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Inter- and Intramolecular Polymerization in Heat-Bodied Linseed Oil[1]

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THERMAL polymerization of drying oils occurs by the formation of direct carbon-to-carbon bonds between the polyunsaturated acid groups present in the triglyceride oil molecules. With conjugated polyene acids the dimerization of the polyunsaturated acid groups is undoubtedly by a Diels-Alder addition reaction while with non-conjugated polyenes it has been proposed that thermal conjugation precedes the Diels-Alder addition of conjugated diene to non-conjugated diene. Whatever the mechanism of polymerization of the polyene acid groups, it is well known that dimerization is the principal reaction, with some trimerization, but probably no higher degree of polymerization.

Triglycerides or other polyesters containing two or more polyene acid groups per molecule can therefore polymerize to very high molecular weights, up to infinity (gelation), theoretically. The composition of drying oils capable of extensive heat bodying are qualitatively in accord with this concept of a functionality of approximately one for heat polymerization of polyunsaturated fatty acid groups.

There have been some considerations whether the dimerization (and trimerization) of the polyene acid groups in bodied oils occurs exclusively between acid groups in different molecules (intermolecular dimerization) or whether there is reaction between acid groups in the same molecule (intramolecular dimerization) (1, 2, 3, 4, 5, 6).

Intermolecular dimerization increases the molecular weight by joining two different molecules. Intramolecular dimerization does not increase molecular weight since reaction is between parts of the same molecule. Intramolecular reaction may occur between acid groups in the same unpolymerized triglyceride molecule, or it may occur between acid groups of the polymeric triglyceride, either between acid groups in the same or different triglycerides in the polymeric triglyceride. Either type of intramolecular reaction would result in less increase in molecular weight of the oil than would be expected from the same extent of intermolecular reaction.

Bradley (1), as well as Adams and Powers (2), suggested intradimerization to explain the observed molecular weights which were lower than would be expected from the extent of reaction, as judged by the change in iodine number. In view of the fact that monomeric acid groups with decreased unsaturation are formed from both linoleate and linolenate groups (7, 8, 9), this method is subject to error. This error is in the direction which would account for the observed molecular weights being lower than calculated from the decrease in iodine number.

Barker, Crawford, and Hilditch (10) considered that in the earliest stages the reaction is largely intramolecular. The sudden rise in viscosity in the later stages of reaction, with very little apparent change in linoleate and linolenate content, suggested that there was rearrangement from intra- to interdimerization by ester interchange. They demonstrated that ester interchange did occur slowly at bodying temperatures with non-polymeric triglycerides. They also converted some of the bodied oils to methyl esters and determined the molecular weight of the methyl esters. The theoretical molecular weight of the glycerides was calculated from that of the derived methyl esters. The most viscous oil which they studied was a 5.4 poise linseed oil with an observed molecular weight of 1,276 compared to the calculated value of 1,481. This difference of 14% may indicate some intradimerization, but not very extensive.

Joubert and Sutton (11) separated a light viscosity (1.2 poises) bodied pilchard oil into monomeric triglycerides (65%) and polymeric triglycerides (35%) by molecular distillation. The monomeric triglycerides were converted to methyl esters and distilled to afford only 1.5% of dimeric ester. They also segregated the polymeric glyceride into fractions ranging from 2,000 molecular weight up to 8,800. The fraction of 2,200 molecular weight was converted to methyl esters and found to contain about 67% monomeric and 33% dimeric esters by weight, which would correspond to a dimeric triglyceride (mol. wt. approximately 1,770) compared to 2,200 mol. wt. found.

Thus in this oil the monomeric triglycerides showed only very slight intrapolymerization, and the lowest molecular weight polymeric triglyceride showed no evidence of appreciable intrapolymerization.

