Observations on the Determination of Iodine Value with Pyridine Sulfate Dibromide[1]

H. J. LIPS, Division of Applied Biology, National Research Laboratories, Ottawa, Canada

THE Rosenmund-Kuhnhenn (11, 12) method for determination of iodine value with pyridine sulfate dibromide was recently modified by Benham and Klee (2, 6) for use with oils containing conjugated double bond systems. Since conjugation is considered to precede polymerization (15), it was felt that the method might be useful in the study of deodorized-polymerized oils (7, 9). However, in preliminary trials, apparent iodine values were found to increase with reaction time and amount of excess reagent, and unexpected results were also obtained in the presence of chloroform or sulfur. These observations led to a study of the Benham-Klee procedure, particularly the action of the mercuric acetate catalyst used.

Materials and Methods

Iodine value studies were made with the following materials: alkali refined and bleached linseed, rapeseed, and weed seed screenings oils; deodorized-polymerized linseed and rapeseed oils; hydrogenated, deodorized-polymerized linseed oil; mineral oil, 1-octadecene, cyclohexene, beta-ionone, benzene, trimethylpentane, methyl myristate, sulfur, and weed seed oil treated with sulfur. The polymerized oils were described in an earlier paper (7).

Iodine values were determined under a variety of reaction conditions, and the results were corrected by appropriate blank determinations carried on concurrently with all experiments. The effects of reaction time, amount of excess reagent, mercuric acetate catalyst, peroxide, and variations in solvent were studied. Hydrobromic acid was recovered from reaction mixtures to check the possibility of halogen substitution. Comparisons of the Benham-Klee method with the Hunter-Hyde modification of Wijs' method (1, 5) were made under some of the reaction conditions studied.

Results and Discussion

1. *Apparent Iodine Value of Polymerized Oils.*

Preliminary trials showed that the Benham-Klee iodine value of linseed and rapeseed oils decreased more slowly than the Hunter-Hyde value with increasing extent of deodorization-polymerization (Figure 1). Both methods also indicated an increase in iodine value with increase in reaction time. Since the changes in iodine value were more pronounced with linseed oil than with rapeseed oil, linseed oil was used for most of the subsequent measurements. Fourteen-hour polymerized linseed oil was chosen as a representative deodorized-polymerized oil.

Effect of Reaction Time. The increase in iodine value with reaction time shown by the Benham-Klee method is illustrated for control and polymerized oils in Table I and Figure 2. The values tended to increase indefinitely although there was some levelling off with time. With prolonged reaction time, values were obtained which exceeded the normal range for these oils. Evidently some halogen disappearance occurred that could not be corrected for by blank determinations under the same conditions. As previously reported for the Rosenmund-Kuhnhenn method (10), values also increased when the mercuric acetate catalyst was omitted (Table I).

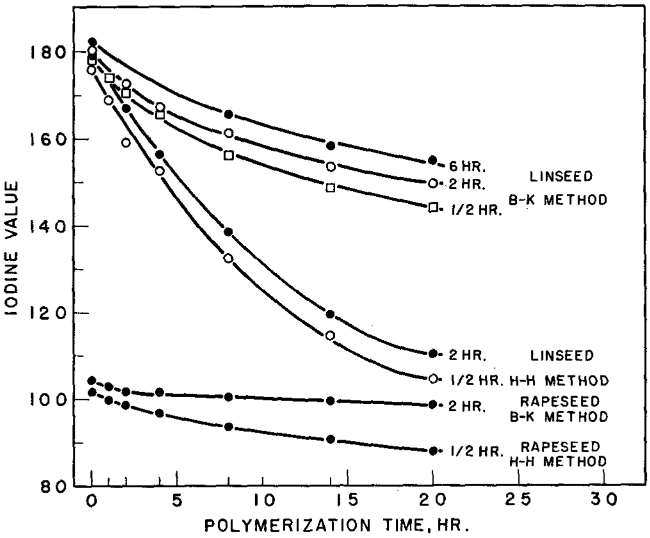

FIG. 1. Decrease in iodine value of linseed and rapeseed oils with increasing time of deodorization-polymerization, Benham-Klee and Hunter-Hyde methods (200-300% excess reagent).

