Isomerization and Trans-Esterification

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IT is our purpose to review rather briefly the fundamental and practical aspects of isomerization and trans-esterification reactions in fats. These two reactions are of considerable interest to all vegetable and animal fat chemists since they represent methods of changing the properties of the fats and oils without the addition of major amounts of modifying reagents. Esterification and its various ramifications, acidolysis, alcoholysis, and trans- or inter-esterification has been studied for more than a century. Indeed, some of the better work was performed before the turn of the century (1). For the most part, of main interest to drying oil chemists are methods which can be used to increase the drying or film-forming constituents of the oil, resin, or other vehicle. Isomerization is of interest to the drying oil chemist primarily because this reaction can lead to products which have conjugated structures similar in nature to the structures present in tung oil, the preferred oil for varnishes.

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Esterification

Direct Esterification. This reaction is most studied of all the types of esterification. The mechanism is established, and it is likely that the mechanism of the other types is similar. The reaction proceeds by mixing, in equal molar proportions, an acid with an alcohol followed by heating. Water is formed with the alcohol contributing the hydrogen and the acid the hydroxyl, as shown in the following equation:

$$\text{R—CO—}\underline{\text{OH}} + \underline{\text{H}}\text{OR} \overset{\text{H}^+}{\rightleftarrows} \text{R—CO—OR} + \text{H}_2\text{O}$$

The reaction is an equilibrium and the extent of this equilibrium is independent of all other variables, provided the reactants and products are retained in the homogenous mixture and sufficient time is permitted for equilibrium to be attained. The rate is proportional to H^+ concentration over a certain range and consequently this reaction is catalyzed by strong acids such as sulfuric, hydrochloric, phosphoric, toluene, sulfonic, and heptafluorbutyric. It is a bimolecular reaction, but the reverse reaction complicates the kinetics. If large excesses of acid or alcohol are used, the reaction is pseudo-first order.

There are several procedures which can be used to effect esterifications and to drive the reaction to completion. They are the use of excess of one reagent, removal of water with return of alcohol or acid to the reaction mixture, the use of catalyst, and the use of higher temperatures. In esterification of fatty acids with polyhydric alcohols, we have a special case of esterification which has some peculiarities of its own:

1. A catalyst increases initial rate and is necessary unless temperature is raised to make the materials homogenous soon after the reaction starts. However higher temperatures of reaction are preferred to acid catalysts.
2. If it is desired to use an excess of reagent to drive the reaction to completion, only an excess of the acid and not of the alcohol is used.
3. Reduced pressure lowers color formation and permits ready removal of volatile products.
4. Use of inert gas is recommended for improved color. As an example we refer to the esterification of linseed fat acids with pentaerythritol, dipentaerythritol, sorbitol, and glycerol in stoichiometric amounts of alcohols and acid (sorbitol 4:1) at 450°F. without a catalyst (2). Results are shown in Table I.

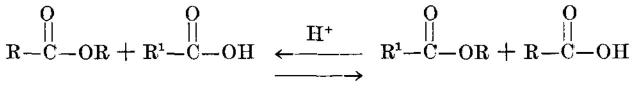
TABLE I

Esterification

Acid and alcohol	Acid value after hours of treatment						
	1	2	3	4	5	6	8
Linseed fatty acid plus pentaerythritol		80	30	18	12		6
Plus dipentaerythritol	24	12	8	5	4		
Plus sorbitol		104	55	44	34	28	22
Plus glycerol		120	65	30	20	14	5

Catalysts normally increase color and do not reduce the total esterification time appreciably. SO_2 as a gas for ebullition promotes bleaching and better color.

Acidolysis. Just as with direct esterification, acidolysis proceeds readily under the influence of acid catalyst as shown in the equation. Indeed, the acid itself is often sufficient catalyst at elevated temperatures. This reaction is promoted by the use of high boiling "replacing" acids so that the displaced acid may be removed by distillation.



$$\text{R—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OR} + \text{R}^1\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH} \overset{\text{H}^+}{\rightleftarrows} \text{R}^1\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OR} + \text{R—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—OH}$$

Examples of commercial use of this reaction are found in the preparation of alkyds with oils rather than fat acids, use of abietic acid to replace fat acid (3), and the use of dimeric fat acids to replace more volatile fat acids in oils (4).

Alcoholysis. This reaction is widely used in both research and commercial operations. It can be effected by either acid or alkaline catalysts, but the alkaline catalysts are much more effective. The equation may be written as follows:

$$\text{R}^1\text{OH} + \text{RCOOR} \overset{\text{OH}^-}{\rightleftarrows} \text{RCOOR}^1 + \text{ROH}$$

Alcoholysis can be effected at higher temperatures without catalysts or even at room temperatures with catalysts. Examples of the experimental and commercial use of this reaction are the following: conversion

