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Cis, Trans Isomerism of the Eleostearate Isomers[1]

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THERE are eight possible cis, trans isomers of the conjugated triene fatty acids which have their double bonds in the 9, 11, 13 positions. Four of the eight are known, but their geometric configurations have not been definitely established. Alpha and beta eleostearic acids are the best known isomers. Alpha eleostearic acid is the principal acid of tung oil or China Wood oil. This acid, m.p. 48°, is easily converted to β eleostearic acid, m.p. 71°, by the action of sulfur, light, iodine, strong acids, or heat. They both form adducts with maleic anhydride. Punicic acid, m.p. 44°, is obtained from pomegranate seed oil. It is also converted to β eleostearic acid by the same catalysts. It does not give a maleic anhydride derivative (1, 2).

Trichosanic acid, m.p. 35°, is a fourth isomer obtained from Japanese snake gourd oil (1). It also converts to β eleostearic acid with catalysts. Its reaction with maleic anhydride has not been reported.

Rossman (3) proposed a cis, cis, cis structure for α eleostearic acid and a trans, trans, trans structure for the β acid. He did not consider the other six possible cis, trans isomers. He ascribed the trans, trans, trans structure to the β acid because it was readily formed from the α acid whereas the reverse change could not be observed by him. The higher melting and boiling point of the β acid seemed more reasonable for the more linear all-trans form than the crooked all-cis form.

Morrell and Samuels (4) studied the structure of the maleic anhydride adducts of α and β eleostearic acids. They suggested that the α acid is "cis" and the β acid is "trans" without stating what bond or bonds they referred to. In a subsequent paper Morrell and Davis (5), with no new experimental evidence, suggest that the α acid is "trans, cis, cis" and that the β acid is "cis, cis, trans." A later paper by Morrell and Davis (6) refers to the "probable X-trans-trans-cis-Y-COOH" structure for the α acid and the "X-cis-cis-trans-Y-COOH" for the β acid. This was evidently a second reinterpretation of the data from the first paper. Recent work on the relation of cis, trans structures to reactivity with maleic anhydride leads to a more definite interpretation of their data, as will be discussed later.

Markley (7) in 1947 stated: "To date no attempt has been made to determine the geometric configuration of these two natural isomers of eleostearic acid (punicic and trichosanic acids) and since the geometric configuration of α and β eleostearic acids is not known with certainty, the exact identity of all four acids remains a problem for future solution."

Pseudoeleostearic acid, m.p. 77°, is a positional isomer of the eleostearic acids, with double bonds at positions 10, 12, and 14 (8, 9). It is made by alkali isomerization of normal linolenic acid. Kass and Burr (9) suggested that it was either trans, trans, trans or trans, cis, trans.

Alpha licanic acid, m.p. 75°C., occurs in oiticica oil and is similar to the eleostearic acids in being a conjugated C_{18} triene acid with double bonds at positions 9, 11, and 13. It differs in having a keto group on carbon 4. It is converted to β licanic acid, m.p. 99.5°C., by the usual catalysts. Both form maleic anhydride adducts, whose positional structures have been determined by Morrell and Davis (6). They assigned the cis-9, trans-11, trans-13 structure to α licanic and the trans-9, cis-11, cis-13 structure to β licanic acid on the same evidence as for α and β eleostearic acids.

It is the purpose of this paper to present evidence for reasonable geometric structures for α and β eleostearic acids, for α and β licanic acids, and for pseudoeleostearic acid and to discuss some of the methods for determining cis, trans structures of conjugated olefins.

Alpha and Beta Eleostearic Acids

From our data we have concluded that β eleostearic acid is the all-trans isomer, trans-9, trans-11, trans-13-octadecatrienoic acid and that α eleostearic acid is the cis-9, trans-11, trans-13 isomer. The evidence is as follows:

a) Since β eleostearic acid has the highest melting point of all known isomers, the all trans form is indicated. Atomic models show that this all-trans structure can assume the most linear configuration, like stearic acid, with least interference to compact crystalline structure.

b) Undoubtedly the all trans isomer is the most stable form since the other isomers, α eleostearic, punicic, and trichosanic acids, all convert readily and extensively to β eleostearic acid. Cis, trans conjugated dienes are similarly known to convert to the trans, trans isomers under like conditions. This has been observed with the conjugated linoleates by Nichols *et al.* (10) and by von Mikusch (11). It has also been observed by Alder and Vogt (12), with simple aliphatic dienes, such as hexadiene 2,4.