Boelhouwer, Jol, and Waterman (12) bodied linseed oil to 33, 73, and 210 poises. The 33-poise oil showed 46% monomeric triglyceride, whose derived methyl esters showed 15% residual dimer plus trimer. The 73-poise oil showed 38% monomeric triglycerides with 29% of residual dimer plus trimer in their de-

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rived methyl esters. The 210-poise oil showed 10% monomeric triglycerides with 20% of residual dimer plus trimer in the derived methyl ester. Molecular weights of the oils were not reported.

Wiseblatt, Wells, and Common (13) bodied linseed oil to 2.72, 4.70, 10.30, and 27.0 poises. They determined the molecular weight of the oils and the percentage of monomer and of dimer (plus trimer) in the methyl esters derived from each oil. They calculated the ''hypothetical'' molecular weight from the determined percentage of monomer and dimer, assuming that only intermolecular dimerization occurred and that the dimer methyl ester which they determined as a distillation residue contained no trimer or higher polymer. The calculated molecular weight was always higher than the observed value: The ratios, calculated/observed molecular weight, ranged from 1,340/1,140 for the 2.72 poise oil to 3,600/1,840 for the 27-poise oil. This was taken as evidence of intrapolymerization between fatty acid radicals in the same monomeric glyceride. They did not separate monomeric from polymeric glycerides.

In the present study linseed oil was bodied at 300° C. to viscosities of 2.47, 10.3, and 52.1 poises. The monomeric triglycerides were separated from polymeric triglycerides by molecular distillation. The whole oil, as well as the monomeric and polymeric glycerides, were converted to methyl esters, which were analyzed for monomer, dimer, and trimer. The polymeric triglycerides were also analyzed for molecular weight. Thus the occurrence of intramolecular dimerization could be detected separately in the monomeric and polymeric glycerides.

Experimental

The linseed oil used was a commercial oil with the following analyses: iodine value 189.0, acid value 2.5, % linolenate 53.5, and % linoleate 16.9 by spectral analysis (16). It was heated in evacuated glass ampoules in a thermostatically controlled heating block for 1.5, 3, and 6 hours. The analyses of the bodied oils are shown in Table I. The analyses of their derived methyl ester are shown in Table II.[2] The polymeric triglycerides were obtained as a residue from distilling the whole bodied oil in a centrifugal cyclic batch molecular still (Distillation Products Industries, model CMS-5) to a maximum rotor temperature of 285-290° at 2-7 microns until distillation practically stopped. Since the total time at 290° during distillation was only a matter of seconds, it is reasonable to assume that no further polymerization or other reactions occurred during the molecular distillation. Materials balance of monomer, dimer, and trimer methyl esters from the molecularly distilled samples plus residue also checked very closely with the whole bodied oil before distillation. Early monomeric fractions of 3 to 5% (coming over at rotor temperatures of 150-200°) were high in free acid (acid values 137 to 151) and apparently contained free monomeric fatty acids produced by thermal cracking, as was shown by Skraup and Hedler (14). The main monomeric triglyceride fractions distilled at rotor temperatures of 260-290° (mostly at 275°), with acid values of 2.1, 4.0, and 12.4 (for the 1.5-, 3-, and 6-hour samples, respectively). The analyses of the methyl esters of the composite monomeric distillates are shown in Table III. These values are for total distillate material. The methyl esters were analyzed for monomer, dimer, and trimer by a micromolecular distillation method (15). The residual polymeric glycerides showed progressively increasing molecular weight, viscosity, and acid values and decreasing iodine values, as shown in Table IV. The composition of the methyl esters derived from the polymeric glycerides is shown in Table V.

TABLE I

Thermal Polymerization of Linseed Oil at 300°C.

