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Cis, Trans Isomerization of Conjugated Linoleates by Iodine and Light[1]

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Cis, trans conjugated aliphatic dienes are converted to the more stable *trans, trans* structure by the action of iodine plus heat or light whether they are the simplest aliphatic dienes (1) or the conjugated linoleate isomers (2).

This conversion was used by Von Mikusch (3) to obtain complete reaction with maleic anhydride ("pandienzahl") of the less reactive *cis, trans* conjugated linoleates by converting them to the reactive *trans, trans* forms. In this case the removal of the active *trans, trans* isomer by reaction with maleic anhydride would favor complete conversion of the *cis, trans* isomers if equilibrium existed.

It is reasonable to expect that an equilibrium will be obtained among the various *cis, trans* isomers with suitable catalysts. No data as to the position of this equilibrium for the linoleate isomers have been reported although it has been shown by infrared spectra that *cis, trans* conjugated isomers are formed from *trans, trans* conjugated isomers and *vice versa* by heating (4).

The present paper presents a study of the equilibration of three isomeric conjugated linoleates, a *cis*-10, *cis*-12; a *cis*-10, *trans*-12; and a *trans*-10, *trans*-12 isomer. The equilibrium is at approximately 32% *cis, trans* and 68% *trans, trans* isomer. *Cis, cis* isomer must be present in small amounts, probably not more than 5–10%, possibly less.

Materials and Equipment

Methyl *trans*-10, *trans*-12 linoleate was that made from castor oil, as previously described (5). The *trans*-10, *cis*-12 linoleate was that prepared as previously described (5), according to Nichols *et al.* (2). Methyl *cis*-10, *cis*-12 linoleate was obtained by the courtesy of R. R. Allen (6). This new isomer, so elegantly synthesized by him, was to us perhaps the most interesting isomer studied. Conjugated dehydrated castor oil methyl esters were the same as previously described (5).

Infrared spectra were run on Beckman IR-3 recording spectrophotometer in CCl_4 from 2 μ to 7.8 μ and in CS_2 from 7.8 μ to 15 μ. Ultraviolet spectra were run on a Cary recording spectrophotometer in iso-octane and occasionally checked on a Beckman DU manual spectrophotometer.

Infrared Studies

The infrared characteristics of the *cis, trans* and *trans, trans* conjugated isomers have been previously described in part (5). In the 10–11 μ region a moderate band at 10.55 μ is characteristic of the *cis, trans* isomer. This isomer also has a strong band at 10.18. The *trans, trans* isomers have a single very strong band at 10.12 μ while the *cis, cis* isomer does not have any band and absorbs very little in this region from 10–11 μ (Figure 1).

Weak bands of some interest are those at 6.0–6.2 μ and at 3.3 μ. The *cis, cis* isomer has a sharp weak single band at 6.2 μ while the *cis, trans* and *trans, trans* isomers have two or three poorly defined bands in this region of C=C stretch. The 3.30 region shows a doublet for the *cis, cis* isomer, a singlet for the *cis, trans* compound, and only a very faint inflection for the *trans, trans* isomer. Nonconjugated *cis* double bonds in fatty esters show a single band which is in proportion to the number of double bonds, with the oleate about the same intensity as the *cis, trans* conjugated isomer. Nonconjugated *trans* double bonds show a doublet of low intensity. This band has been attributed to the CH stretch of methylenes adjacent to the double bond.

The bands in the 10–11 μ region appeared interesting for following the isomerization of the various isomers to equilibrium mixtures since absorption at 10.55 μ would be a direct measure of *cis, trans* isomers, with little correction for absorption from other isomers. *Trans, trans* isomers could be estimated from the absorption at 10.12 μ, correcting for the considerable absorption of the *cis, trans* isomer at this wavelength. *Cis, cis* isomers would be estimated by the difference.

The *cis*-10, *cis*-12 isomer was the first compound studied. A solution in CS_2 (0.300 g./100 cc.) containing .01 g. of iodine/100 cc. was prepared in the dark and scanned in the instrument (1-mm. cell), where it is in the entrance beam illuminated by chopped radiation of the Nernst glower. Since the first spectrum (at three minutes) showed some isomerization, the sample was left in the instrument and was scanned at intervals. The characteristic peaks of conjugated *cis, trans* diene appeared at 10.55 μ and 10.18 μ, followed by the decrease of the 10.55 μ peak to a lower equilibrium value with an increase in the 10.13 μ peak. This required two hours, and no further change occurred after another hour (Figure 2).