c) Beta eleostearic acid is more reactive than the α acids in the Diels-Alder addition reaction. It reacted with maleic anhydride more rapidly than the α acid; the β acid required 3¾ hours to discharge the yellow color of the intermediate complex while α eleostearic acid required 11 hours in boiling benzene. Its ester polymerized with heat twice as fast as the α ester (13). These facts indicate the all-trans structure of β eleostearate for the following reasons: von Mikusch (11) has recently shown that the cis, trans conjugated linoleates react very slowly if at all with maleic anhydride at temperatures of about 100° or lower whereas the trans, trans isomers react readily in the diene number determination under these conditions. Alder and Vogt (12) observed the same effect with the simple cis, trans and trans, trans conjugated hexadiene, 2,4 and other dienes. The trans, trans isomer reacted readily in boiling benzene

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whereas the cis, trans isomer did not react under these conditions (but did react when heated at 150° for 15 hours to produce an adduct different from that of the trans, trans isomer). A pair of conjugated acyclic double bonds must therefore be trans, trans in order to react with maleic anhydride at 100° or lower.

The reason for this is evident from atomic models of conjugated isomeric dienes, and from the fact that a planar, bent-back, "semi-ring" structure is necessary for easy attack by the maleic anhydride or other dieneophile (12).

Models of the trans, trans isomer show no steric interference to forming this structure. The cis, trans isomer shows some interference while the cis, cis isomer shows great interference and probably could not react at all as such.

Beta eleostearic acid, with all three trans double bonds, has two pairs of adjacent trans, trans conjugated dienes with one double bond in common. Atomic models show that it can form two planar "semi-ring" structures very easily with very little interference to approach of dieneophile to either of the two. The all-trans β acid should therefore be the most reactive diene in the Diels-Alder reaction. Experimental data confirm this expectation.

Alpha eleostearic acid must have two adjacent, conjugated trans double bonds since it reacts readily with maleic anhydride at temperatures of 100°C. or below but less rapidly than the β acid. Since the addition was across the 11 and 13 double bonds (4), they are both trans, and the 9 double bond is cis. This means that the structure of α eleostearic is cis-9, trans-11, trans-13 octadecatrienoic acid.

d) If the structures are as proposed, the isolated double bond outside of the cyclohexene ring should be trans in the maleic anhydride adduct of the β acid and cis in the adduct of the α acid. Infrared spectroscopy permits experimental testing of these expectations since isolated trans double bonds have a characteristic absorption peak at 970 cm.$^{-1}$.

The maleic anhydride adducts were prepared and the spectrum of the adduct of β eleostearic acid was found to have an absorption band at 970 cm.$^{-1}$ while that of α eleostearic adduct did not have it. The spectra of the two adducts were essentially identical otherwise (Fig. 1).

e) Infrared absorption curves on the α and β acids or their methyl esters were consistent with the proposed structures, namely that the β acid is all-trans and that the α acid contains a cis double bond. The β ester showed a single, very strong band at 993 cm.$^{-1}$ while the α ester showed a doublet, stronger at 991 cm.$^{-1}$ and weaker at 963 cm.$^{-1}$ (Fig. 2, curves B and A). Analogously trans, trans conjugated linoleates show a single strong band at 988 cm.$^{-1}$ while conjugated cis, trans linoleates show a doublet, stronger at 982 cm.$^{-1}$ and weaker at 948 cm.$^{-1}$ (14).