The Benham-Klee iodine value of hydrogenated polymerized oils also increased with increased reaction time. Typical results with 200-300% excess reagent are shown below:

		Iodine value
Linseed polym. 4 hr., hydrog.	4-hr. reaction time	130.9
	6-hr. reaction time	132.8
	24-hr. reaction time	140.5
Linseed polym. 8 hr., hydrog.	4-hr. reaction time	124.9
	6-hr. reaction time	127.5

Observed changes of iodine values on hydrogenation were about 10% higher than calculated from hydrogen consumption, perhaps due to the length of reaction time chosen. The observed drop was similar, using both the Hunter-Hyde and Benham-Klee methods, and paralleled decrease in refractive index (7).

Effect of Excess Reagent. Apparent iodine value by the Benham-Klee method also increased with in-

TABLE I

Effect of Reaction Time on the Apparent Iodine Value of Deodorized-Polymerized Oils

(Benham-Klee method, 200-300% excess reagent)

Reaction time	Apparent iodine value			
	Linseed oil		Rapeseed oil	
	Control	Polym. 14 hr.	Control	Polym. 14 hr.
1 hr.				
without catalyst	169.8	126.0	99.8	91.8
with catalyst	179.6	150.6	103.8	98.1
24 hr.				
without catalyst	175.1	141.3	102.6	97.0
with catalyst	187.3	167.5	108.4	102.3

---

[1] Issued as Paper No. 287 of the Canadian Committee on Food Preservation and as N.R.C. No. 3054.

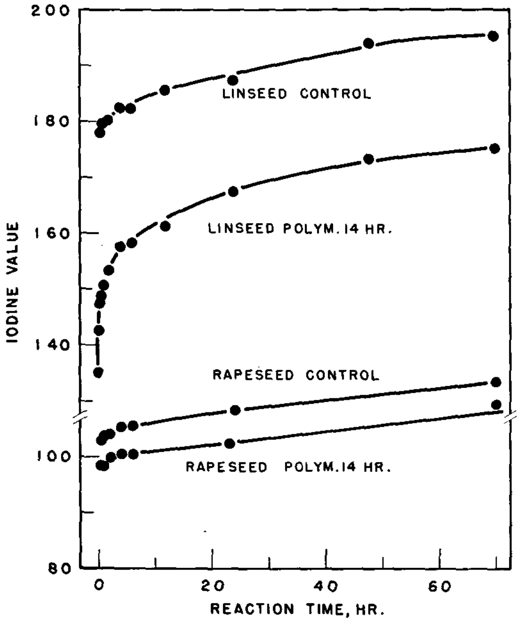

FIG. 2. Increase in iodine value of linseed and rapeseed oils with reaction time, Benham-Klee method (200-300% excess reagent).

creasing amounts of reagent, as illustrated in Figure 3. However this increase in iodine value levelled off appreciably, and useful and reproducible values could be obtained by selecting arbitrary conditions, *e.g.*, 4-hr. reaction time with 300-400% excess reagent. Results for 6- and 9-hour reactions (not shown in Figure 3) were almost the same as those for 4-hr. The titration end-point was not as sharp as in the Hunter-Hyde method, and color returned more quickly in titrated solutions on standing. It was necessary to observe the arbitrary conditions closely to ensure duplication of results.

Secondary Reactions. To check the possibility of secondary reactions in the Benham-Klee procedure, recovery of hydrobromic acid from reaction mixtures by silver bromide precipitation (6) was carried out several times with 0.1-g. samples of polymerized (14-hr.) linseed oil after a contact of 48 hr. with catalyst and 200-300% excess reagent. Average recovery of silver bromide (0.1014 g.) from seven oil samples was slightly larger than from corresponding blanks (0.0795 g.), suggesting a halogen substitution equivalent to about 15 units of iodine value on prolonged contact of the polymerized oil with pyridine sulfate dibromide. The possibility of halogen substitution in polymerized oils, acids, and esters has been raised by other workers (8). Reaction of iodine chloride with hydroxyl groups, which might occur to some extent in polymerized oils, has also been demonstrated in the presence of mercuric acetate (13).

The possibility of secondary reactions suggested with polymerized oils was supported by Benham-Klee iodine values obtained for pure compounds. Whereas stable values close to the theoretical were obtained for 1-octadecene and cyclohexene, the more complex systems of beta-ionone and benzene gave increasing values on standing with the reagent. Furthermore trimethylpentane, methyl myristate, and mineral oil showed appreciable apparent unsaturation on prolonged contact. Hunter-Hyde values were close to the theoretical ones, except for beta-ionone, which gave a higher result than expected for the one double bond normally reacting in the side chain.