Similarly the *trans, trans* and the *cis, trans* isomers were equilibrated. The courses of these equilibrations are shown in Figure 3. The curve labeled 10.13 μ actually starts at 10.18 μ for the *cis, trans* isomer and at 10.12 μ for the *trans, trans* isomer, reaching the equilibrium value at 10.13 μ because of the overlap of the bands of the two components at equilibrium.

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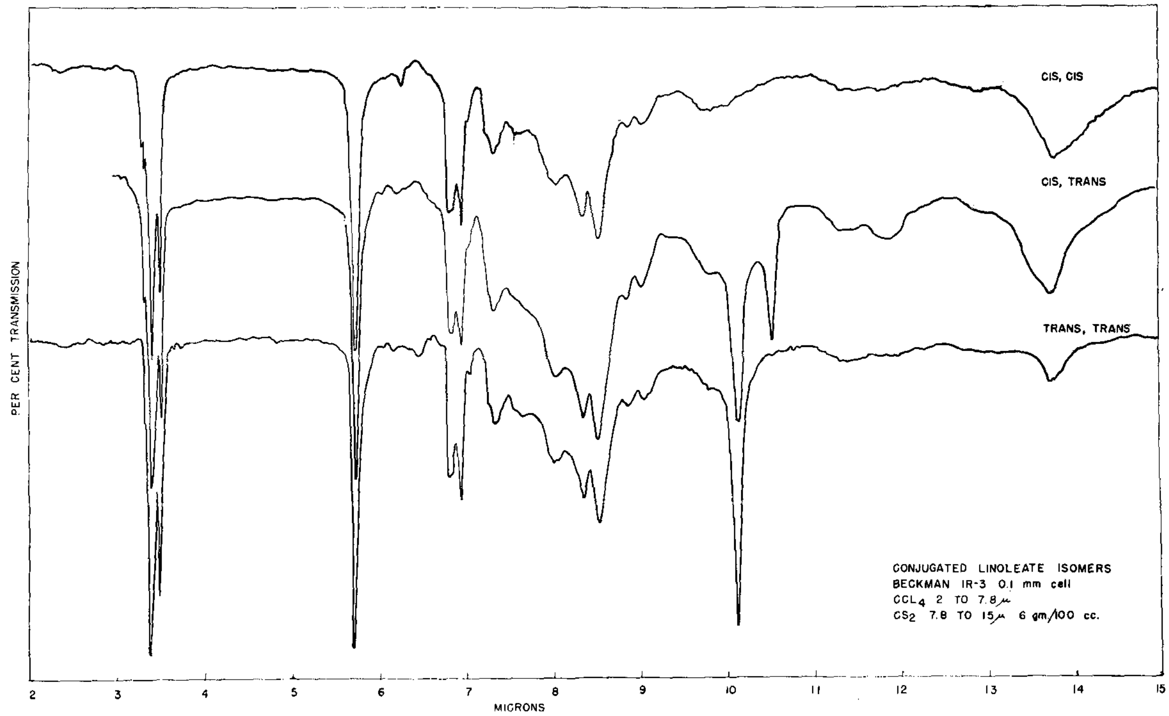

FIG. 1. Infrared absorption of conjugated linoleate isomers.

Table I shows the equilibrium value of k (1 cm., 1 g./1,000 cc.) for the various methyl esters. These values were all obtained by using the same 1-mm. cell within a few days' time. Since the cell thickness was not calibrated, but was assumed to be the thickness of the spacer used for construction, these actual k values are approximate, probably accurate to within 5 or 10%. This would not affect the calculations of total conjugation or of *cis, trans* isomers shown below. Transmissions were determined from a base line equal to transmission at 11 μ. Taking the highest equilibrium value, found for the *cis, trans* isomer as representing 100% conjugation, the total percentage conjugation was calculated for the other isomers by dividing $k_{10.13}$ after equilibraiton by 1.06, the value for the *cis, trans* isomer at 10.13 μ.

The *trans, trans* isomer showed 98% conjugation. Its k value at 232 mμ in ethanol (105.9) is 95% of that reported for pure 10-*trans,* 11-*trans* linoleate in ethanol (111.4 calculated to methyl ester) (7).

