

Thermal Polymerization of Methyl Linolenate, Alpha- and Beta-Eleostearates¹

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PREVIOUS STUDIES on the kinetics of thermal polymerization of the linoleate isomers (1, 2) indicated that dimerization of the conjugated diene isomers is by a Diels-Alder addition between two moles of conjugated diene. Dimerization of non-conjugated (1, 4 diene) linoleates was considered to occur by thermal conjugation, followed by a Diels-Alder addition between a conjugated linoleate (as diene) and non-conjugated linoleate (as dienophile).

The Diels-Alder mechanism for thermal polymerization of polyunsaturated fatty esters was supported by the findings of Waterman's group (3, 4) that residual dimers of linoleate contained about 1.3 rings per molecule while those of linolenate and eleostearate contained about 2 rings per mole. Their statistical method did not prove the size of the rings.

Definite proof of the cyclohexane ring with four adjacent substituents (as demanded by the Diels-Alder mechanism) was recently shown by Clingman, Rivett, and Sutton (5). They aromatized molecularly distilled dimers by bromination with N-Bromosuccinimide and dehydrobromination with N,N-diethyl aniline. Oxidation with permanganate afforded prehnitic acid (benzene, 1,2,3,4 tetra carboxylic acid) identified as the tetramethyl ester. Beta-eleostearate dimer afforded 9%, linolenate dimer 2%, and linoleate dimer 3-4% of the theoretical amount of isolated prehnitic ester. It is not clear whether the low yields are due to

low content of cyclohexene structure or due to inherently low yields in the degradation steps involved. Their work for the first time, by classical organic methods, satisfactorily proved the presence of a six-membered ring in these thermal dimers. While the low yields of derivative do not prove this as the predominant structure, they do not preclude it.

Discussion of Results

The present study is on the kinetics of the polymerization of normal methyl linolenate and of methyl α - and β -eleostearates.

Normal Linolenate. The general picture on normal linolenate is rather similar to those on the non-conjugated linoleates (1, 2) in that conjugation (dienic) rapidly appears at a low level, remains fairly constant during most of the reaction, and then drops off. Dimer forms more rapidly at first, and trimer forms more rapidly later on so that the dimer-trimer ratio is high at low conversions, and relatively low at high conversion (Table I). However dimer is the predominant polymer at all stages. No triene conjugation was evident in any samples. In the triene region general absorption was quite low $k_{1\text{cm}}^{\text{cm}^{-1}} > 1$, with no peak. The iodine number of the recovered monomer dropped off rapidly, indicating side reactions, such as cyclization or disproportionation. Also isomerization to form isolated *trans* double bonds was evident by infrared adsorption at 10.32μ . This was more rapid than with normal linoleate. In view of the known effect of *trans*

TABLE I
Normal Linolenate, Thermal Polymerization

270° Large Samples											
Hours	Monomer %	Dimer %	Trimer %	Ln _s ^a %	Conj. Diene k ₂₃₃	n _D ²⁰ Whole	n _D ²⁰ Monomer	n _D ²⁰ Dimer	I.V. Monomer	I.V. Whole	k, First Order ^b
12	74.3	19.6	6.3	58.7	7.3 ^c	1.4734	1.4678	1.4866	229.7	0.0415
24	53.9	30.9	14.8	28.8	5.5 ^c	1.4784	1.4686	1.4885	208.4	0.0595
48	39.5	36.4	25.0	10.0	3.6 ^c	1.4824	1.4691	1.4887	179.7	0.0441
290° Large Samples											
3	78.7	16.8	4.7	62.1	7.5 ^c	1.4726	1.4677	1.4885	229.4	0.148
6	57.4	31.9	9.9	33.2	6.5 ^c	1.4769	1.4683	1.4881	206.3	0.209
12	44.0	35.4	19.8	13.5	4.8 ^c	1.4812	1.4688	1.4890	180.5	0.150
24	29.8	40.1	29.8	2.0	3.0 ^c	1.4845	1.4690	1.4892	157.1	0.159
290° Small Samples											
0.75	92.9	6.9 ^d	1.4687	245.7	0.0522
1.5	83.4	8.2 ^d	1.4700	232.4	0.1474
3	65.5	9.1 ^d	1.4728	210.1	0.1595
6	38.6	8.2 ^d	1.4768	180.6	0.1756
12	14.9	5.8 ^d	1.4815	152.1	0.1589
24	4.1	3.9 ^d	1.4851	138.1	0.1075

^a % linolenate in whole esters calculated from % monomer \times % Ln_s in monomer, except small samples, where analysis was made on whole bodied esters.