TABLE II

Effect of Mercuric Acetate Catalyst on Apparent Iodine Value (Benham-Klee method, 200-300% excess reagent)

Oil	Apparent iodine value		
	1 hr. reaction	36 hr. with catalyst, 1 hr. reaction	36 hr. reaction
Linseed control	179.6	179.8	195.1
Linseed polym. 14 hr	150.6	151.8	175.1
Rapeseed control	103.8	104.4	113.2
Rapeseed polym. 14 hr	98.1	99.2	109.3

2. *Effects of the Mercuric Acetate Catalyst.*

Degeneration of the Blank. Mercuric acetate accelerated degeneration of the Benham-Klee reagent in the absence of oil. For example, the titration value of reagent plus catalyst in one trial decreased by 0.8 ml. of 0.1 *N* thiosulphate in 50 hr., but the value for the reagent alone was unchanged.

Dehydrogenation. Thomas reported that mercuric acetate may act as a dehydrogenating agent (16). To test this possibility under conditions similar to those of the Benham-Klee reaction, storage experiments were set up with 30 g. of weed seed oil in 150 ml. of chloroform plus 10 or 50 ml. of glacial acetic acid saturated with mercuric acetate. These mixtures were stored in glass-stoppered flasks in the dark at room temperature for times up to seven days. After standing, they were filtered and then washed with distilled water until the washings gave no color with hydrogen sulphide. The solvent was removed under vacuum. Iodine numbers by both Benham-Klee and Hunter-Hyde methods showed a slight decrease (1 to 10 units) for all samples instead of the anticipated increase. The decrease might be ascribed to uptake of mercuric acetate (3) or oxygen, or both, at the double bonds of the oil.

In a further storage experiment to check the possibility of dehydrogenation, samples of linseed oil were dissolved in 5 ml. carbon tetrachloride, and 10 ml. of 1.5% mercuric acetate catalyst added. After 36 hr. reagent was added, and samples were titrated in the usual manner after 1-hr. reaction time. Parallel samples were stored with oil, catalyst, and reagent for 36 hr. and then titrated. Two blanks were run with each

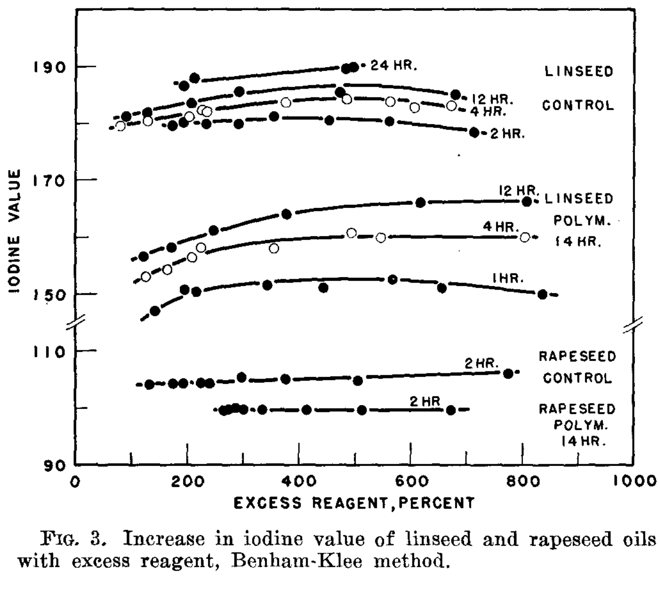

FIG. 3. Increase in iodine value of linseed and rapeseed oils with excess reagent, Benham-Klee method.

set, and 200-300% excess reagent was used. Results are shown in Table II. Again, no direct dehydrogenating action of mercuric acetate on the oil was observed (cf. first and second columns of the table). However the high values in the third column of Table II might be due in part to dehydrogenation of oil by the catalyst in the presence of pyridine sulfate dibromide. This possibility was not ruled out. Even after prolonged reaction, iodine values obtained with reagent plus catalyst were appreciably greater than those obtained with reagent alone (Table I).

