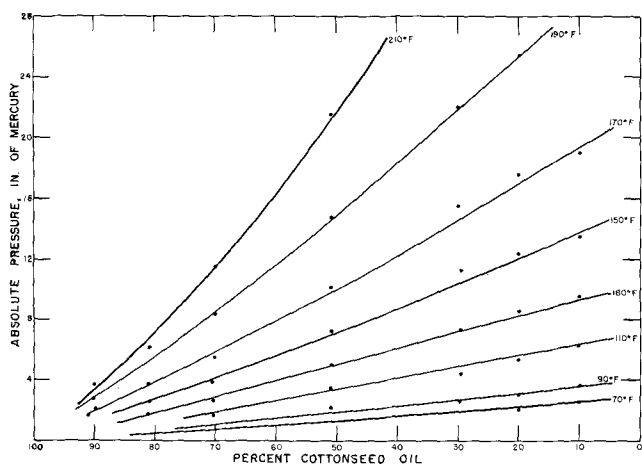


Fig. 4. Vapor pressure-composition curves for trichloroethylene-cottonseed oil miscellas at various constant temperatures.

at a given pressure for any increase in oil content. As the percentage of oil in the miscella is increased, the slope of the curves increases, gradually approaching a straight line for higher oil content miscella over the lower temperature portion. These relations are similar to those found previously in the laboratory for soybean oil-trichloroethylene miscellas (5).

The data obtained in this investigation were compared with values calculated from Raoult's law. No

agreement between the observed and calculated values was found; the observed values in all cases were lower than the calculated values. According to Pollard, Vix, and Gastroek (3) the agreement between observed and calculated values of vapor pressure for hexane-cottonseed oil miscellas is good below approximately 50% oil. Above 50% there is appreciable deviation, which becomes increasingly great as the oil concentration approaches 100%. If we assume compound formation between the glycerides of the cottonseed oil and the trichloroethylene as postulated by Johnstone, Spoor, and Goss (2) for soybean oil and trichloroethylene, the reason for the low vapor pressure values of the cottonseed oil-trichloroethylene miscellas even below 50% oil is evident. This variation from the theoretical makes the experimental data desirable for the successful design and operation of solvent extraction plants.

Summary

The boiling points of crude cottonseed oil-trichloroethylene miscellas for pressures below atmospheric have been determined. The data indicate that the temperature-pressure relations for these miscellas differ from those of cottonseed oil-hexane miscellas in that, even below 50% oil concentrations, they are lower than those calculated by Raoult's law. Above 50% the deviation from the calculated values becomes greater.

REFERENCES

- Harris, W. D., "Solvent Extraction of Cottonseed Oil," A. and M. College of Texas Eng. Exp. Sta. Bul. 12, 1941.
- Johnstone, H. F., Spoor, I. H., and Goss, W. H., *Ind. Eng. Chem.*, **32**, 832-835 (1940).
- Pollard, E. F., Vix, H. L. E., and Gastroek, E. A., *Ind. Eng. Chem.*, **37**, 1022-1026 (1945).
- Russell, R. F., "Extraction of Certain Oil-Bearing Materials with Trichloroethylene," Ph.D. Thesis, Iowa State College, 1950.
- Sweeney, O. R., Arnold, L. K., and Hollowell, E. G., "Extraction of Soybean Oil by Trichloroethylene," *Iowa Eng. Exp. Sta. Bul.* 165 (1949).

[Received December 8, 1952]

The Volatile Decomposition Products and the Organoleptic Characteristics of the Oxidative Polymers of Ethyl Linoleate¹

S. S. CHANG² and F. A. KUMMEROW, Department of Food Technology, University of Illinois, Urbana, Illinois

STUDIES (1, 2, 3) involving the volatile decomposition products formed by successive heat reversion and deodorization of soybean oil have led to the identification of a number of carbonyl compounds which have been suspected of contributing to the reversion flavor and odor. Similar results were obtained when soybean oil or methyl linolenate was autoxidized at room temperature (4, 5). In both cases acetaldehyde, propionaldehyde, and 2-pentenal were identified in the volatile decomposition products. However hexanal was found in the volatile de-

composition products obtained from soybean oil but not methyl linolenate. Since hexanal was also found in the volatile decomposition products obtained from cottonseed oil which had been autoxidized at 70°C. (6), hexanal may be a degradation product of linoleic acid.