^b Calculated from % Ln_s.

^c On monomer.

^d On whole esters.

TABLE II
 Eleostearate Polymerization 270°C.

Alpha Eleostearate								
Hours	Monomer %	Dimer %	Trimer %	α Eleo %	β Eleo %	Total Eleo %	n_D^{20} Whole	k, Second Order
(Heat-up)								
0.....	66.0	29.5	4.5	43.2	17.7	62.5	1.4939
0.047.....	55.6	38.6	5.8	33.0	16.0	50.4	1.4968	0.0818
0.094.....	51.2	41.1	7.7	29.1	15.0	45.6	1.4961	0.0455
0.19.....	45.3	46.1	8.6	19.6	14.6	36.4	1.4943	0.0590
0.38.....	36.8	53.0	10.2	13.1	11.4	25.9	1.4926	0.0593
0.75.....	28.6	55.4	16.0	6.2	8.1	15.4	1.4912	0.0702
1.5.....	24.4	55.4	20.2	3.1	5.3	9.1	1.4905	0.0600
3.0.....	21.3	55.0	23.7	1.3	3.4	7.3	1.4900	0.0181
Beta Eleostearate								
(Heat-up)								
0.....	50.6	45.6	3.8	1.6	42.3	45.0	1.4969
0.047.....	43.6	50.3	6.1	2.5	33.9	37.1	1.4950	0.1007
0.094.....	41.7	51.4	6.9	6.6	25.2	34.2	1.4944	0.0486
0.19.....	35.9	57.4	6.7	4.4	22.7	28.9	1.4933	0.0557
0.38.....	29.6	58.8	11.6	4.9	15.7	21.9	1.4922	0.0589
0.75.....	25.8	55.4	18.8	3.4	11.3	15.3	1.4911	0.0550
1.5.....	23.6	53.2	23.2	1.6	7.8	10.3	1.4908	0.0423
3.0.....	21.1	48.5	30.4	1.0	4.6	6.1	1.4905	0.0446

isomers on the ultraviolet spectral analysis of linoleate, it is very probable that the analyses shown for linolenate are only an approximation and are probably lower than the true value for total non-conjugated linolenate. The much more complicated problem of analysis for total non-conjugated linolenate has not been solved, as is the case with linoleate (6). It is therefore somewhat presumptuous to make kinetic studies and deduce reaction mechanisms from the rates of disappearance of linolenate or of monomer. However, if one does yield to the temptation to calculate orders of reaction from the data, the disappearance of linolenate is found to follow a first order reaction at 270° and 290° (Figures 1 and 2). When percentage monomer is similarly plotted to determine the order of reaction, it appears as first order for the 270° (Figure 1) but fits a second order of reaction at 290°. This is very similar (except the last case) to the kinetics of the non-conjugated linoleate polymerizations, and along with the similarity of pattern of development of conjugation, dimer and trimer, suggests that the general mechanism is the same as that suggested for linoleate (2):

- (1) $N \longrightarrow C$ slow, 1st order rate determining step
- (2) $N + C \longrightarrow D$ fast, 2nd order dimerization as principal reactions, and:
- (3) $D + C \longrightarrow T$
- (4) $C + C \longrightarrow D$
- (5) $N \text{ or } C \longrightarrow X$
as reactions of lesser importance.