Effect of Solvent. A comparison of the relative results obtained with carbon tetrachloride and chloroform in stored reaction mixtures is shown in Tables III and IV. The contact of iodine reagent and catalyst, even in the absence of oil, gave an apparent iodine value (Table III). Chloroform with mercuric acetate caused a greater deterioration of Benham-Klee than Hunter-Hyde reagent. With Benham-Klee reagent the separate effects of chloroform and catalyst appeared to be greatly enhanced when they were used together.

TABLE III

Effect of Carbon Tetrachloride and Chloroform on Iodine Value Blanks (Reaction mixture stored five days at room temperature in the dark)

Components of stored reaction mixture	Additions after storage	Titration, ml. of 0.1*N* thiosulphate	
		Carbon tetrachloride solvent	Chloroform solvent
Benham-Klee method			
Solvent, catalyst	reagent	47.3	47.3
Reagent	solvent	47.2	47.3
Solvent, reagent	....	47.2	46.4
Solvent, reagent	catalyst	47.2	45.9
Solvent, reagent, catalyst	....	45.6	33.1
Hunter-Hyde method			
Solvent, catalyst	reagent	37.8	37.8
Reagent	solvent	37.7	37.7
Solvent, reagent	....	37.8	37.0
Solvent, reagent	catalyst	37.7	36.7
Solvent, reagent, catalyst	....	36.8	36.0

Prolonged contact of oil and catalyst in the absence of reagent caused a marked decrease in Benham-Klee iodine value (Table IV), as noted earlier. This effect was slightly offset when the oil and catalyst were stored in solvent under purified nitrogen (17). Higher iodine values were also obtained when the reaction time following storage was lengthened. This increase continued with time when carbon tetrachloride was the solvent but was not sustained when chloroform was used. With the latter solvent the expected iodine value was not attained, and after an early maximum was reached, the iodine value again decreased (Table IV). With the Hunter-Hyde method (values not shown) the increase in iodine value was sustained in the presence of either carbon tetrachloride or chloroform.

Lowering of iodine value when chloroform and catalyst were used together also occurred at shorter reaction times with the Benham-Klee method, but not with the Hunter-Hyde method. With the Benham-Klee method, using chloroform and catalyst, the observed iodine values for a linseed oil were: 1 min., 171.6; 1 hr., 160.3; and 6 hr. 130.9.

The addition of small amounts of water to the Benham-Klee reagent had little effect on the observed iodine value of linseed and rapeseed oils (Table V). The value of the blank remained unchanged with addition of 2 ml. of water.

TABLE V

Effect on Apparent Iodine Value of Adding Water to Reaction Mixture (Benham-Klee method, 200-300% excess reagent, reaction time 2 hr.)

Amount of water added to reaction mixture, ml.	Apparent iodine value	
	Linseed oil polym. 14 hr.	Rapeseed oil polym. 14 hr.
0	152.5	98.6
1	150.1	99.6
2	149.8	99.0
5	146.2	97.5
10	140.8	96.8
15	136.3	95.5

Effect of Peroxides. Attempts were made to relate effect of mercuric acetate catalyst with peroxide value (4) of the sample. However the catalyst interfered with iodimetric peroxide determination, perhaps by promoting reaction, at the double bonds, of iodine liberated from potassium iodide. For example, 1 g. of linseed oil with a peroxide value of 71 ml. of 0.002 *N* thiosulphate showed a peroxide value of zero in the presence of 0.1 g. of mercuric acetate, and a value of 63 ml. in the presence of 0.0025 g. of acetate. Removal of catalyst from carbon tetrachloride solutions of oil by water washing prior to peroxide determinations also resulted in low peroxide values.

Unrefined linseed oil of zero peroxide content gave about the same iodine value and showed the same apparent increase in unsaturation with reaction time as refined linseed oil with a peroxide content equivalent to 60 ml. 0.002 *N* thiosulphate per g. This was observed for both iodine value methods, with and without catalyst, using carbon tetrachloride as solvent.