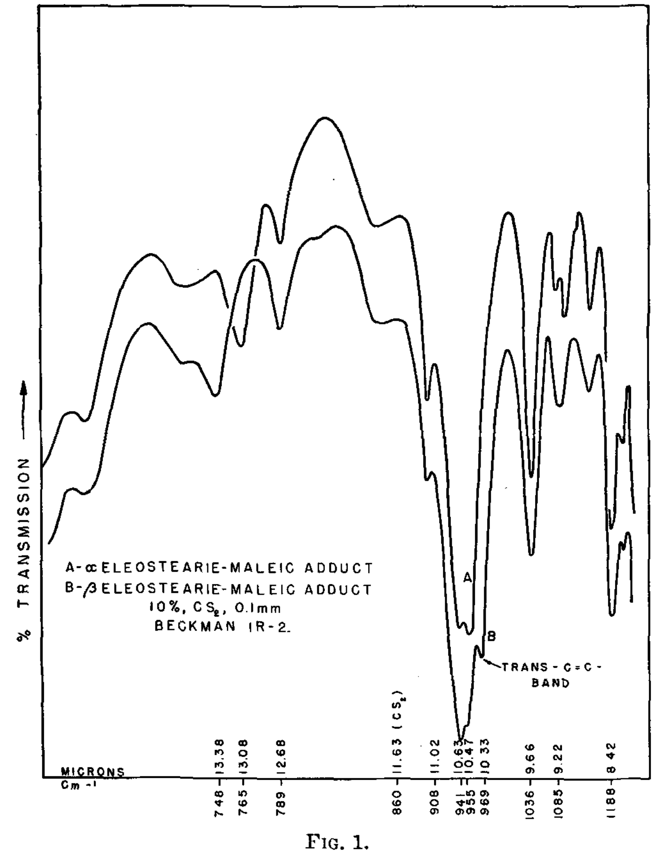

FIG. 1.

We believe that the behavior of α and β eleostearates toward maleic anhydride, the configuration of the exocyclic double bond as determined by infrared, and the infrared spectra establish the structures of these two isomers.[2]

Punicic Acid

Since punicic acid from pomegranate seed oil is reported not to form a maleic anhydride adduct (2), it must not have two adjacent trans double bonds according to the considerations discussed above. This leaves five of the eight cis, trans isomers as possible structures:

	C_9	C_{11}	C_{13}
1.	cis	cis	cis
2.	cis	cis	trans
3.	trans	cis	cis
4.	trans	cis	trans
5.	cis	trans	cis

A sample of pomegranate seed oil was made available to us by R. T. Holman of the Hormel Institute. The infrared curve showed a strong band at 992 cm.$^{-1}$ and a weaker one at 941 cm.$^{-1}$ (Fig. 2, curve P). This doublet with a stronger band at 992 indicates a cis, trans diene pair which would eliminate the all-cis structure (cis-9, cis-11, cis-13). However all-cis conjugated aliphatic dienes and trienes are unknown at the present, and it is evident that further work is necessary to establish the exact cis, trans configuration of punicic acid.

Alpha and Beta Licanic Acids

Morrell and Davis (6) showed that α and β licanic acids both formed maleic anhydride adducts readily, that the α adduct was by addition to the 11, 13 pair of double bonds, and that the β adduct was by addition to the 9, 11 pair, as in α and β eleostearic acids. This, and the fact that α licanic acid, m.p. 75°C., is easily converted by catalysts to the β form, m.p. 99.5° C., suggest that the β form is all-trans and that the α form is cis-9, trans-11, trans-13, as with the eleostearates. The confirmatory evidence as to relative reactivity in the Diels-Alder diene reaction and the cis or trans configuration of the exocyclic double bond in the maleic adducts is not available for the licanic acids. It appears reasonable that α licanic acid is 4-keto-cis-9, trans-11, trans-13 octadecatrienoic acid, and that β licanic acid is 4-keto-trans-9, trans-11, trans-13, octadecatrienoic acid.

Pseudoeleostearic Acid

Pseudoeleostearic acid is a conjugated 10,12,14-octadecatrienoic acid produced by alkali conjugation of normal linolenic acid, according to Kass and Burr (9).

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[2] In a conversation with W. G. Bickford, C. H. Mack, and R. T. O'Connor of the Southern Regional Research Laboratory on May 1, 1952, one of the authors (D. H. Wheeler) learned that identical observations and conclusions had been made by them. On the basis of these observations and other experiments (recognition of the existence of two geometric isomers of the β eleostearic acid maleic anhydride adduct through selective oxidation of their exocyclic trans double bonds) these investigators had arrived independently at views completely in accord with those herein presented.