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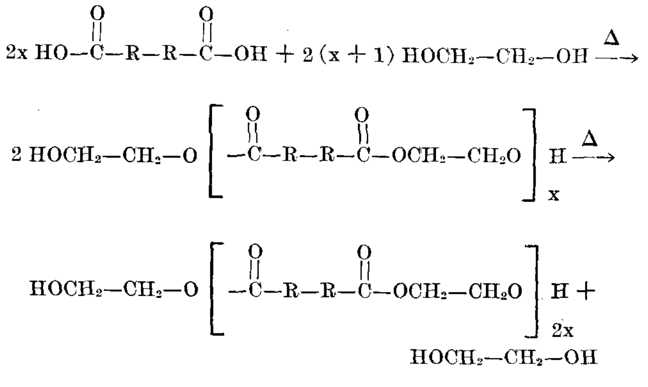
[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Report of a study in which certain phases were carried on under the Research and Marketing Act of 1946.

of glycerides to pentaerythritol esters, conversion of glycerides to methyl esters for glycerol recovery (5), and preparation of superpolyesters with ethylene glycol and other glycols which decompose. This latter reaction is of interest mainly in the preparation of polyester rubbers (6), as shown in the accompanying equation:



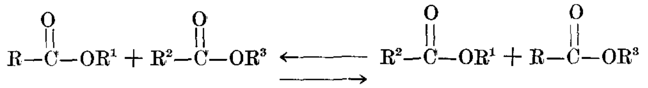
$$2x\,HO{-}\overset{O}{\overset{\|}{C}}{-}R{-}R{-}\overset{O}{\overset{\|}{C}}{-}OH + 2\,(x+1)\,HOCH_2{-}CH_2{-}OH \xrightarrow{\Delta}$$

$$2\,HOCH_2{-}CH_2{-}O\left[{-}\overset{O}{\overset{\|}{C}}{-}R{-}R{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{-}CH_2O\right]_x H \xrightarrow{\Delta}$$

$$HOCH_2{-}CH_2{-}O\left[{-}\overset{O}{\overset{\|}{C}}{-}R{-}R{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{-}CH_2O\right]_{2x} H + HOCH_2{-}CH_2{-}OH$$

Several examples of alcoholysis and acidolysis are listed in Table II.

Inter-esterification or Trans-esterification. Until recently, undirected or random inter-esterification of esters was the main type known. In this reaction two esters are reacted either with or without a catalyst to give all the expected products as shown in the equation. If the simple esters were completely dissimilar, i.e., contained different acids and bases, the expected products would be four different esters including both the reactants and the products of the reactants. This reaction is of direct interest to all



$$R{-}\overset{O}{\overset{\|}{C}}{-}OR^1 + R^2{-}\overset{O}{\overset{\|}{C}}{-}OR^3 \rightleftarrows R^2{-}\overset{O}{\overset{\|}{C}}{-}OR^1 + R{-}\overset{O}{\overset{\|}{C}}{-}OR^3$$

drying oil chemists since it can be performed on the original oil used as a vehicle, and it undoubtedly occurs to a greater or less extent in the polymerization or bodying of an oil at 300°C. The occurrence of interchange at bodying temperature is best illustrated by reference to experiments with saturated glycerides, shown in Table III. In the absence of catalyst it is doubtful if interchange is complete in a bodied oil, but unquestionably it has occurred to a considerable extent.

Directed Inter-esterification. There are essentially two types: one in which the direction is effected by crystallizing one reactant from the reaction mixture, and the other in which direction is achieved by fractionally distilling a more volatile constituent.

Strong acids, bases, sodium alkoxides, alkali and alkaline earth metals, tin and zinc metals, hydroxides, and chlorides are catalysts. The alkoxides are probably the best catalysts. One example of the directed inter-esterification with distillation would be the conversion of glycerol triacetate to glycerol trieleostearate with methyl eleostearate. The methyl acetate could be removed at a sufficiently low temperature to give the required alkaline catalyst a long life.

The use of lower temperatures with alkoxide catalysts and the crystallization of fully saturated glycerides thus formed has been recently patented and discussed at some length (14). For example, refined and dried cottonseed, menhaden, and soybean oil were mixed for 15 minutes at given temperatures with 0.2 sodium methoxide in a xylene suspension. The mixtures were cooled in the presence of the catalyst to somewhat lower temperatures to permit the crystal to form. Table IV shows the results which were obtained.

In this directed inter-esterification the distribution of the fat acid is changed from a random or even arrangement to one in which the saturated groups are

TABLE II

Acidolysis and Alcoholysis

Type of reaction	Reactants	Utilization
Acidolysis	Drying oil + polymeric fat acids	Tung oil replacement
Acidolysis Esterification and alcoholysis	Drying oil + phthalic anhydride and glycerol	Alkyd resins
Acidolysis	Drying oil + abietic acid	Varnish oil and resin
Alcoholysis	Methanol + oil No catalyst — 175°-200°C. (7) 10 hrs. NaOMe — 70°C. (5) 10 min.	Soap manufacture Polymeric fat acids
Alcoholysis	Glycerol + oil	Alkyd resins Emulsifying agents
Glycolysis	Polyester — 200°C. (6) 10 hrs.	Synthetic rubber