On the other hand, Sims (7) could find no correlation between flavor stability and polyunsaturation. Soybean oil hydrogenated so as to free it of linolenic and linoleic acid still reverted. Furthermore Mattil (8) chromatographed soybean oil and hydrogenated soybean oil and found no reduction in linolenic and linoleic acid content although the flavor stability of soybean oil was slightly improved and that of hydrogenated soybean oil was markedly improved. These

¹Funds for this study were furnished by a grant-in-aid from Armour and Company, Chicago, Ill.

²Portion of a thesis presented by S. S. Chang as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology. Presented at the American Oil Chemists' Society meeting, Cincinnati, O., Oct. 21, 1952.

observations were difficult to correlate with the idea that linolenic and linoleic acid *per se* served as a source of reversion compounds. However these two polyunsaturated fatty acids may have been present in a form which could not be detected by spectrophotometric analysis and could not be hydrogenated completely. In the present study a polymeric structure of this nature was found in autoxidized ethyl linoleate.

Experimental

Preparation of Oxidative Polymers of Ethyl Linoleate. Two batches of pure ethyl linoleate of approximately 250 g. each were prepared by a bromination and debromination method. The ethyl ester was oxidized by bubbling oxygen through it at $30 \pm 0.5^\circ\text{C}$. for 250 hours and then separated into 13 fractions by extraction with solvent pairs made up of redistilled Skellysolve F and successively increasing amounts of anhydrous ethyl ether as reported in a previous paper (9). The 10th, 11th, and 12th fractions, with an average molecular weight of 865, 1,046, and 1,070, respectively, were combined and used as oxidative polymers for this investigation (Table I).

TABLE I

Comparison of the Physical Constants of the Polymer Fractions and Ethyl Linoleate

Fractions	10	11	12	Ethyl linoleate
Solvent				
% Skellysolve F.....	76	68	60	100
% Diethyl ether.....	24	32	40	0
Density (25°C).....	1.061	1.065	1.068	0.8571
Ref. index ($n_D^{25^\circ\text{C}}$).....	1.4778	1.4788	1.4810	1.4569
Molecular weight.....	865	1,046	1,070	308
Weight (grams).....	16.4	10.0	12.8
Ultimate analysis				
C%.....	64.91	64.90	64.72	77.81
H%.....	9.42	9.58	9.39	11.78
O%.....	25.67	25.52	25.89	10.61

Catalytic Hydrogenation. Two different procedures were used; one involved low and the other high pressure hydrogenation. The low pressure hydrogenation was carried out in a No. 3910 Parr low pressure shaker type of hydrogenation apparatus, and the high pressure hydrogenation was carried out in an Aminco super-pressure hydrogenator. Raney nickel or platinum oxide prepared according to the method of Adams, Voorhees, and Shriner was used as catalyst (10). Five to 15 g. of sample diluted with absolute ethanol was used in each case. Temperatures ranging from 25 to 110°C ., pressures ranging from 60 to 1,800 p.s.i., and time ranging from one to 500 hours were used.

Organoleptic Evaluations. The organoleptic tests were conducted in a manner similar to the one designed by the Northern Regional Research Laboratory (11). The sample to be evaluated was dissolved in

fresh shortening (Crisco) at various concentrations, kept at 37°C . and submitted to a panel of five individuals with organoleptic testing experience. A score of 10 was given to the blank as an arbitrary standard.

Reautoxidation. Fifteen g. of the oxidative polymers were reoxidized by bubbling oxygen through it for two weeks at $30 \pm 0.5^\circ\text{C}$. The volatile decomposition products were collected in two glass traps connected in series and immersed in acetone and solid CO_2 . The condensate was removed from the traps every four days by washing them with ethyl alcohol. Fifteen g. of each of the hydrogenated polymers were reoxidized in the same manner.

Analysis of Carbonyl Compounds. The carbonyl compounds in the volatile decomposition products were converted into their hydrazones and then separated by chromatographic absorption according to the method of Gordon *et al.* (12). The alcoholic solution of the carbonyl compounds was added slowly with stirring into a saturated solution of 2,4-dinitrophenylhydrazine in 2 N. hydrochloric acid. The precipitate was digested at 0°C . for one hour and then filtered and dried.

Thirty to 60 mg. of the hydrazones were dissolved in 10 to 20 ml. of chloroform and the solution was poured into a 35×200 mm. column of a mixture of two parts of silicic acid (Mallinckrodt, 100-mesh, analytical reagent) and one part Celite analytical filter aid (Johns-Manville Company). Fifty ml. of pentane-hexane were added after complete absorption of the chloroform solution. The bands were then developed by a mixture of 1% diethyl ether in pentane-hexane. As separation of the bands occurred, the diethyl ether content was gradually increased to a maximum of about 6% by volume. The rate of percolation was adjusted by applying nitrogen at a pressure of 2 to 5 pounds per square inch. The column was then dried, free of solvent, the bands separated, and eluted with diethyl ether. The eluate was freed of ether under reduced pressure.