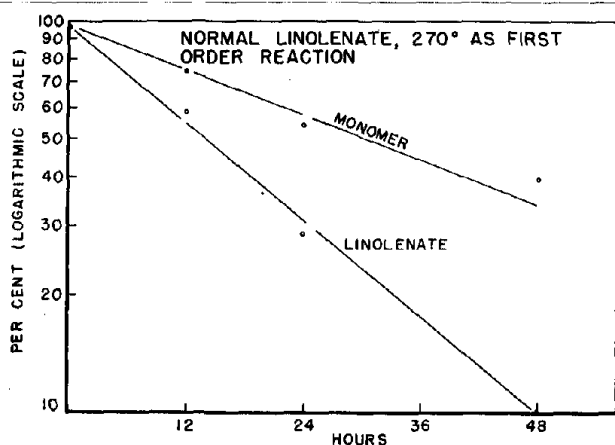


Fig. 1

Here N = non-conjugated linolenate, C = dienically conjugated linolenate, D = dimer, T = trimer, and X represents cyclic or other isomers of linolenate incapable of participating in polymerization, and isomers which are not analyzed by the present spectral method.

The principal differences between normal linoleate and normal linolenate are that the linolenate develops conjugation and *trans* isomers more rapidly and polymerizes more rapidly. This is reasonable since linolenate has two active methylenes between two double bonds while linoleate has only one.

Alpha- and Beta-Eleostearates. Since these isomers are conjugated and each has at least one pair of adjacent *trans*, *trans* conjugated double bonds, they should polymerize rapidly and directly by a second order Diels-Alder addition. This is shown to be the case whether total eleostearate or monomer is plotted (Figures 3 and 4, Tables II and III). The faster rate of polymerization of the beta-eleostearate is very reasonable in view of its all-*trans* conjugated structure, compared to the *cis*, *trans*, *trans* structure of the alpha isomer (7, 8).

This follows from the fact that a *trans*, *trans* acyclic conjugated diene is much more reactive as

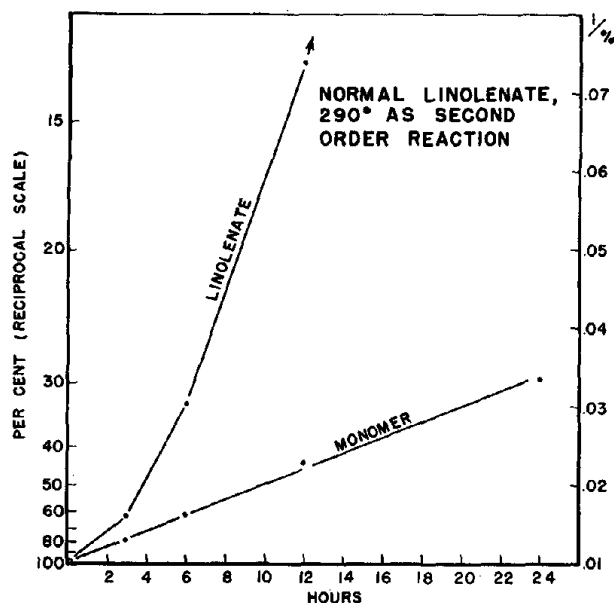


Fig. 2

TABLE III
 Eleostearate Polymerization 230°C.

Alpha Eleostearate								
Hours	Monomer %	Dimer %	Trimer %	α Eleo %	β Eleo %	Total Eleo %	n_D^{20} Whole	k, Second Order
(Heat-up)								
0.....	90.6	8.4	1.0	78.3	14.2	93.0	1.5044
0.047.....	88.3	10.9	0.8	72.1	15.3	88.4	1.5035	0.0119
0.094.....	84.7	13.4	1.9	65.1	18.9	85.7	1.5032	0.0076
0.19.....	81.8	16.1	2.1	58.1	19.5	80.5	1.5017	0.0080
0.38.....	71.2	25.3	3.5	49.9	17.3	69.3	1.5005	0.0107
0.75.....	58.0	38.1	3.9	38.7	14.3	54.6	1.4982	0.0104
1.5.....	44.0	51.3	4.7	24.7	11.9	38.1	1.4956	0.0106
3.0.....	27.8	60.9	11.3	13.1	8.6	22.6	1.4932	0.0120
6.0.....	21.4	61.9	17.4	6.4	5.0	12.2	1.4918	0.0126
Beta Eleostearate								
(Heat-up)								
0.....	84.1	14.6	1.3	neg.	91.3	83.5	1.5035
0.047.....	77.5	21.4	1.1	neg.	83.3	77.3	1.5022	0.0204
0.094.....	73.8	24.8	1.4	neg.	76.3	74.8	1.5014	0.0092
0.19.....	66.8	32.1	1.1	neg.	68.2	67.1	1.5001	0.0163
0.38.....	56.6	41.3	2.1	0.6	51.0	56.2	1.4980	0.0168
0.75.....	42.4	54.7	2.9	36.8	38.1	1.4954	0.0226
1.5.....	30.9	64.2	4.9	2.1	21.3	25.8	1.4934	0.0167
3.0.....	21.4	68.9	9.7	2.3	12.9	16.4	1.4920	0.0148
6.0.....	18.1	69.7	12.2	1.2	8.4	10.4	1.4913	0.0117