Time, hrs.	Viscosity poises, 25°	Acid No.	Iodine No.	Ln$_2$ %	Ln$_3$ %	Polym. glyc. %
0 (orig.)	0.42 (A)	2.5	189.0	16.9	53.5	(0)
1.5	2.47 (J)	6.9	156.9	17.4	33.1	39.5
3	10.3 (W)	10.2	139.9	12.1	14.1	60.5
6	52.1 (Z_3)	15.0	130.2	7.6	4.6	72.5

TABLE II

Methyl Esters from Polymerized Linseed Oils

Sample	Monomer, % wt.	Dimer, % wt.	Trimer, % wt.	D/T
0 hrs. (orig.)................	99.7	0.2	0.1	....
1.5 hrs.........................	83.5	14.2	2.3	6.2
3 hrs............................	71.6	22.5	5.9	3.8
6 hrs............................	60.3	27.3	12.4	2.2

TABLE III

Methyl Esters from Monomeric Glycerides

Sample	Monomer, % wt.	Dimer, % wt.	Trimer, % wt.	% of total D + T found in mon. glyc.
1.5 hrs.........................	98.7	1.3	0	4.7
3 hrs............................	97.9	1.8	0.3	3.0
6 hrs............................	94.0	5.2	0.8	4.2

TABLE IV

Polymeric Glycerides of Polymerized Linseed Oils

Sample	Viscosity poises, 25°	Acid value	Iodine value	Mol. wt.	Ln$_2$ %	Ln$_3$ %
1.5 hrs.	30.5	1.5	150	1760	14.7	18.5
3 hrs.	73.4	3.1	136	2066	10.8	10.1
6 hrs.	503	5.7	129	2724	7.9	4.9

TABLE V

Methyl Esters from Polymeric Glycerides

Sample	Monomer, % wt.	Dimer, % wt.	Trimer, % wt.	D/T
1.5 hrs....................	59.3	33.4	7.3	4.6
3 hrs....................	53.7	35.8	10.5	3.4
6 hrs....................	48.8	36.5	14.7	2.5

Discussion

The analytical values recorded for linoleic and linolenic acids on the polymerized oils and fractions are probably lower than the true values. They are based on the 25-min. isomerization in KOH-glycol in air, using the coefficients of the pure acids, as reported by Brice *et al.* (15). Infrared curves indicated appreciable amounts of isolated trans double bonds. Since the effect of cis-trans isomerism on spectral analysis of linolenate isomers has not been determined, as is the case with linoleate (16), the values must be considered as only approximations. The amount of linoleate plus linolenate which apparently disappears during polymerization is considerably greater (ca. 50%) than the amount of dimeric plus trimeric acid groups formed (cf. Tables I and II). The formation of cyclic monomers may in part account for this excessive disappearance of linolenate

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[2] To prepare the esters one part of oil was refluxed 30 minutes with ½ part KOH in 3 parts 95% ethanol. Recovered acids were refluxed 30 minutes with 10-15 parts methanol containing 1% H_2SO_4, and esters were recovered in the usual manner.

and linoleate (17, 18), but the effect of trans isomers on spectral analysis is also probably quite important. Also the iodine numbers are at best only empirical indications of the extent of polymerization since cyclic monomers have lower iodine values, and also dimers and trimers have rather similar iodine values which vary considerably with the conditions of their determination (19).

The dimeric and trimeric acid groups should be most directly related to actual polymerization. That very little intramolecular dimerization of acid groups occurs in the monomeric glycerides is evident from Table III. Furthermore the percentage of total dimerization of acid groups which occurs intramolecularly in monomeric glycerides is small (3-5%) and essentially constant (last column, Table III). This is contrary to the idea that in the early stage intrapolymerization occurs extensively in the monomeric glycerides, followed by ester interchange in later stages to produce interpolymerization with little or no change in amount of dimeric and trimeric acid groups.

Whether intradimerization of acid groups (in the same triglyceride or in different glycerides) occurs in the polymeric glycerides is not so readily determined. It is possible to derive an equation for calculating the theoretical number of average molecular weight from the monomer, dimer, trimer composition of the methyl esters derived from a polymeric glyceride. This equation is: $M_n = n \cdot W = \frac{W(1+d+2t)}{1-2d-4t}$

where:

M_n = number average molecular wt. of polymeric triglycerides.
W = molecular weight of monomeric triglyceride.
n = average number of triglycerides in one mole of polymeric triglycerides.
m = mole fraction of monomer in derived methyl esters.
d = mole fraction of dimer in derived methyl esters.
t = mole fraction of trimer in derived methyl esters.