In order to obtain enough material for identification, the hydrazones from the corresponding bands of 4-6 runs were combined, re-chromatographed, and re-crystallized from ethyl alcohol. The hydrazones were identified by comparing their melting points, ultimate analyses, and absorption spectra in the ultraviolet region with those of known carbonyl compounds and by determining their mixed melting points with 2,4-dinitrophenylhydrazones of authentic carbonyl compounds.

Results

The present results indicated that the oxidative polymers and the hydrogenated oxidative polymers of ethyl linoleate could be decomposed by autoxida-

TABLE II

Identification of 2,4-dinitrophenylhydrazones Prepared from Volatile Decomposition Products of the Oxidative Polymers of Ethyl Linoleate

2,4-Dinitrophenylhydrazone	Color	M. P.	Mixed M.P. with authentic specimen	Maximum absorption ($m\mu$)	Ultimate analyses		
					C%	H%	N%
0.1.....	Orange	140-148	148-150	356	45.31	4.02	23.88
Propionaldehyde.....	Orange	155	356	45.38	4.23	23.52
0.2.....	Yellow	105-106	106-107	356	49.99	5.33	21.20
n-Pentanal.....	Yellow	107	356	49.43	5.27	20.95
0.3.....	Yellow	104	105-106	357	51.23	5.60	19.86
n-hexanal.....	Yellow	107	356-357	51.40	5.78	20.01

tion to yield carbonyl compounds. The carbonyl compounds collected in the cold traps when oxygen was bubbled through 15 g. of the polymers at 30°C. for two weeks were converted into 963 mg. of 2,4-dinitrophenylhydrazones. Characterization of these hydrazones led to the identification of propionaldehyde, n-pentanal, and n-hexanal (Table II). An attempt to characterize the dark red band of the 2,4-dinitrophenylhydrazone on top of the column met with failure. No solvent could be found for its recrystallization.

The oxidative polymers, when in pure form, had a bitter, painty, and rancid odor and flavor. However, in a dilution up to 10 parts per million, their odor and flavor were undetectable organoleptically (Table III). All the five individuals on the panel considered the mixture of shortening (Crisco) with 10 p.p.m. of oxidative polymers as bland. At a concentration of 1,000 and 10,000 p.p.m. the mixture was definitely rancid, while at a concentration of 100 p.p.m. the flavor was barely perceptible.

TABLE III

Organoleptic Evaluations of Oxidative Polymers of Ethyl Linoleate Diluted with Fresh Crisco

Concentration (p. p. m.)	Average score	
	Odor	Flavor
0.....	10.0	10.0
10.....	9.6	9.4
100.....	8.4	8.2
1,000.....	5.2	4.6
10,000.....	1.2	1.0

The molecular weights and refractive indices of the hydrogenated products formed under widely varying conditions indicated that catalytic hydrogenation cannot completely break up the oxidative polymers (Table IV). Conditions of hydrogenation much more drastic than those used in manufacturing shortening and margarine stocks were used, yet the products were still higher in molecular weights and refractive indices than monomers. Furthermore the hydrogenated products remained insoluble in non-polar solvents like pentane-hexane. However higher concentration of catalyst, longer time, and higher temperature and pressure of hydrogenation gave products of lower molecular weight and lower refractive index.

The hydrogenated products seemed to be able to react further with oxygen as indicated by the increase in refractive index in all the samples which were reautoxidized. At a dilution of 1,000 parts per million all the hydrogenated products as well as their reautoxidized products had bitter, beany, and painty flavors and odors (Table V). It is interesting to note that reautoxidation of the hydrogenated products af-

TABLE V
Results of Organoleptic Evaluations

Sample number	Treatment of sample	Odor score	Flavor score
1.....	Polymers without treatment	3.3	4.5
2.....	Sample No. 1 hydrogenated	5.7	4.3
3.....	Sample No. 2 reautoxidized	5.7	3.5
4.....	Sample No. 1 hydrogenated	6.0	5.5
5.....	Sample No. 4 reautoxidized	5.5	5.3
6.....	Sample No. 1 hydrogenated	4.8	5.8
7.....	Sample No. 6 reautoxidized	4.5	3.5
8.....	Sample No. 1 hydrogenated	6.0	6.3
9.....	Sample No. 8 reautoxidized	5.0	4.3
10.....	Fresh Crisco	10.0	10.0

fecting the score for odor and flavor to only a slight extent. This was evidently due to the volatility of the odorous constituents formed during reautoxidation. Since the reautoxidation was carried out by bubbling oxygen through the samples at 30°C. for 250 hours, the volatile odorous principles should be carried away by the effluent oxygen instead of remaining in the sample. The odor of condensate collected in the cold traps indicated that this must have occurred.