diene in the Diels-Alder reaction than is a *cis-trans* diene (2, 8, 9, 10, 11). The *trans, trans, trans* conjugated β -isomer has two pairs of *trans, trans* conjugated dienes (with one double bond in common) whereas the α -isomer has only one such pair.

The reason that a *trans-trans* conjugated diene reacts more readily than the *cis-trans* or *cis-cis* isomer in the Diels-Alder diene addition reaction is evident when one considers that a planar "bent-back" or "half-ring" or *s-cis* configuration is required for facile approach of the dieneophile in a manner which will produce the cyclohexene ring of the adduct after reaction. It is difficult to describe, but very evident from inspection of scale models, that *trans, trans* acyclic dienes can most readily assume this planar *s-cis* configuration whereas the *cis-trans* diene shows some interference (with the "outside" H of the *trans* double bond) in assuming this configuration while the (so far unknown) *cis-cis* conjugated isomer has great interference between the H's of the methylenes adjacent to the double bonds.

The α -eleostearate isomer, with only one *trans-trans* conjugated diene pair, is faster than the *trans, trans* conjugated linoleate (2). There may be several reasons for this:

- the *cis-trans* pair has some activity as a diene;
- the α -form isomerizes to the more active β -form during the polymerization (Table II);
- the double bonds (particularly the central double bond activated by two adjacent double bonds) may be a more active dieneophile than the double bond of a simple diene; and
- comparisons of scale models of α -eleostearate with *trans, trans* linoleate show even less interferences with α -eleostearate than with the *trans, trans* linoleate.

As a summary and comparison of the relative polymerization rates of the linoleate and linolenate iso-

mers studied by us, the following chart of relative speeds is shown. This is based on normal linoleate as unity and using the (reciprocal of) time required for formation of 60% polymer as an indication of speed, at comparable temperatures.

The non-conjugated isomers are all in a slow class where the number of double bonds is more important than *cis-trans* configuration. The conjugated isomers are all much faster and depend greatly on the *cis-trans* configuration. These relative rates are explainable by the conjugation and Diels-Alder addition mechanism of dimerization, assuming thermal dimerization of non-conjugated isomers, and considering the effect of *cis, trans* isomers on the diene activity of conjugated isomers.

Experimental

Methyl linolenate was obtained from the Hormel Foundation. Infrared absorption at 10.32μ indicated that about 5-10% of the double bonds were *trans*. This value rose rapidly to a maximum of about 50% in 1.5 hours at 290°C . and then gradually decreased as the reaction progressed. Analyses on the starting material were: I.V. = 259.4 (theory 260.4); after alkali isomerization at 180°C . for 25 min. (KOH, glycol) (12) $k \frac{\text{gm./liter}}{233, 1 \text{ cm.}} = 59.2$ $k \frac{\text{gm./liter}}{268, 1 \text{ cm.}} = 49.2$.