However increase in peroxide content ultimately reduced observed iodine value of fat samples. When

TABLE IV

Effect of Carbon Tetrachloride and Chloroform on Apparent Iodine Value of Linseed Oil (Benham-Klee method, 150% excess reagent, reaction mixture stored five days at room temperature in the dark)

Components of stored reaction mixture	Additions after storage	Reaction time after storage	Apparent iodine value	
			Carbon tetrachloride solvent	Chloroform solvent
Oil, solvent	reagent	1 min.	158.4	159.6
Oil, solvent	reagent, catalyst	1 min.	168.3 (167.6)[a]	168.3
Oil, solvent, reagent	....	0	174.8	173.6
Oil, solvent, reagent	catalyst	1 min.	176.6	174.1
Oil, solvent, reagent, catalyst	....	0	190.0	112.0
Oil, solvent, catalyst	reagent	1 min.	120.9	117.4
Oil, solvent, catalyst, under purified nitrogen	reagent	1 min.	128.3	128.1
Oil, solvent, catalyst	reagent	30 min.	154.4	157.7
Oil, solvent, catalyst	reagent	1 hr.	169.9	161.2
Oil, solvent, catalyst	reagent	2 hr.	172.0	157.2
Oil, solvent, catalyst	reagent	4 hr.	176.8	147.9

[a] Iodine value of this oil without storage.

the peroxide value of lard was increased from zero to 150 by storage at 50°C., the Hunter-Hyde number decreased from 63 to 56. Similarly the Benham-Klee result decreased from 63 to 58 at a peroxide value of 175. With linseed oil, storage at 50°C. progressively lowered iodine value, but measured peroxide content tended to level off or even decrease erratically after an initial high value was attained.

The promotion of peroxide formation by phosgene was also considered. The chloroform used in these experiments was reagent grade, free from phosgene, and stabilized with 0.7% ethanol. However the sulfuric acid in the Benham-Klee reagent might induce formation of phosgene from carbon tetrachloride or chloroform (14, p. 435). This possibility might explain why iodine values by the Benham-Klee method decreased in the presence of chloroform and catalyst whereas those by the Hunter-Hyde method did not (Table IV).

Addition of Mercuric Acetate at the Double Bond. The evidence already presented indicated that lowering of iodine value of oil on prolonged contact with catalyst only was partly due to oxidation at the double bond. The possibility of reaction of mercuric acetate itself at the double bond (3) was next considered.

Stored mixtures of linseed oil, solvent, and catalyst were washed with water until the washings gave no test for mercury with hydrogen sulphide. Subsequent washing with 5% hydrochloric acid yielded appreciable mercury, which was precipitated with hydrogen sulphide and weighed. Assuming that mercuric acetate formed a diacetate compound at the double bond (3), the weight of the recovered mercury accounted for most of the decrease in iodine value of oil samples stored with catalyst. The rest of the change in iodine value could be ascribed to oxidation of the oil.

The increase in iodine value obtained when the reaction time was lengthened after storage with catalyst (Table IV) was apparently due to instability of the mercuric acetate addition compound in the presence of the halogen ions of the iodine value reagents (3). With Benham-Klee reagent and chloroform the increase was offset by the apparent oxidizing action of chloroform in that medium.

3. *Effect of Sulphur.*

The use of pyridine sulfate dibromide reagent with mercuric acetate catalyst gave unexpectedly high values for oils treated with sulfur. The increase in iodine value varied with the amount of sulfur present, and all values were much higher than those obtained by the Hunter-Hyde (uncatalyzed) method (Table VI).

In a study of this effect, apparent iodine values were obtained for sulfur alone with both methods under varying conditions. The Benham-Klee method gave appreciable iodine values for colloidal sulfur or sulfur flowers in suspension in carbon tetrachloride and for colloidal sulfur in solution in carbon disulfide. The Hunter-Hyde method gave only small values, even in the presence of mercuric acetate catalyst. Samples of 0.1 g. of sulfur in 10 ml. of solvent were used throughout. Detailed results for colloidal sulfur are shown in Table VII.

TABLE VI

Apparent Iodine Value of Oils Treated with Sulphur
(Sulphur treatment: one hour at 130°C.)

Oil	Apparent iodine value (150% excess reagent)	
	Hunter-Hyde method	Benham-Klee method
Weed seed treated with 2% sulphur	111.3	138.4
Weed seed treated with 5% sulphur	113.5	160.7
Weed seed treated with 10% sulphur	111.4	177.9
Weed seed treated with 15% sulphur	112.0	173.1