The *cis, cis* compound showed 91% conjugation. The hydrogenation-iodine value of 163 reported by Allen (6) corresponds to 89.5% diene and 10.5% monoene. (The method of synthesis presumably precludes nonconjugated diene.) The dehydrated castor conjugated ester fraction showed 82% conjugation. From k at 232 mμ (71.1), on the original material, the percentage conjugation is estimated as 76% (using k = 94 for pure *cis, trans* conjugated linoleate at 232 mμ). The crude alkali conjugated linoleate showed 93% conjugation whereas the k at 232 mμ on the original was 79.5, corresponding to 85% conju-

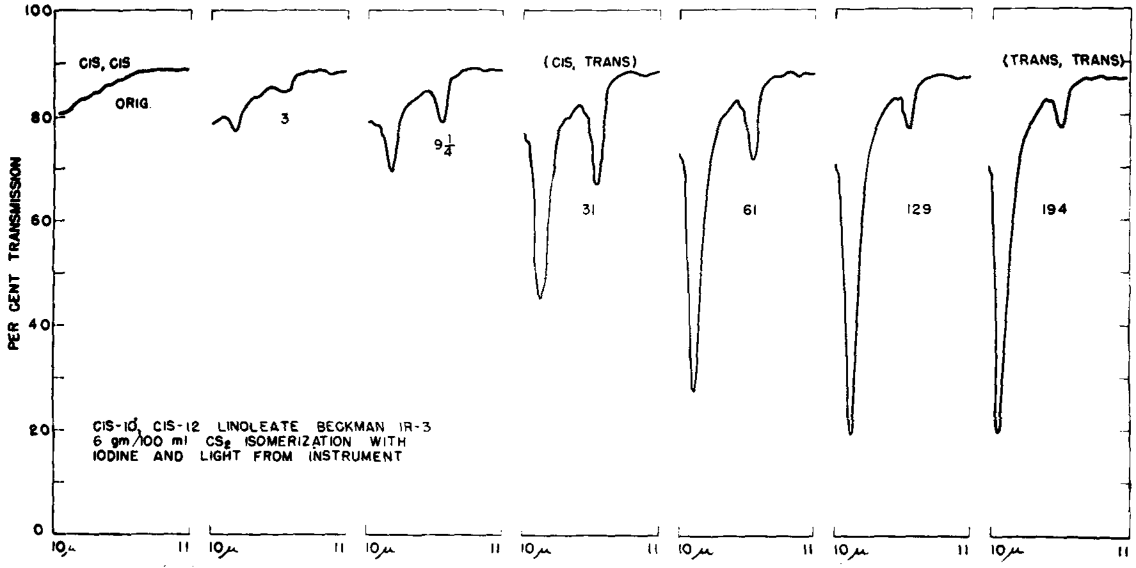

FIG. 2. Isomerization of *Cis*-10, *Cis*-12 linoleate. Infrared from 10 to 11 microns.
(Numbers below curves indicate minutes of exposure)

TABLE I

Infrared Studies of Equilibrated Conjugated Linoleates

Compound	k before equil.			k after equil.		Total conj.	Ct.	Ct. of total conj.
	10.12 μ	10.18 μ	10.55 μ	10.13 μ	10.55 μ			
						%	%	%
Cis, trans	[0.39]	0.495	0.295	1.06	0.091	100	31	31
Trans, trans	1.43[a]	[0.60]	......	1.04	0.088	98	30	31
Cis, cis	......	......	......	0.96	0.082	91	28	31
Dehyd. c.o.	......	......	......	0.85	0.077	80	26	32
Alk. conj.	......	......	......	0.99	0.096	93	33	35

[a] Corrected to 100% purity, k at 10.12 μ = 1.46, and k at 10.18 = 0.61, assuming 98% purity as estimated by equilibration. The bracketed values are at nonmaxima wavelengths.

gation (using k = 94 for pure *cis, trans* as above). These agreements are rather good.

The table also shows the calculated percentage of *cis, trans* isomer in the equilibrium mixtures and the percentage of total conjugation present as *cis, trans* isomers. This later value averages 32%, which means that about 16% of all conjugated double bonds are *cis* (assuming no *cis, cis* isomer is present at equilibrium). This is much lower than the 33% of *cis* double bonds in the oleic, elaidic equilibrium. The greater resonance stabilization of the *trans, trans* conjugated isomer may account for this effect. However allowance for 4% of *cis, cis* isomer (*cf.* below) would result in total of 24% of all double bonds as *cis*, and 8.5% of *cis, cis* isomer would give a total of 33% of all double bonds as *cis*.

Chipault (8) has obtained a higher value, 0.316, for $k_{10.57}$ of a *cis, trans* conjugated linoleate than our value (0.295), using the plateau near 11 microns as a base line. He also obtained a lower ratio of $k_{10.18}$ to $k_{10.57}$, which would indicate greater purity of his product. The ratio of $k_{10.18}$ to $k_{10.57}$ should be an indication of purity of *cis, trans* isomers if the *trans, trans* is the impurity. Available data do not permit quantitative estimates however. Using his value of 0.316 for $k_{10.57}$, our *cis, trans* isomer would be only 93% *cis, trans*, and the equilibrium value would be about 30% instead of 32% of *cis, trans* isomer.