TABLE III

Undirected Trans-Esterification

Reactants	Temperature	Time	Remarks
Ester I Ester II	°C.	Hrs.	
Ethyl benzoate + Benzyl acetate (8)	210	44	Low yield of products
Ethyl benzoate + Amyl acetate (9)	240	60	Some amyl benzoate
Ethyl benzoate + Amyl acetate No catalyst	300	3-5	Interchange occurs in appreciable amounts
Tristearin (10 pts.) + Soybean oil (10)	250	17	M.p. —43°C. (original 54°C.)
Tristearin (10 pts.) + Soybean oil	250	24	M.p. —34°C. (original 54°C.)
Beef stearin + Soybean oil (11)	275	8	M.p. —39.8°C. (original 42.5°C.)
Beef stearin + Soybean oil No catalyst	275	16	M.p. —36.1°C. (still dropping)
Tristearin + Triolein (12) Catalyst—NaOMe	205	3½	Obtained mixture with 12.5 tristearin present
Linseed oil + Sunflower seed oil	200	6	.01-0.06 Ca naphthenate Products equal to linseed oil (1)

TABLE IV

Directed Inter-Esterification

Oil	Directed procedure		Crystallization from petroleum ether 40°F.		Remarks
	Time	*Temp.*	*Yield*	*I.V.*	
Cottonseed	16 hrs. at	120°F.	0.8	....	Undirected
Cottonseed	70 hrs. at	70°F.	10.4	3.0	Other fraction I.V.—130(1)
Menhaden	20 hrs. at	80°F.			
	26 hrs. at	70°F.	21.9	4.6	Other fraction I.V.—210(1)
	96 hrs. at	60°F.	20°F.		
Soybean	....		8	....	Other fraction I.V.—150(1)
Triacetin plus methyl eleostearate		60-100°C. Catalyst NaOME	....	....	Me acetate removed by vacuum distillation(2)

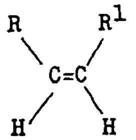
(1) Iodine value approximation.

predominantly located on the same glycerol molecule. The theory of even distribution applied to glyceride molecules would only give appreciable amounts of trisaturated glyceride as the amount of saturated acid increases above approximately 67%. The theory of random distribution which applies when a catalyst such as sodium methoxide is used or perhaps even in the natural fats would give a larger amount of saturated glyceride than the theory of even distribution but much lower than when the reaction of inter-esterification is directed by crystallization. The amount of triglyceride in a fat which has been randomly distributed is equal to the cube of the mole fraction of saturated fat acids.

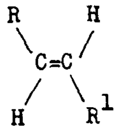
Isomerization

Types of Isomers of Fat Acids. The term isomers is generally applied to those compounds which have the same molecular formula but which differ in at least one of their physical or chemical properties. The term isomerization is applied to reactions which effect changes among isomers.

With the mono-unsaturated fatty acids the isomeric forms are limited to the cis-trans isomers of the different positional isomers with the omega-unsaturated fatty acid existing in only one form. The different forms of mono-unsaturated fatty acids can be represented as follows:



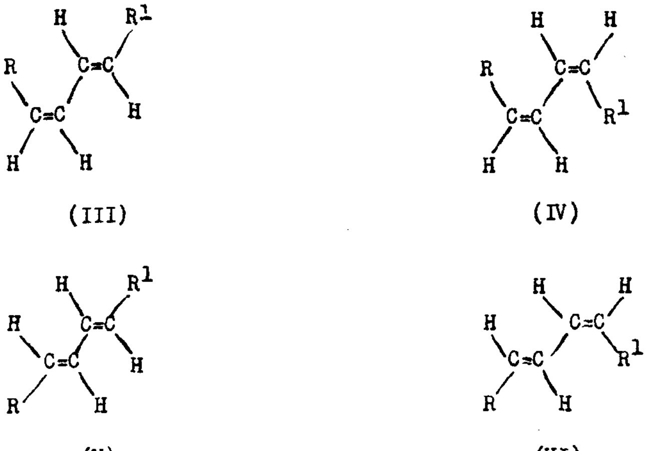
(I)



(II)

Formula I would be considered the cis isomer; II, the trans isomer. R equals H or alkyl radicals from methyl N to pentadecyl and R^1 equals any radical from carboxyl group to the hexadecanoate radical. Cycloparaffinic isomers also may exist.

The isomers of octadecadienoic and octadecatrienoic acids differ considerably in their complexity and number as compared with the isomers of octadecenoic acid. For example, most positional isomers of linoleic acid may exist in four different cis-trans forms as shown:



(III) (IV) (V) (VI)

Cis-trans isomers of octadecadienoic acid

III is a cis-trans; IV, a cis-cis; V, a trans-trans; VI, a trans-cis isomer. In addition to these four forms of octadecadienoic acid where R is not hydrogen, there are two cis-trans forms when R = H, and three or more different types of positional isomers depending on the position of the double bonds with respect to each other. These may be classified as conjugated or a 1,3-butadiene (VII), a 1,4-pentadiene (VIII), and isolated diene types such as 1,5-hexadiene (IX):

$R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}R^1$ (VII)
$R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}R^1$ (VIII)
$R{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}R^1$ (IX)

Position isomers of octadecadienoic acid

The allenic, acetylenic, and the cyclolefinic acids also, as well as isomers in which the unsaturated bonds are conjugated with the carboxylic group, should be included.

With the octadecatrienoic acids there are eight possible isomers for most of the positional isomers, plus a number of different types of positional isomers.