TABLE VII

Apparent Iodine Value of Colloidal Sulphur

Reaction time	Apparent iodine value			
	Carbon disulphide solvent		Carbon tetrachloride solvent	
	Catalyst	No catalyst	Catalyst	No catalyst
Hunter-Hyde method (25 ml. of reagent)				
3 min.	−0.7	1.5	1.8	0.6
30 min.	1.6	4.8	4.3	5.3
1 hr.	2.5	5.9	5.0	6.0
2 hr.	3.3	8.8	6.1	14.0
4 hr.	6.2	17.8	13.6	24.1
6 hr.	8.9	31.4	19.5	31.1
Benham-Klee method[a] (50 ml. of reagent)				
1 min.	45	5.4	88	3.4
30 min.	−66	27.6	69	4.1
1 hr.	−71	47.0	66	18.5
2 hr.	−82	113.2	60	39.0
4 hr.	−85	130.4	59	95.8
6 hr.	−85	142.0	53	114.3

[a] Because the titration end point was unstable in the presence of catalyst, results with catalyst are given only to the nearest whole number.

With the Hunter-Hyde method, apparent iodine values of colloidal sulfur increased slowly with reaction time, and the increase was greater in the absence of catalyst.

With the Benham-Klee method, values increased markedly with reaction time in the absence of catalyst. In the presence of catalyst, negative results were obtained for carbon disulphide solutions and longer reaction times. For carbon tetrachloride suspensions containing catalyst, values tended to decrease slightly with reaction time. The titration endpoint was unstable when catalyst was used; the blue color of the starch indicator tended to regenerate itself indefinitely. Hence an arbitrary time of color disappearance (one minute) was chosen, and results were calculated only to the nearest unit.

The values obtained in the presence of sulfur were apparently due to reaction of sulfur with halogens. There was no evidence that sulfur reacted with sodium thiosulfate during the titration. No compounds of iodine and sulfur have been described, but sulfur chlorides and bromides are known (14, p. 658). Presumably the bromine of the Benham-Klee reagent was more reactive toward sulfur than the iodine-chlorine combination of the Hunter-Hyde reagent. However no explanation can be offered for high negative values obtained with the Benham-Klee method when carbon disulfide and catalyst were used together in prolonged reactions (Table VII).

Summary

Iodine values determined with pyridine sulfate dibromide tended to increase with reaction time and amount of excess reagent. There was some evidence of halogen substitution in polymerized linseed oil and in pure compounds. Mercuric acetate used to catalyze halogen addition in this method also appeared to promote degeneration of the reagent. In the absence of reagent, the catalyst had no dehydrogenating action

on oils, but reduced their iodine value, apparently by promoting oxidation, and by reacting at the double bond. Iodine value decreased with reaction time when the catalyst was used in the presence of chloroform, and high and erratic results were obtained in the presence of sulfur. Comparative iodine values with an iodine-chlorine reagent also tended to increase with prolonged reaction, but were only slightly affected by the presence of sulfur or chloroform.

Acknowledgments

The technical assistance of P. E. Diotte, J. W. Halcero, and A. L. Promislow is gratefully acknowledged.

REFERENCES

1. American Oil Chemists' Society, "Official Methods," Chicago, 1946.
2. Benham, G. H., and Klee, L., J. Am. Oil Chem. Soc., *27*, 127-129 (1950).
3. Chatt, J., Chem. Rev., *48*, 7-43 (1951).
4. French, R. B., Olcott, H. S., and Mattill, H. A., Ind. Eng. Chem., *27*, 724-728 (1935).
5. Hunter, L., and Hyde, F. F., Analyst, *58*, 523-527 (1933).
6. Klee, L., and Benham, G. H., J. Am. Oil Chem. Soc., *27*, 130-133 (1950).
7. Lips, H. J., Promislow, A. L., and Grace, N. H., J. Am. Oil Chem. Soc., *30*, 213-216 (1953).
8. Mikusch, J. D. von, and Frazier, C., Ind. Eng. Chem. (Anal. Ed.), *15*, 109-113 (1943).
9. Nergaard, R., and Jakobsen, F., Tids. Kjemi, Bergv., Met., *1*, 177-180 (1941).
10. Norris, F. A., and Buswell, R. J., Ind. Eng. Chem. (Anal. Ed.), *15*, 258-259 (1943).
11. Rosenmund, K. W., Z. angew. Chem., *37*, 58-59 (1923).
12. Rosenmund, K. W., and Kuhnhenn, W., Z. Untersuch. Nahr. Genuss., *46*, 154-159 (1923).
13. Skell, P. S., and Radlove, S. B., Ind. Eng. Chem. (Anal. Ed.), *18*, 67-68 (1946).
14. Taylor, F. S., "Inorganic and Theoretical Chemistry," Heinemann, London, 1948.
15. Taylor, R. S., and Smuli, J. G., Ind. Eng. Chem., *28*, 193-195 (1936).
16. Thomas, G., Bull. Soc. Chim. Belg., *54*, 181-185 (1945).
17. Uhrig, K., Roberts, F. M., and Levin, H., Ind. Eng. Chem. (Anal. Ed.), *17*, 31-34 (1945).