The amount of *trans, trans* isomer in the equilibrated *cis, trans* mixture was estimated by correcting for the absorption of the 31% of *cis, trans* isomer at 10.12 μ. The percentage of *trans, trans* isomer was found to be 64. A similar calculation of the equilibrated *trans, trans* isomer gave about the same proportion of isomers. This indicates a possible 4% of *cis, cis* isomer present at equilibrium (by difference). The over-all accuracy of the method would probably preclude the presence of more than 10% of *cis, cis* isomer.

Ultraviolet Studies

Since the infrared studies showed that essentially the same equilibrium was obtained from the three geometrically isomeric types of conjugated linoleate, it was of interest to confirm this by ultraviolet studies. The three isomers have somewhat different ultraviolet curves (Figure 4). It is interesting to note that the *cis, cis* and the *trans, trans* isomers show definite shoulders on each side of the main peak while the *cis, trans* isomer does not show this structure. The broad bands and slight difference in position of the maximum absorption of the *cis, cis* at 235.5 mμ, of the *cis, trans* at 233.0 mm., and of the *trans, trans* isomer at 231.5 mμ obviously preclude optical resolution of mixtures by ultraviolet spectroscopy.

Equilibration should produce a mixture from each conjugated isomer (or any mixture) from which total diene conjugation could be calculated, knowing the k value after equilibration obtained from a pure diene standard.

Preliminary tests with alcohol as a solvent showed that a reaction with iodine was occurring on illumination. However isooctane was sufficiently stable with iodine on exposure to light. An amount of 0.005 g./100 ml. was a suitable concentration of iodine which did not absorb at 230 mμ and which rapidly catalyzed equilibration. Two minutes of exposure at 15 in. from a No. 2 Photoflood lamp caused complete equilibration, unchanged after additional exposures up to 10 min. or more. In fact, if the preparations were made in the ordinary fluorescent laboratory light, isomerization was almost complete by the time the solutions were made and put in the machine. Two to four minutes of exposure to the Photoflood lamp was generally used. At twice the concentration of iodine used, the solutions were somewhat less stable after reaching the same equilibrium values, and prolonged exposure to room light or to the Photoflood

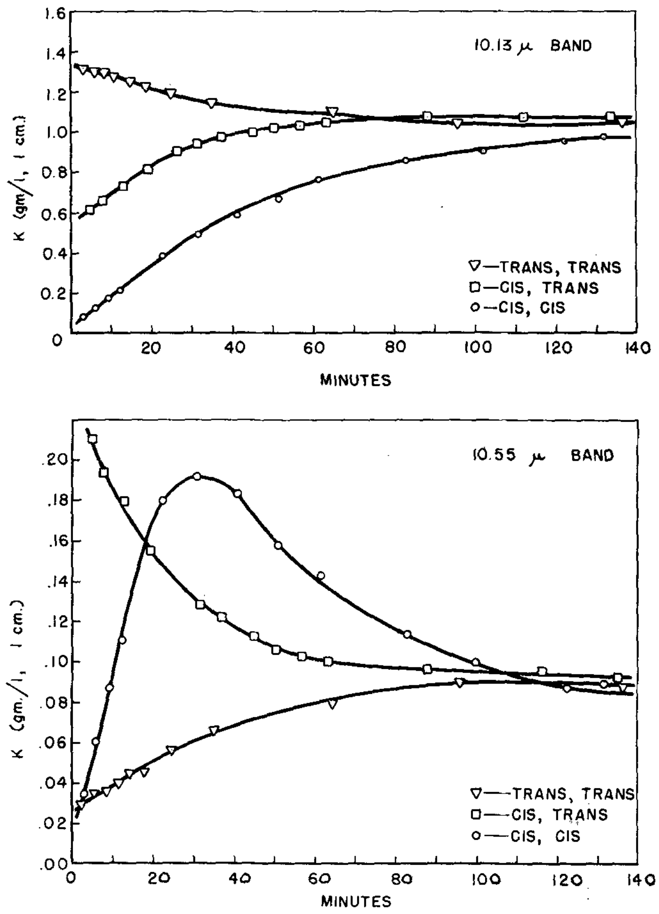

Fig. 3. Isomerization of conjugated linoleate isomers. Infrared bands at 10.13 and 10.55 microns.