$R{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}R^1$ (X)
$R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}R^1$ (XI)
$R{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}R^1$ (XII)
$R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R$ (XIII)
$R{-}CH{=}CH{-}CH_2{-}$
$CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}R^1$ (XIV)

Position isomers of octadecatrienoic acid

These positional isomers may be classified as follows: a conjugated triene radical (X); a conjugated diene radical with an allylic (XI) or with an isolated double bond (XII); a 1,4,7-octatriene radical (XIII); and a 1,4-pentadiene radical with an isolated double bond (XIV). In addition, all double bonds can be isolated one from another. The main difference between one isolated double bond and one in the 2,3 position to a second double bond is the ease with which the hydrogen may shift to give conjugation. In a 1,4-pentadiene radical (VIII) and (XIV) the hydrogen on the active methylene merely needs to undergo a 1,3 shift whereas in a 1,5-hexadiene (IX) and (XIV) or with isolated double bonds a greater initial shift or a great number of 1,3 shifts would be required. If a 1,3 shift occurred first to give a trans isomer, additional energy would be required to effect a second shift since the trans form would be more stable. Allenic, acetylenic, and cyclic isomers also can exist.

Mechanism of Reaction

Numerous attempts have been made to determine the mechanisms by which isomerization occurs in organic compounds. According to Marvel's chapter on cis-trans isomerization in Gilman's "Organic Chemistry" (15), the following explanation is probably the best general mechanism for cis-trans isomerism: the double bond is polarized by the result of a collision with an activating catalyst such as selenium. The polarized carbon atom and its adjoining carbon are now free to rotate and the forces are such as to make the deficient carbon atom essentially planar. When the system then moves to relieve these forces set up as a result of the collision, then both cis and trans isomers are formed. Ultraviolet light acts differently from most isomerizing agents. It usually converts a trans isomer to a cis isomer. Since ultraviolet light imparts energy to the mixture, the cis form is more easily achieved than by chemical methods.

Shifting in polyunsaturated compounds to form isomeric compounds containing displaced unsaturation appears to depend on either the removal of an hydrogen atom or of a proton. Alkali is a strong catalyst for many rearrangements to conjugated systems, and it appears to act as a proton acceptor. This leaves a molecule with an excess of electrons and a 1,3 shift occurs to a more stable form.

$$\begin{aligned}
&\mathrm{R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R^1} + \mathrm{NaOH} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{-}CH{=}CH{-}R^1} + \mathrm{H^+\,[NaOH]} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH{-}R^1} + \mathrm{H^+\,[NaOH]} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}R} + \mathrm{NaOH}
\end{aligned}$$

Mechanism of alkali isomerization

This is one method of describing how the change occurs. The unsatisfied electrons are neutralized by the catalyst complex, and the proton is returned to the fatty acid molecule. By this mechanism one would expect substantially complete conversion to the conjugated isomer unless one of the unconjugated forms that might arise should be more stable than the conjugated forms or too stable to undergo isomerization with alkali.

With certain other materials a different mechanism appears probable since different percentages of conjugation are achieved and alkali-stable isomers lose conjugation on treatment with some of these catalysts. Examples are nickel-carbon and iodide catalysts. It appears likely that many more catalysts similar in type to these will be discovered since they probably isomerize by a free radical mechanism:

$$\begin{aligned}
&\mathrm{R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R^1} + \mathrm{Ni} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{-}CH{=}CH{-}R^1} + \mathrm{NiH} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH{-}R^1} + \mathrm{NiH} \longrightarrow \\
&\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH_2{-}R} + \mathrm{Ni}
\end{aligned}$$

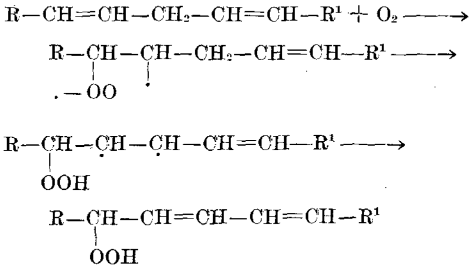
Mechanism of nickel isomerization

Nickel-carbon is a strong hydrogen acceptor, and it produces approximately the percentage of conjugation which would be expected from a free radical mechanism—for example, 66% from methyl linoleate (16). This same approximate percentage is achieved when alkali-conjugated isomers are the starting material and are treated with a nickel-carbon catalyst. Table V shows the amounts of conjugation achieved with nickel-carbon catalyst and with alkali on dehydrated castor-fatty-acid radicals. This is believed to indicate that some equilibrium does exist in the reaction, but the exact nature of it is unknown. Quite possibly, the reaction is complex, having a number of different courses and with different end products resulting when a different catalyst is used.