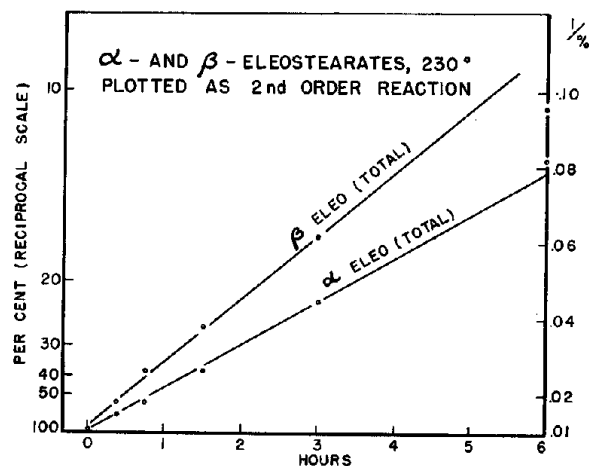
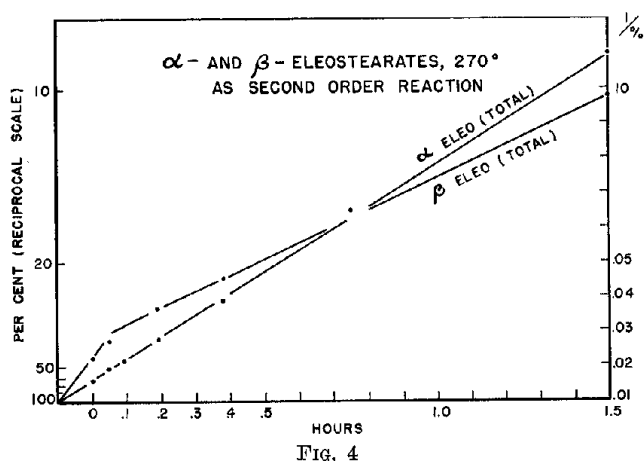


FIG. 3

 TABLE IV
 Linoleate and Linolenate Polymerization

Relative Speed	Conjugation	Double Bonds	<i>Cis, trans</i>
0.74.....	no	2	<i>cis, trans</i>
1.0.....	no	2	<i>cis, cis</i>
1.2.....	no	2	<i>trans, trans</i>
2.4.....	no	3	<i>cis, cis, cis</i>
5.8.....	yes	2	<i>cis, trans</i>
26.0.....	yes	2	<i>trans, trans</i>
170.0.....	yes	3	<i>cis, trans, trans</i>
340.0.....	yes	3	<i>trans, trans, trans</i>



Micromolecular distillation (14) showed 100% monomer.

Methyl β -eleostearate was made from β -eleostearic acid by agitation under CO_2 with 20 parts of absolute methanol containing 0.4% *p*-toluene sulfonic acid for 3 hrs. at room temperature. The esters were recovered by dilution with water, extracted with Skelly F and benzene, washed free of toluene sulfonic acid, washed free of fatty acids with dilute NaOH, and dried over Na_2SO_4 . The solvent was removed under vacuum with only mild heat ($<50^\circ$). The esterification at room temperature was necessary because it was found that the usual method of refluxing with methanol and strong acid promoted $\beta \rightleftharpoons \alpha$ isomerization. The ester showed the following values in cyclohexane, calculated to the basis of free acid: $k_{269} = 201.0$; $k_{271.5} = 165.4$; $k_{276.5} = 120.7$. The values of O'Connor *et al.* (13) for the β acid were: $k_{269} = 202.4$; $k_{271.5} = 178.1$; $k_{276.5} = 122.5$. Our values agree well with theirs except at 271.5 μ . The errors involved in calculations of α - and β -content from differences in absorption between curves at points of steep slope have been discussed by them (13). If their formulae are used, the above ester would show 98.5% total eleostearate, 122.0% β^2 and -30.8% α eleostearate. It showed only a trace of the infrared band at 10.37 μ which the α isomer shows (8). It showed 99.5% monomer and 0.5% dimer by micromolecular distillation (14). $n_D^{20} = 1.5067$, M. P. 14.0°C .

The β -eleostearic acid was prepared from raw tung oil. The 1,000 g. of tung oil, 400 g. of KOH in 270 cc. water plus 2,000 cc. of ethanol were refluxed 20 min. It was diluted with 2,000 cc. of H_2O , acidified under CO_2 with excess cold 20% H_2SO_4 , and extracted with Skellysolve B. The mineral acid was washed out with water. The Skellysolve solution was dried with Na_2SO_4 , diluted to 4,000 cc. with Skellysolve B, and treated with 85 cc. of 0.005 N I_2 in diffused outdoor light for one hour. It was diluted with 3,000 cc. of methanol and stored for two days in a cold room at 4°C . It was filtered on a Buchner filter and washed with 3,000 cc. of methanol cooled to -10°C . The wet crystals were esterified directly as described above. Yield of methyl esters was 16% of crude oil. The crude oil analyzed 81.0% total, 79.9% α - and 1.3% β -eleostearic acid.