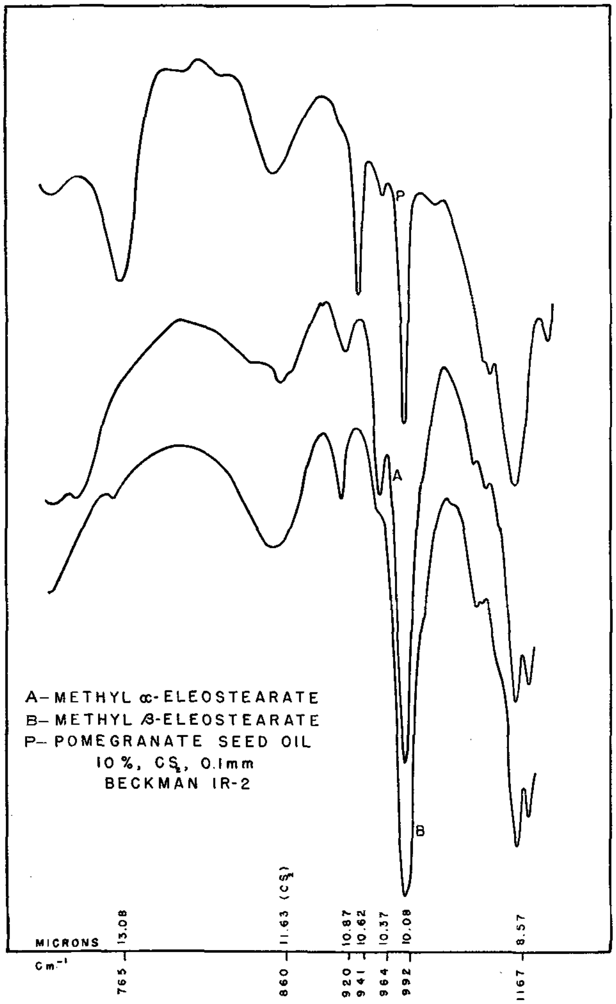

FIG. 2.

Nichols *et al.* (10) predicted that this isomer should be trans-10, cis-12, trans-14 from certain rules concerning double bond shift during alkali conjugation.

This acid was prepared and was found to have a single strong absorption peak at 993 cm.$^{-1}$. This indicates that it is all-trans like β eleostearate. It is quite possible that the trans-cis-trans isomer is first formed, as predicted by Nichols *et al.* (10), but that it is converted to the all-trans isomer under the influence of the heat and alkali used to produce it. We have found, for example, that α eleostearate converts to the β form during the thermal polymerization (and much more rapidly than does cis, trans linoleate convert to the trans, trans isomer). Since the all-trans form is the highest melting and least soluble form, any of it which was produced would be the form isolated by crystallization. Perhaps under less vigorous conditions of isomerization the intermediate trans-10, cis-12, trans-14 isomer could be isolated.

General Discussion

Infrared spectra are valuable in characterizing cis, trans isomers of conjugated double bond systems. Conjugated cis, trans and trans, trans linoleates have characteristic absorption bands by which they can be determined even in mixtures. The spectrum of β eleostearate is analogous to that of conjugated trans, trans linoleate and that of α eleostearate to conjugated cis, trans linoleate. From these spectra and those of their reaction products with maleic anhydride we have confirmed the analogy. The spectrum of punicic acid with a doublet at 941 and 992 cm.$^{-1}$ is also analogous to the doublet spectrum of the cis trans isomers. Until the spectrum of a known triene system has been observed to have bands identical with those of punicic acid, no assignment of structure to any of the double bonds can be made.

Ultraviolet absorption spectra are less specific than infrared in distinguishing conjugated isomers. X-ray diffraction spacings have been used to distinguish between conjugated cis, trans isomers (2, 10), but, as in infrared spectra, known standards are necessary for assignment of structure.

The work of Alder and Vogt (12) on simple conjugated dienes and of von Mikusch on linoleates (11) as to their cis, trans isomers points to the use of maleic anhydride as an aid in determining cis, trans structures of conjugated polyenes. The ability to form the semi-ring structure as indicated by atomic model spacings is definitely related to ease of reaction with maleic anhydride.

The rate and temperature of formation of the adduct, the structure of the exocyclic double bond or bonds as shown by infrared spectra, and the identification of cleavage products will clearly establish the structure and position of the double bonds in conjugated polyene acids.

Summary

The cis, trans isomers of the conjugated trienes present a difficult problem for complete determination of structure.

Several methods of attack have been outlined, and application of two of them have been made to α and β eleostearic acids, α and β licanic acids, and to pseudoeleostearic acid.

These results indicate the following structures:

α eleostearic:	cis-9, trans-11, trans-13
β eleostearic:	trans-9, trans-11, trans-13
pseudoeleostearic:	trans-10, trans-12, trans-14
α licanic:	4-keto, cis-9, trans-11, trans-13
β licanic:	4-keto, trans-9, trans-11, trans-13

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