TABLE V
Effects of Nickel-Carbon Catalyst on Dehydrated Castor Oil-Methyl Ester

Catalyst	Conjugation, %
None	30.7
Nickel-carbon	43.8
Alkali	55.8
Alkali plus nickel-carbon	41.6

The autoxidation of drying oils also results in isomerization reactions. The mechanism of autoxidation is not fully established. It may be similar to the free radical mechanism already discussed for nickel, or it may be a direct addition of oxygen to the double bond with subsequent rearrangement. With a 1,4-pentadiene structure like linoleic acid, the reaction could be pictured as follows:



$$\begin{aligned}
&\mathrm{R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}R^1} + \mathrm{O_2} \longrightarrow \\
&\mathrm{R{-}}\underset{\cdot-\mathrm{OO}}{\mathrm{CH}}\mathrm{{-}}\underset{\cdot}{\mathrm{CH}}\mathrm{{-}CH_2{-}CH{=}CH{-}R^1} \longrightarrow \\
&\mathrm{R{-}}\underset{\mathrm{OOH}}{\mathrm{CH}}\mathrm{{-}}\underset{\cdot}{\mathrm{CH}}\mathrm{{-}}\underset{\cdot}{\mathrm{CH}}\mathrm{{-}CH{=}CH{-}R^1} \longrightarrow \\
&\mathrm{R{-}}\underset{\mathrm{OOH}}{\mathrm{CH}}\mathrm{{-}CH{=}CH{-}CH{=}CH{-}R^1}
\end{aligned}$$

Effects of Isomerization on Properties of Drying Oils

It is well known that trans isomers are higher melting and more stable than cis isomers. Consequently oils which contain substantial amounts of trans forms of octadecenoic acids might be expected to dry more slowly than other oils. This is true with the whole oil

TABLE VI
Absorption of Oxygen by Oleic and Iso-Oleic Acids

Time	Oleic	Elaidic	Oleic		Elaidic	Iso-oleic
			I[a]	II[b]	III[a]	IV[b]
Min.						
10				3[d]		0.8[d]
30	2[c]	3[c]	61[c]	7.5	7[c]	2.8
50				11.3		4.0
60				13.3		4.9
120	2	5	250		10	
240	14	13	423		21	
300	19	18	475		25	

[a] Catalyst, Hemin.
[b] Catalyst 0.1% cobalt naphthenate.
[c] Ml. of O_2 at 37°C.
[d] Millimoles of oxygen at 37°C.

when only cis-trans isomerization has occurred. The trans forms however appear to be less affected by the addition of oxidation catalysts than do the cis forms. Table VI shows the results obtained when hemin and cobalt naphthenate are used as oxidation catalysts (17, 18). The slow oxidation of these trans forms may account for after-tack in films from isomerized oils.

Further support for the possible adverse effect of cis-trans isomerization is found in the oxidation rates of the conjugated trienoic acids (19). Table VII shows how the oxygen absorption of three different conjugated octadecatrienoic acids varies with respect to differences in position and cis-trans isomerization.

TABLE VII

Oxidation of Octadecatrienoic Acids

Acid	Mole O_2/mole acid/100 min.
α-Eleostearic acid	2.68
β-Eleostearic acid	1.02
Pseudoeleostearic acid	0.63
Methyl pseudoeleostearate	0.41
Linolenic acid	0.52
Ethyl linolenate	0.24

α-Eleostearic acid, according to Morrell and Davis (20), is probably a trans-cis-cis and β-eleostearic acid is a cis-cis-trans. Morrell makes these selections on the basis of reactions with maleic anhydride to give crystalline adducts. This selection assumes that cis forms do not react so readily with maleic anhydride to form the normal adduct. The assumption has been confirmed in other dienes such as piperylene or 1,3-pentadiene. Steric hindrance may be responsible for the failure of certain cis forms of this conjugated diene to form maleic anhydride adducts, and the steric effects in the fatty acid isomers certainly would be more powerful. Using the same reasoning as Morrell, Kass and Burr assigned a trans-trans-trans, or a trans-cis-trans configuration to pseudo-eleostearic acid since it gave a mixture of α- and β-type of maleic anhydride adducts (21). Note that it is the slowest to react with oxygen of the three conjugated dienes.

Since drying is established as an oxidative, polymerization phenomenon, it appears sound to assume that although conjugated isomers do oxidize and dry faster than the unconjugated, trans isomers oxidize and dry much slower than the corresponding cis forms both in the conjugated and nonconjugated isomers. The information on conjugated isomers led Spitzer, Ruthruff, and Walton (22) to suggest the explanation that certain anomalies in the drying of alkali-isomerized linseed oils might be due to position and cis-trans isomerization of conjugated acids. Further support for Spitzer's contention is found in the behavior of cis- and trans-piperylene toward oxygen and maleic anhydride (23). The cis form polymerizes and copolymerizes readily as compared with the trans form which polymerizes slowly or forms adducts. However it appears more reasonable to assume that trans forms of octadecenoic acid, nonconjugated octadecadienoic acid, and possibly cyclic isomers of octadecatrienoic acid are responsible for the unusual after-tack in certain isomerized oils.

The adverse effect of conjugation processes has questioned to some extent the feasibility of having trans forms of conjugated structures in drying oils. A review of the comparative properties of films from linseed oil and tri-10,12-linolein is sufficient to demonstrate that even trans-isomers of conjugated acids are not responsible for adverse effects in films of conjugated oils (24). The films are compared in Table VIII.