Methyl α -eleostearate was made by esterifying α -eleostearic acid in the same manner as described above

² Such an extraordinarily high content can only be ascribed to the fact that this paper was presented at the Paul Bunyan Meeting of the Society. R.I.F.

for the β -isomer. The methyl α -eleostearate showed the following extinction coefficients calculated to the acid: $k_{269} = 159.0$; $k_{271.5} = 178.3$; $k_{276.5} = 125.9$. The values of O'Connor *et al.* (13) for the α acid are: $k_{269} = 149.5$; $k_{271.5} = 168.6$; $k_{276.5} = 122.5$. In this case all of our values are higher than theirs.

By their formulae our α -eleostearate would analyze 102.8% total, 103.8% α , and 1.9% β -eleostearate. Distillation on a micromolecular still (14) showed 99.7% monomer and 0.3% dimer.

The α -eleostearic acid was made from the same crude tung oil. The crude acids from 1,000 g. of oil were crystallized once from 5,000 cc. of Skellysolve B at 4°C . and twice from 4,000 cc. of methanol at -30°C . The wet crystals were esterified directly, as described above, to afford a 15% yield of ester based on oil.

Polymerization was done by heating samples sealed in evacuated glass ampoules. They were heated in a thermostatically controlled, electrically heated aluminum block which had suitable holes drilled into it. With linolenate 70 g. samples were used. Heat-up time was 30 min. on this size of batch. One set of linolenate polymerizations at 290° was also done with 1 g. samples in small tubes. Heat-up time was 10 min. on these samples. The eleostearates were all polymerized as 1 g. samples in the small tubes, with a 10-min. heat-up time. The heat-up time is quite significant only in the case of eleostearates at 270° (Table II) since 1/3 to 1/2 of the reaction has occurred in this period. The intersection of the line with the base line in Figure 8 at -0.1 hr. indicates that the 10-min. heat-up time is equivalent to about 6 min. at reaction temperature.

Analyses for monomer, dimer, and trimer on the large linolenate samples were made by alembic distillation as in previous studies on linoleate isomers. On the eleostearate and the small-sample linolenate runs, analyses for monomer, dimer, and trimer were made with a micromolecular still, which required only 0.5 g. (14). Spectral analyses on linolenate were by essentially the method of Mitchell *et al.* (12) (KOH glycol, 180° 25 min.). Apparent linolenate (non-conjugated) was calculated from the difference between k_{268} before and after analytical conjugation, by dividing this difference by 51.0. Comments on the possible effect of *trans* double bonds on the inherent accuracy of this method on the thermally polymerized linoleate have been given above. Analyses for total α - and β -eleostearates were made by the equations of O'Connor *et al.* (13). The rate constants were calculated from the values for total eleostearate. The values for α and β isomers are approximations since it is not known whether other isomers are formed or how they would affect the method. The values certainly do indicate qualitatively that *cis-trans* isomerization does occur with heat and that the β form is the favored isomer.

Summary

The rates of polymerization of alpha and beta eleostearates agree with second order kinetics, as would be expected for a bimolecular Diels-Alder addition. The all-*trans*, beta isomer reacts faster than the *cis*, *trans*, *trans* alpha isomer, in agreement with known *cis*, *trans* effects on diene activity.

The polymerization of normal linoleate follows an apparent first order reaction. It is suggested that conjugation is the slow rate determining monomo-

lecular reaction, as has been proposed for the non-conjugated linoleate isomers.

Acknowledgment

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Cyclization of Eleostearic Acid¹

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ROSSMAN, in 1933, was the first to consider seriously the cyclization of fatty acids (1). For many years the problem was of only mild academic interest. However in 1951 Professor Crampton and his associates at McGill University began an intensive study of cyclic isomers of linolenic acid (2, 3, 4, 5).