This formula assumes that all dimerization and trimerization is intermolecular, that no other process of intermolecular combination occurs, and that no process of degradation occurs.[3] The calculated molecular weights are compared with the observed molecular weights in Table VI. The fact that the calculated molecular weights are higher than the observed molecular weights indicates intrapolymerization. However these polymeric glycerides showed appreciable acid numbers. One could assume that these are carboxylic acid groups of a dimeric acid grouping which resulted from splitting of a polymeric glyceride into two smaller polymeric glycerides, one with an acid end-group and one with a neutral end-group (propene-1, diol-2, 3 ester). This type of splitting has been proven on monomeric triglycerides by Skraup and Hedler (14). If the acidity of the polymeric triglycerides is so formed, it is possible to calculate a corrected molecular weight, allowing for the end-groups thus formed. The calculated values, corrected for observed acid values on this basis, are shown in Table VI. Even these corrected values are higher than the observed values so intradimerization is still indicated. With the known molecular weights and the calculated molecular weights (after correction for acid end-groups, as above) it is possible to estimate the percentage of intradimer in the total dimer (plus trimer) of the polymeric glycerides. The 1.5-hr. sample shows 20%, the 3-hr. sample 17%, and the 6-hr. sample 10% intradimer of the total dimer plus trimer groups present.

TABLE VI

Molecular Weights of Polymeric Glycerides

Sample	Mol. wt. detd.[a]	Acid No.	Mol. wt. calc.	Mol. wt. Calc. + corr.[b]
1.5 hrs.	1760	1.5	2490	2150
3 hrs.	2066	3.1	3500	2900
6 hrs.	2724	5.7	5370	3500

[a] Signer isothermal distillation (21) on .02 M soln. in ether.

[b] Calculated from composition of derived methyl esters, corrected for acid end-groups, as described in text.

Viscosities of the whole bodied oils and of the polymeric glycerides are shown in Tables I and IV. Plots of the viscosities of the whole bodied oils or of the polymeric glycerides *vs.* time showed the typical concave upward shape. Plots of log viscosity *vs.* time showed a straight line for the polymeric esters but a slightly concave downward curve for the whole oils. The plot of log of viscosity *vs.* square root of molecular weight was nearly linear for the polymeric glycerides. This would indicate a fairly constant ratio of weight average to number average molecular weight in the polymeric glycerides since weight average molecular weight more nearly governs this relationship. The relationship of number average molecular weight to viscosity will vary with factors which affect the molecular weight distribution. Such factors might be: temperature of polymerization, composition of fatty acids, polymerization or ester interchange catalysts, and any other factor which would affect the dimer to trimer ratio in the polymeric acid groups.

The sudden rise in viscosity with very little apparent reaction in the later stages of polymerization may be explained by the following factors:

1. Viscosity increases progressively more rapidly with increase in molecular weight, a phenomenon inherent in the general properties of liquid polyesters and polymers in general. The logarithm of viscosity is proportional to the square root of the (weight average or viscosity average) molecular weight.

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[3] The derivation is as follows:

For a given degree of polymerization, n, a definite relationship exists between M, D, and T (respectively the number of moles of monomeric, dimeric, and trimeric fatty acid groups present as glyceride ester per mole of polymeric glyceride). The results, found by empirical trial and error fitting for increasing values of T, are shown in the following table, with a generalized relation in the last column for M and D in terms of T and n:

M	n+2	n+3	n+4	n+5	n+(T+2)
D	n—1	n—3	n—5	n—7	n—(2T+1)
T	0	1	2	3	T
Σ	2n+1	2n+1	2n+1	2n+1	2n+1

(1) $t = \frac{T}{2n+1}$ = mol. fraction in trimer in derived methyl esters.