TABLE VIII

Comparative Evaluation of Film From Conjugated Glyceride (24)

Characteristics	Linseed oil	Tri-10,12-linolein
Viscosity	A	J
Color	6	5
Conjugation	None	100% (some lost in preparation)
Drying tests		
Set-to-touch	9.5 hours	3.75 hours
After 9 days	Moderate tack	Tack-free
Cold-water immersion (24 hours)	Very white Dull 18 hours after *removal*	Slightlycloudy Recovered in 2 minutes
Hot-water immersion (60 min.)	White and soft White after 24 hours	Very slightly cloudy Immediate recovery
Alkali immersion tests 5% NaOH	Completely dissolved 1.5 hours	Intact after 1.5 hours
Accelerated weathering		
1 coat	Disintegrated at 510 hours	661 hours
3 coats	Disintegrated at 400 hours	2550 hours

The film of 10,12-trilinoleate dried set-to-touch rapidly and was tack-free at 9 days. It had excellent water and alkali resistance and excellent durability in accelerated weathering tests. Although this sample was too small to prepare a varnish, the evidence favored the belief that conjugation itself was beneficial and that objectionable features of conjugation processes might be due to side reactions.

The rapid rates of polymerization which have been reported for the different conjugated oils are to be expected from their composition. For example, an alkali-isomerized linseed oil having a viscosity of 135 poises (Gardner Z-6) is reported to have a gelation time at 600°F. of 12 minutes whereas that for tung oil is 6 minutes and that for linseed oil of Z-6 viscosity is 113 minutes. Table IX shows the relative bodying rates of nickel-carbon isomerized oils as compared with dehydrated castor oil and alkali-refined linseed and soybean oils (25). Finally, conjugated oils will copolymerize much more readily than nonconjugated oils with styrene and other vinyl compounds.

TABLE IX

Relative Bodying Rates (25)

Oil	Relative times required *to body oil*		
	2-15 poises at		2-46.4 poises at
	590°F.	560°F.	590°F.
Isomerized linseed	0.21	0.37	0.22
Dehydrated castor	0.39	0.35	0.27
Isomerized soybean	0.93	0.72	1.01
Alkali-refined linseed	1.00	1.00	1.00
Alkali-refined soybean	2.23	....	2.43

Method of Analysis for Isomerization

Measurement of cis-trans isomers can be effected by obtaining the relative proportion of saturated and solid acids by crystallization and oxidation techniques. The difference would be a good measure of trans form present in an oil. All cis forms are relatively low-melting and all trans forms are relatively high-melting. The preferred method for determining the presence and amount of trans isomers is infra-red spectrophotometric analysis. There are many methods for measuring conjugation in drying oils, but the best is the use of ultraviolet spectrophotometric analysis. Space does not permit a description of these two methods, but newcomers to these procedures may obtain information sufficient for most purposes by reference to recent papers.

Methods of Conjugation

Alkali Isomerization of Drying Oils. The most studied of all known methods of conjugation (excluding oxidation) is alkali-isomerization at elevated temperatures. As early as 1840, Varrentrapp (26) treated oleic acid with fused potassium hydroxide and obtained palmitic and acetic acids and hydrogen. Consequently it was believed for many years that oleic acid was a substituted acrylic acid. Apparently the fused alkali isomerized the unsaturated bond until it became conjugated with the carboxyl group and then cleavage occurred.

In 1931, Morton, Heilbron, and Thompson (27) reported on the unusually high absorptions obtained when certain vitamin A-containing oils were saponified and the absorption of the total acid fraction obtained after ether extraction. Unfortunately, these absorptions were believed to result from acid decomposition products formed from materials associated with vitamin A. No study of the effect of time or temperature on the saponification was made. Two years later Dann and Moore (28) reported their studies on the effect of varying the duration of alcoholic potassium hydroxide saponification. They clearly demonstrated that the increased absorption resulting from the prolonged alkali treatment was achieved by some change in the polyunsaturated acids and that the most probable explanation was isomerization. Moore (29) later demonstrated that the linolenic acid was converted to an isomeric material which had an absorption curve similar to eleostearic acid but not identical; Kass and Burr (21) demonstrated that this solid conjugated acid melting at 77° C. was 10,12,14-octadecatrienoic acid.

It is difficult to make comparisons among different methods of alkali isomerization because of the lack of uniformity in the analysis of oils and in the raw materials treated. Bradley (30) demonstrated that aqueous sodium or potassium hydroxide under pressure could be used. However aqueous alkali isomerization is somewhat slower than isomerization when organic solvents are used; alcohols and glycols appear to be well suited as media for alkali isomerization. The ethers of the glycols appear to be somewhat superior; in particular, glycol monomethyl ether appears to be superior to ethylene glycol. In addition, the conjugation can be effected with alkali in substantially anhydrous conditions in short periods at 285° to 300°C.

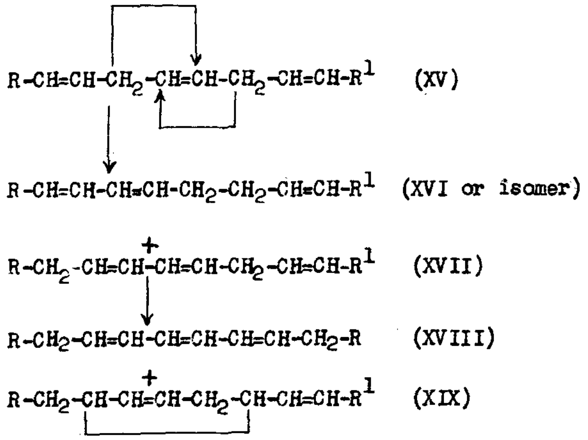
The behavior of the two most important acids in nonconjugated oils, linoleic acid and linolenic acid, toward alkali is considerably different. Whereas linseed oil contains substantially more linolenic acid than does soybean oil, the proportion of conjugated triene formed is not proportionate to this difference.