[Received April 22, 1953]

The Isolation and Characterization of the Polymers Formed During the Autoxidation of Ethyl Linoleate[1]

S. S. CHANG[2] and F. A. KUMMEROW, Department of Food Technology,
University of Illinois, Urbana, Illinois

THE oxidative polymerization of ethyl linoleate could involve the formation of polymers through carbon to oxygen or carbon to carbon linkages. Triebs (1) and Farmer (2) favored the former viewpoint, but each proposed a different kind of carbon to oxygen bond. Triebs proposed that two moles of fatty ester were combined through a 2,5-dihydroxy-dioxane ring while Farmer suggested that they were joined through a polymeric peroxide of high stability. On the other hand, Powers (3) and Powers, Overhold, and Elm (4) suggested that carbon to carbon linked polymers were produced as a result of a peroxide catalyzed reaction and that the link was formed through a vinyl or a Diels Alder type reaction.

Whether polymers are formed through carbon to oxygen or carbon to carbon linkages has been difficult to ascertain as polymers are not easily isolated in pure form. Most of the mechanisms suggested to date (5) have been based on unfractionated oxidation mixtures and on interpretations of the changes in the physical or chemical properties which accompany the polymerization step. In order to overcome these objections Swern *et al.* (6) attempted to separate oxidized methyl oleate by subjecting it to molecular distillation. However Kass (7) has pointed out that the thermal effect may have altered the nature of the components. Similarly, chromatography is not applicable for this type of separation as Privett, Lundberg, and Nickell (8) have shown that chemical changes in the autoxidation products may take place on the chromatograph column.

TABLE I

Analysis of the Solvent Extracted Fractions

Fractions	Solvents		Weight of Extract (grams)	Density 25°C.	Refractive Index $n_D^{25°}$	Molecular Weight
	% Skelly Solve F	% Diethyl Ether				
1	100	0	47.60	0.0948	1.4651	406
2	98	2	19.91	1.004	1.4671	494
3	96	4	16.48	1.011	1.4679	472
4	94	6	15.15	1.021	1.4691	516
5	92	8	17.31	1.026	1.4706	536
6	90	10	13.50	1.030	1.4711	543
7	88	12	12.14	1.038	1.4725	586
8	84	16	12.72	1.043	1.4739	646
9	80	20	14.80	1.051	1.4759	808
10	76	24	16.40	1.061	1.4778	865
11	68	32	9.99	1.065	1.4788	1046
12	60	40	12.84	1.068	1.4810	1070
13	50	50	7.14	1.077	1.4821	1130

In the present work the oxidized products of pure ethyl linoleate were separated into various fractions by solvent extraction at room temperature. The more polar polymer fractions were then characterized and the molecular structure which corresponded most closely to these analytical results was determined. This structure was then substantiated by characterization of the depolymerized products of the polymer fractions.

Experimental

Preparation of Material. The ethyl linoleate was prepared from corn oil according to a modification of Rollet's method (9). The ethyl ester had a Wijs iodine number of 164.1 (theoretical 164.6), a peroxide value of zero and a specific absorption coefficient of 0.2 at 2320 Å.

Oxidation Procedure. Two different batches of ethyl linoleate of approximately 250 g. each were weighed into a 50 x 460 mm. glass tube, the tube suspended in a constant temperature bath kept at 30 ± 0.5°C., and the ester aerated with dry air for 350 hours. The air was introduced through a fritted glass disk sealed into the bottom of the tube.

Solvent Extraction. The oxidized product was separated into 13 fractions with a solvent pair made up of redistilled Skellysolve F and anhydrous diethyl ether. The amount of solvent used in each solvent

---

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

[2] Portion of a thesis presented by S. S. Chang as partial fulfillment of the requirements for the degree of Doctor of Philosophy in Food Technology.