The 2,4-dinitrophenylhydrazones obtained from the volatile decomposition products showed that the hydrogenated polymers could be cleaved by oxygen to carbonyl compounds. The condensate collected in the cold traps during the autoxidation of 15 g. of the hydrogenated polymers (60 p.s.i., 25-30°C., 1% Raney Nickel, and 2 hours) gave 453 mg. of 2,4-dinitrophenylhydrazones. Characterization of these hydrazones led to the identification of n-pentanal and 2-heptenal (Table VI). The carbonyl compound responsible for the third yellow band was not identified.

Discussion

Three of the carbonyl compounds obtained from the reautoxidized oxidative polymers and the reautoxidized hydrogenated polymers of ethyl linoleate have been isolated from reverted soybean oil and reverted hydrogenated soybean oil by previous workers. The propionaldehyde and n-hexanal isolated from the autoxidized oxidative polymers of ethyl linoleate were identified by Kawahara and Dutton (4) as constituents of the painty fractions of the volatile decomposition products from reverted soybean oil. The 2-heptenal isolated from the autoxidized hydrogenated polymers of linoleate was identified by Schepartz and Daubert (2) as a reversion compound of hydrogenated soybean oil. However both n-hexanal and 2-heptenal were absent in the volatile cleavage products of autoxidized linolenate (5). It is therefore possible that both of these two aldehydes could have arisen from polymerized linoleic acid.

It seems surprising that linoleic acid could be one of the precursors of reversion flavors, as oils which

TABLE IV
Treatment of the Oxidative Polymers

Sample number	Treatment of sample	Conditions of treatment				Properties of product	
		Pressure, p. s. i.	Temperature, °C.	Time, hrs.	Catalyst	Refractive index n_D^{25}	Molecular weight
1.....	None	1.4778	865
2.....	Sample No. 1 Hydrogenated	60	25-30	500	1.4639	588
3.....	Sample No. 2 Reautoxidized	Atmos.	30	250	1% Pt.	1.4670
4.....	Sample No. 1 Hydrogenated	60	25-30	2	1% Ni.	1.4694	617
5.....	Sample No. 4 Reautoxidized	Atmos.	30	250	1.4701
6.....	Sample No. 1 Hydrogenated	1,800	60-62	6	1% Ni.	1.4590	405
7.....	Sample No. 6 Reautoxidized	Atmos.	30	250	1.4608
8.....	Sample No. 1 Hydrogenated	60	110	1	0.1% Ni.	1.4688	602
9.....	Sample No. 8 Reautoxidized	Atmos.	30	250	1.4682

TABLE VI
 Identification of 2,4-Dinitrophenylhydrazones Prepared from Volatile Decomposition Products of the Hydrogenated Polymers of Ethyl Linoleate

2,4-Dinitrophenylhydrazone	Color	M. P.	Mixed M. P. with authentic specimen	Maximum absorption ($m\mu$)	Ultimate analyses		
					C%	H%	N%
H-1..... 2-heptenal.....	Red Red	123-127 132	127-129	377 377-378	53.74 53.41	5.40 5.52	19.39 19.17
H-2..... n-pentanal.....	Yellow Yellow	103-104 107	105-107	356 356	50.14 49.43	5.26 5.27	20.78 20.95
H-3.....	Yellow-orange	82-83	48.30	4.48	24.18

contain no linolenic or other more highly unsaturated acids do not revert easily. However the behavior of mixtures of esters does not always parallel to the behaviors of pure esters. Gunstone and Hilditch (13) found that the autoxidation of methyl oleate was strongly accelerated and the induction period much reduced in the presence of small proportions of linoleate. They considered that oleo-glycerides were also responsible for the oxidative rancidity of oils if small amounts of linoleo-glycerides were present and served as a catalyst. Therefore it is not impossible that the linolenate present in soybean oil could accelerate the autoxidation of linoleate with the formation of polymers, which in turn decomposed and yielded these aldehydes.