TABLE X

Composition of Soybean and Linseed Oils Before and After Isomerization Compared With Tung Oil (24)

Acids	Composition, %				
	Soybean		Linseed		
	Before	After	Before	After	Tung
Saturated acids	15	....	11	....	2-7
Oleic acids	30	....	22	....	1-20
Dienoic					
Nonconjugated	50	10	16	3	1-10
Conjugated	....	40	....	13	....
Trienoic					
Nonconjugated	2-5	....	52	13	....
Conjugated diene	....	4	....	27	....
Conjugated triene	....	2	....	13	74-95

If alkali isomerization to conjugation were complete, isomerized linseed oil would approach tung oil in the percentage of conjugated acids present but fall far short of the tung oil in the amount of conjugated triene present. Table X shows that tung oil contains approximately 25 to 45% more triene than linseed oil. However, since only 25% of the nonconjugated triene is converted to conjugated triene, alkali isomerized linseed oil contains only approximately 13% of conjugated triene. However alkali-isomerized linseed oil does contain some 40% conjugated diene which results both from linoleic and linolenic acid. The cause for this apparent anomaly can be seen by an examination of what may occur in the alkali isomerization of linolenic acid. We obtain 25% trienoic, 50% dienoic, and 25% cyclic isomers (24).



Isomerization of an octadecatrienoic acid

These products can be explained by the series of reactions shown above. The hydrogens may move in the directions indicated from either active methylene group to give a 1,3 shift and a dienoic isomer which should be relatively stable. Formula XVI represents one of the two possible isomers. However if the hydrogens move in the opposite directions to those indicated, a relatively unstable dienoic isomer (XVII) is obtained. It can undergo isomerization to form a conjugated trienoic acid (XVIII) or a cyclic isomer (XIX). A cyclic isomer also may result from the conjugated trienoic acid.

The main chemical disadvantages of the alkali process appear to be the formation of cyclic isomers from the linolenic acid and the loss of the glyceride structure. Esterification to give glycerides or other polyalcohol esters results in polymerization which produces oils of high viscosity suitable for varnishes and enamels. The polymerization reduces versatility of the oils. After-tack in the films of varnishes is another reported disadvantage of such oils.

Sulfur Dioxide

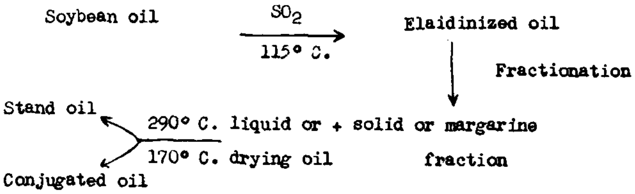
Sulfur dioxide has been proposed by Waterman and his coworkers as a catalyst for the commercial isomerization of fats to produce: higher melting fats and faster drying oils (31). Waterman describes this process as operating at three different temperatures:

For cis-trans isomerization, 115° to 130°C.

For conjugating 160° to 220°C.

For polymerization, 290° to 300°C.

He suggests that soybean oil might be treated as follows:



Isomerization with sulfur dioxide

With linseed oil at 160° to 220°C. at 80 atmospheres, the iodine value was reduced from 180 to 150 and the diene value increased to 25.5. This oil polymerized very rapidly. It is reported that one major interest in this reaction in Holland is the production of margarine, but detailed information is not available. The commercial scale polymerization of linseed oil with sulfur dioxide as a catalyst has been reported from Holland.

Use of Iodide Compounds

Another process for the isomerization of polyene compounds to give conjugated oils was recently patented by Ralston and Turinsky of Armour and Company (33). This process involves the heating of fatty acids or their esters with iodide compounds in which the iodine is loosely combined. Representative catalysts are ammonium iodide, dodecylamine hydroiodide, triethanolamine hydroiodide, turpentine-iodine addition product, iodoform, phosphorus iodide, aluminum iodide, etc. Although these compounds vary considerably in their isomerization activity, all appear to be active to some extent. This development probably stems from earlier observations that iodine is a catalyst for cis-trans isomerization of unsaturated fatty acids.

From a commercial standpoint the process appears to be the simplest to operate. If conjugation can be effected without the production of undesirable side reactions, the process may become commercially important. Table XI indicates the success of our attempt to repeat Ralston and Turinsky's work (24). The turpentine-iodine addition product appears to offer an excellent oil for industrial use since it contains over 30% conjugation: the oil can be readily removed from the catalyst, and the oil has good color.

TABLE XI

Isomerizations of Soybean Oil With Iodine Compounds (24)

Catalyst used	Increase in n_D 30°		Conjugation, %			Viscosity (Gardner)
	Reported	Found	Diene	Triene	Total	
CHI_3	0.0057	0.0039	16.2	2.00	18.3[a]	....
Turpentine-iodine addition product	0.0052	0.0067	31.0	0.12	31.12	E-F Color 5-6
AlI_3	0.0086	0.0080	28.0	4.99	33.33[a]	B-C
PI_3	0.0061	0.0079	26.9	4.63	31.79[a]	C

[a] Includes tetraene 0.10 to 0.34%.