(2) $d = \frac{n-(2T+1)}{2n+1}$ = mol. fraction dimer in derived methyl esters.

(3) $m = \frac{n+(T+2)}{2n+1}$ = mol. fraction monomer in derived methyl esters.

(4) from (1): $T = 2nt + t$.

(5) from (2): $n - 2T - 1 = 2nd + d$.

(6) or: $T = -nd - d/2 + n/2 - 1/2$.

(7) equating (4) and (6): $2nt + t = -nd - d/2 + n/2 - 1/2$.

(8) solving (7) for n: $n = \frac{1+(d+2t)}{1-2(d+2t)}$.

(9) Whence: $M_n = n \cdot W = \frac{W(1+d+2t)}{1-2d-4t}$.

2. Molecular weight increases progressively more rapidly for a given extent of a bifunctional or higher order polymeric addition reaction, as the extent of reaction increases.
3. Methods of measurement of extent of reaction of polyunsaturated acids such as by iodine number, polybromide number, and spectral analysis become less accurate as the extent of reaction increases, giving lower than true values, due to interference by trans double bonded isomers and by cyclic monomers.

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Summary

1. Linseed oil has been polymerized at 300° for 1.5, 3, and 6 hours. The polymeric glycerides have been separated from the monomeric glycerides, and the derived methyl esters of each fraction have been analyzed for monomer, dimer, and trimer.

2. The monomeric glycerides show very little intradimerization, ranging from 1.3 to 6% of their acid groups, or 3 to 4% of the total polymeric acid groups in the whole oil.

3. The polymeric glycerides show appreciable intradimerization, from 10 to 20% of their total polymeric acid groups.

4. There is no evidence that a shift from intra- to interdimerization is the major cause of the sudden increase in viscosity in the later stages of thermal polymerization.

5. The rapid rise in viscosity is due to the nature of the relationship of viscosity to molecular weight and of molecular weight to extent of reaction in the difunctional polymerization system present.

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Effects of High Temperature Storage Upon Lard as a Raw Material for Shortening Manufacture[1]

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IT is well known that the meat food fats, in contrast to the vegetable oils, contain a minimum of natural antioxidants (1, 2). As a result, prior to the development of the use of phenolic antioxidants (3, 4, 5, 6), lard was low in keeping quality. Therefore it was of interest to study the effect of storing lard upon its quality as a raw material for the manufacture of stabilized shortenings.

It is known that lard develops strong flavors during aging. We have found in some cases that samples with peroxide values near 20 me./kg. (7, 8) were considered objectionable by panel members.[2] Analytically, the only other difference between fresh and rancid samples noted was an increase in the percentage of conjugated dienes.

Colors of the aged lards after deodorization were found to be considerably darker than those of the fresh, and the flavor stabilities of the former were poorer. Stabilization with synergistic combinations of antioxidants was not fully effective in preventing the development of peroxides in the aged, deodorized lards. Consequently the fresh, deodorized, and stabilized lards had higher A.O.M.'s.

Partial hydrogenation did not stabilize the aged lards nearly as markedly as the fresh lards. The former had darker colors, lower A.O.M.'s and poorer flavor stabilities.

Each experiment described here was repeated at least twice, and in some cases three or four tests were run to establish with certainty that the results could be reproduced. Although data from only one representative series of tests are reported here, the same trends with respect to color, A.O.M., and flavor stability were observed each time a test was repeated.

Experimental

A 200-lb. sample of prime steam lard was centrifuged, using a laboratory model Sharples centrifuge to remove suspended solids and excess moisture. Then 100 lbs. of this lard were stored at —22°C.(—8°F.) to retard deterioration.

The remaining 100 lbs. were aged at 35°C.(95°F.) in a covered can until its peroxide value had increased from an initial figure of 2.0 to 10.0 me./kg. This re-

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[2] Lard with a peroxide value of 20 or greater is considered rancid.