Organoleptic characteristics of the polymers which had been formed during the autoxidation of ethyl linoleate indicated that oxidative polymers could be involved in the flavor reversion of soybean oil. The present results indicated that if such polymers were present in oils up to a concentration of 10 parts per million, they could not be detected organoleptically. However these polymers could decompose to yield various aldehydes which had been isolated from reverted soybean oil by previous investigators.

This postulation seems to have the advantage of being applicable to several questions which have to date been unanswered. Among these are: a) that flavor stability bears no relationship to the content of polyunsaturated glycerides, as hydrogenated soybean oil free of linoleate and linolenate can still be reverted easily (7); b) that an extremely small amount of oxygen is required to produce the reversion compounds (14, 15); c) that chromatography could markedly improve the flavor stability of hydrogenated soybean oil without any apparent alternation in the polyunsaturated fatty acids content of the oil (8, 16).

If oxidative polymers are precursors of reversion compounds, then these questions may be answered in the following manner: a) these polymers cannot be detected by the spectrophotometric method generally used for the quantitative determination of fatty acids, and since these polymers cannot be completely removed by catalytic hydrogenation, the polymers will remain in the hydrogenated oil and would eventually cause reversion; b) each molecule of linoleate in the oxidative polymers contained two extra moles of oxygen besides those in the ester group (9), and this high content of oxygen would enable them to decompose without further absorption of much more oxygen; c) chromatography may have removed the oxidative polymers of polyunsaturated fatty esters. Since these polymers may serve as the source of

reversion compounds, the flavor stability of the chromatographed product would improve.

Summary

The polymers formed during autoxidation of ethyl linoleate at 30°C. were isolated by a solvent extraction method using pentane-hexane and diethyl ether as solvents. These polymers were only partially decomposed by catalytic hydrogenation at temperatures ranging from 25 to 110°C. and pressures ranging from 60 to 1,800 p.s.i. with Raney Nickel as catalyst. Both the polymers and their hydrogenated products had a bitter rancid flavor and painty odor. However in a dilution up to 10 parts per million, the polymers as well as the hydrogenated polymers could not be detected organoleptically.

Both the polymers and their hydrogenated products were reautoxidized at 30°C. and the volatile material obtained in each case characterized. The volatile material which was obtained from the polymers contained n-propionaldehyde, n-pentanal, and n-hexanal; and the volatile material from the hydrogenated polymers contained n-pentanal and 2-heptenal. Since n-hexanal was also identified in the volatile decomposition products from autoxidizing soybean oil and 2-heptenal from the reversion compounds of hydrogenated soybean oil and since both these aldehydes were absent in the volatile cleavage products from autoxidizing linolenate, it is therefore possible that these reversion compounds could have arisen from the oxidative polymers of linoleate.

REFERENCES

1. Martin, C. J., Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **25**, 113-117 (1948).
2. Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **27**, 367-373 (1950).
3. Stapp, R. J., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **27**, 374-377 (1950).
4. Kawahara, F. K., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, **29**, 372-377 (1952).
5. Kawahara, F. K., Dutton, H. J., and Cowan, J. C., *J. Am. Oil Chem. Soc.*, **29**, 633-635 (1952).
6. Swift, C. E., O'Connor, R. T., Brown, L. E., and Dollear, F. G., *J. Am. Oil Chem. Soc.*, **26**, 297-300 (1949).
7. Sims, R. J., *J. Am. Oil Chem. Soc.*, **29**, 347-350 (1952).
8. Mattil, K. F., *J. Am. Oil Chem. Soc.*, **24**, 243-246 (1947).
9. Chang, S. S., and Kummerow, F. A., *J. Am. Oil Chem. Soc.* (in press).
10. Adams, R., Voorhees, V., and Shriner, R. L., "Organic Synthesis," John Wiley and Sons Inc., New York, Col. Vol. 1, 463-470.
11. Moser, H. A., Jaeger, C. M., Cowan, J. C., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, **24**, 291-296 (1947).
12. Gordon, B. E., Wopat, F. Jr., Burnham, H. D., and Jones, L. C. Jr., *Anal. Chem.*, **23**, 1754-1759 (1951).
13. Gunstone, F. E., and Hilditch, T. P., *J. Chem. Soc.*, 1022-1025 (1946).
14. Golumbic, C., and Daubert, B. F., *Food Ind.*, **19**, 1075-1077 and 1174 (1947).
15. Bailey, A. E., "Industrial Oil and Fat Products," Interscience Publishers Inc., New York, 1951, p. 67.
16. Lange, W., and Folzenlogen, R. G. (The Procter and Gamble Company) U. S. Patent No. 2,589,097.

[Received December 8, 1952]