The patents indicate that some after-tack was encountered but the cause was attributed to failure to remove catalyst.

Nickel-Carbon Isomerization. Nickel catalysts in various forms effect cis-trans isomerization as well as a shift of unsaturated bonds to conjugation (16). Table XII shows the amounts of conjugation which can be obtained with one of the most active of nickel catalysts. This catalyst appears to show steric hindrance effects. Table XIII shows how the change in molecular weight from methyl ester to polymeric glyceride affects the amount of conjugation produced. After-tack in the films of protective coatings from these oils was the major drawback to their use (25).

TABLE XII

Nickel-Carbon Isomerization of Drying Oils (16)

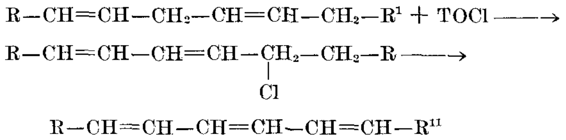
Material	Time	Temperature	Conjugation, %
	Hours	°C.	
Soybean oil	6	160	20.1
	6	170	32.1
	4	180	34.9
	4	190	35.7
Linseed oil	6	160	24.7
	6	170	28.0
	4	180	32.5
	4	190	33.3
Dehydrated castor oil	4	175-185	38.8

TABLE XIII

Effect of Nickel-Carbon Catalyst on Linseed Fatty Acid Derivatives (16)

Derivative	Conjugation,%
Methyl ester	46
Glyceryl ester	33
Pentaerythrityl ester	10
Polymeric glyceride (X-viscosity)	0.9

Tertiary Butyl Hypochlorite. A new procedure for isomerization of fat acids in drying oils which is probably related to some extent to the iodide and the oxygen isomerization. When tertiary butyl hypochlorite (TOCl) is reacted with soybean oil, chlorine is introduced with a shift of double bonds to conjugation. Subsequent removal of chlorine gives additional unsaturation conjugated to this intermediate form of conjugation. The following equations depict how this reaction probably occurs:



$$\mathrm{R{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}R^1 + TOCl} \longrightarrow$$

$$\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}}\underset{\overset{|}{\mathrm{Cl}}}{\mathrm{CH_2}}\mathrm{{-}CH_2{-}R} \longrightarrow$$

$$\mathrm{R{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}R^{11}}$$

How tertiary butyl hypochlorite affects soybean oil and what changes occur in conjugation before and after removal of chlorine by heating (34) are shown in Table XIV.

Dehydrated Castor Oil

The industrial value of dehydrated castor oil in varnishes and other protective coatings is well established. Discussion here will be limited primarily to the isomeric fatty acids present in the oil and their relation to the problem of finding a tung oil replacement (24). Castor oil contains a high proportion of ricinoleic acid, approaching the amount of eleostearic

TABLE XIV

Properties of Chlorinated Soybean Oil, Before and After Dehydrochlorination (34)

Treatment	Cl, %	Conjugation,%				Color (Gardner)	Viscosity (Gardner)
		Diene	Triene	Tetraene	Total		
Original	10.97	16.6	2.5	0.3	19.4	10-11	H
Heated 5.75 hr., 150°-160°C	5.33	11.0	15.7	4.4	31.1	13-14	J-K
Heated 8 hr., 175°-185°C	5.04	12.8	15.9	2.9	31.6	13-14	T-U
Heated 7.75 hr., 180°-220°C	4.10	13.2	6.9	0.6	20.7	14-15	Z_2
Heated 2 hr., 180°-220°C	2.72	11.3	2.8	0.2	14.3	16-17	Z_6

acid present in tung oil. However commercial methods of converting ricinoleic acid to an octadecadienoic acid have so far failed to convert a high percentage of the latter to the conjugated form; indeed, only 17 to 26% of the conjugated acid is formed (35). Reports of laboratory work indicate that at least a 50% yield can be obtained. In commercial practice some alcoholysis occurs and results in forming esters of ricinoleic acid (36). In the commercial oils this percentage of conjugated dienoic acid appears to be a mixture of cis-cis and cis-trans-9,11-octadecadienoic acid. The nonconjugated isomers likewise are a mixture of the natural linoleic acid and a cis-trans isomer in which isomerization has occurred in 12,13 position. As discussed under the relation of isomerization to the drying phenomenon, this isomer should oxidize more slowly than the natural linoleic acid, and it may be responsible for the slight after-tack which occurs in films of dehydrated castor oil paints and varnishes.

Comparison of the composition of dehydrated castor oil with that of tung oil, as shown in Table XV, clearly demonstrates that dehydrated castor oil is not a chemical replacement for tung oil. It is rather an oil which is intermediate in reactivity between tung oil and nonconjugated oils.

TABLE XV

Comparative Composition of Tung and Dehydrated Castor Oil (24)

	Dehydrated castor, %	Tung,%
Fatty acid, % of		
Solid	3	2-7
Oleic	14	1-20
Conjugated diene	27	....
Nonconjugated diene	43	1-10
Conjugated triene	....	74-94

Summary

Inter-esterification and isomerization reactions offer opportunities to modify drying oils by changing the arrangement of the acids in the fats and oils and by changing the arrangement of double bonds and the groups around the double bonds in the fat acid chains. Although much work has been completed, much more remains to be done.

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