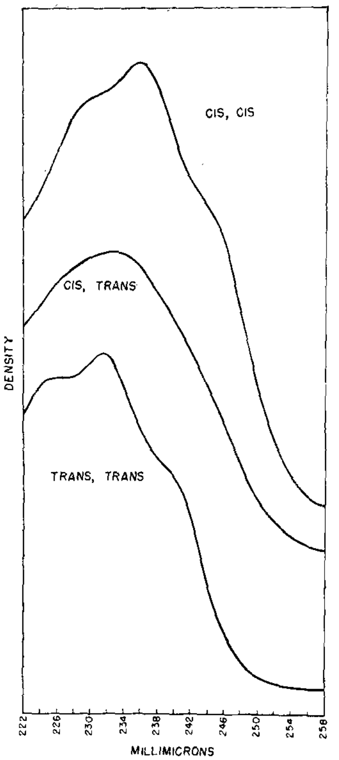

FIG. 4. Ultraviolet absorption curves of conjugated linoleate isomers.

produced decreased values for k. The results of equilibration are shown in Table II. Percentage conjugation was calculated on the basis of the *cis, trans* isomer as 100% conjugated by dividing the equilibrium values by 102.4.

The isomerization was done on the solutions used to measure absorption at concentrations suitable for accurate measurements by the instrument.

The agreement between the infrared and ultraviolet values are excellent for the *cis, cis* and *trans, trans* compounds. On the dehydrated castor oil ester fraction and the alkali conjugated linoleate, the infrared values are higher. In the former case, at least, this is probably attributable to the isolated *trans* structure, which has a peak at 10.3 μ and would contribute to the 10.13 μ band.

The equilibrated *cis, trans* isomer, assumed to be 100% conjugated, has a value of $k_{231.5} = 102.4$. The calculated value, by adding 64% of the corrected $k_{231.5}$ of the unisomerized *trans, trans* isomer plus 32% of $k_{231.5}$ of the unisomerized *cis, trans* isomer, plus 4% of $k_{231.5}$ of the unisomerized *cis, cis* isomer, is k = 102.8 (if the conjugated *trans, trans* isomer is assumed to be 95% pure) or k = 100.6 if the *trans, trans* isomer is assumed to be 98% pure.

TABLE II

Compound	mμ max.	k, before equil.		k, equil. 231.5 mμ	Conj.	
		Cary	D.U.		U.V.	I.R.
					%	%
Cis, trans	233.0	93.7	93.9	102.4	100	100
Trans, trans	231.5	103.1	103.6	97.3	95	98
Cis, cis	235.5	80.8	......	90.9	89	91
Deh. c.o.	232.0	67.7	......	74.0	72	82
Alk. conj.	233.0	79.5	......	88.6	87	93

Discussion

In the absence of much isolated *trans*, the iodine-equilibrated mixture should afford a convenient infrared spectrophotometric method for analyzing mixtures of conjugated diene isomers for total conjugation. Since it is reported that iodine does not cause conjugation of isolated double bands under similar conditions (2), it should be applicable to mixtures of conjugated diene isomers with *cis* nonconjugated dienes. It is spectrally somewhat analogous to the chemical "pandienzahl" of Von Mikush (3). Ultraviolet absorption on the equilibrated mixture would give total conjugation without interference by *trans* isomers. For determination of *cis, trans* and *trans, trans* conjugated isomers (in the absence of much isolated *trans*) infrared absorption is useful.

Summary

Infrared and ultraviolet studies have shown that the three geometrically isomeric types of conjugated linoleates (*cis, cis*; *cis, trans*; and *trans, trans*) are readily equilibrated by dilute iodine and light. Infrared shows that the equilibrium is at 32% *cis, trans* and 64% *trans, trans* isomer. Probably no more than 5–10%, if any, *cis, cis* isomer exists at equilibrium. The equilibrated mixture can be used to determine total conjugation in mixtures of conjugated geometric isomers by either infrared or ultraviolet absorption.

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Fractionation and Glyceride Composition of Fats[1, 2, 3]

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This paper deals with a new method of correlating fractionation data for natural fats, which provides further information on the glyceride composition of the fats. In particular it relates to the distribution of the unsaturated fatty acids among the glyceride types GS_2U, GSU_2, and GU_3.

The present work was begun when it was noted that a direct relation existed between the linolenic acid content and iodine value for fractions obtained from rapeseed oil. Such a regular relation must stem from some definite pattern for the separation of the glycerides on fractionation, and the form of the rela-

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[2] Presented at fall meeting, American Oil Chemists' Society, Cincinnati, O., September 30–October 2, 1957.

[3] Issued as N.R.C. No. 4779.