Our own interest began with our earlier work with methyl linoleate (6). It was noted that after prolonged polymerization 60% of the monomer was monoolefinic and did not hydrogenate to methyl stearate. The material was considered to be cyclic. Investigation of this material is now in progress.

This paper describes our study of the cyclic isomer of methyl eleostearate. Eleostearate is known to cyclize readily at temperatures of 250° or less. Linoleate however requires much more drastic conditions (290° or above), and disproportionation or even rupture of carbon to carbon bonds may occur. Hence, since the eleostearate would give a cleaner product and higher yields, it was chosen for our first study. The determination of the structure of cyclic eleostearate was only a secondary purpose. The primary purpose was to develop methods (aromatization, oxidative degradation, etc.) and to obtain data (infrared and ultraviolet spectra, analytical constants, etc.) for use in the study of cyclic materials from other sources.

Experimental

A. Preparation of Alpha-Eleostearic Acid. The acids from 2 kg. of American tung oil (alcoholic KOH saponification, 20-min. reflux) were crystallized from 11.3 liters of Skellysolve Fat -25°. The original oil showed 81% total, 79.9% alpha, and 1.3% beta eleostearic acid. The crystals (m.p. 46°), isolated by inverse filtration (silk bolting cloth on a thistle tube), were recrystallized twice from 7.5 liters of Skellysolve F at +5°. The product was clarified by dissolving it in 2.25 kg. of A. R. acetone, filtering (Buchner), and evaporating the solvent finally at 100°C. with a mechanical pump with swirling (10). Yield was 790 g. (m.p. 49.0-49.5 cor.; literature 48.4 [19]) Infrared showed characteristic bands for *cis*, *trans* conjugation at 10.09 and 10.38 μ (7).

B. Preparation of Methyl Eleostearate. Methyl esters were prepared by esterification (10 vol. methanol, 2% sulfuric acid, 3 hrs. reflux), crystallization, and high vacuum distillation. They showed about 50% β - and 50% α -eleostearate by ultraviolet analyses (8). Both heat and mineral acid catalyze *cis*, *trans* isomerization of the double bonds of eleostearates. In the above case the mineral acid was probably the principal cause.

C. Cyclization of Methyl Eleostearate (Figure 3). The cyclization of the methyl eleostearate was done

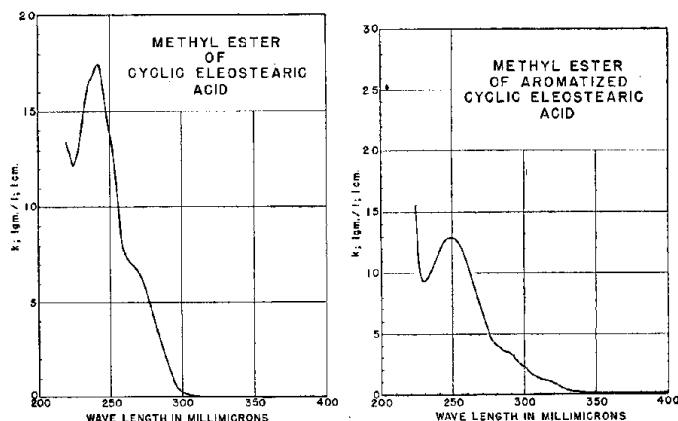


FIG. 1

as a 10% solution in methyl laurate to promote the presumably monomolecular cyclization reaction and to minimize bimolecular reactions, such as dimerization and disproportionation. Thus 58.5 g. (0.2 mole) of eleostearate was heated with 540 g. methyl laurate at 250° C. for 48 hrs. in a sealed, evacuated ampoule. Methyl laurate was stripped off through a short column to a pot temperature of 145° at 0.05 mm. The residue (67.5 g.) showed 39.9% monomer, 48.2% dimer, and 11.9% residual trimer by micromolecular distillation (11). In contrast, undiluted eleostearate would be 80% or more polymerized in only 3 hrs. at only 230°C. (9).

Cyclized eleostearate was concentrated from this residue by removal of noncyclic material as urea adducts (5), followed by distillation to separate it from polymers. Thus 64 g. of the residue in methanol (*ca.*

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