

9. Lemon, H. W., *Can. J. Research*, **22F**, 191 (1944).
10. Lemon, H. W., *ibid.*, **25F**, 34 (1947).
11. Lemon, H. W., Lips, A., and White, H. W., *ibid.*, **23F**, 295 (1945).
12. Lips, H. J., Lemon, H. W., and Grant, G. A., *ibid.*, **25F**, 44 (1947).
13. Rebello, D., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **28**, 177 (1951).
14. Report of the Spectroscopy Committee, *ibid.*, **26**, 399 (1949).
15. Frankel, J. S., and Brown, J. B., *J. Am. Chem. Soc.*, **65**, 415 (1943).
16. Wheeler, D. H., *Oil and Soap*, **9**, 89 (1932).
17. Evans, C. D., Lancaster, E. B., Dutton, H. J., and Moser, H. A., *J. Am. Oil Chem. Soc.*, **28**, 118 (1951).
18. Wearn, R. B., Murray, W. M., Ramsey, M. P., and Chandler, N., *Anal. Chem.*, **20**, 922 (1948).
19. Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **27**, 367 (1950).
20. Galat, A., *J. Am. Chem. Soc.*, **68**, 376 (1946).
21. Nystrom, R. F., and Brown, W. F., *ibid.*, **69**, 1197 (1947).
22. Delaby, R., and Guillot-Allegre, S., *Bull. Soc. Chim.*, **53**, 301 (1933).
23. Roberts, J. D., and Green, C., *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).
24. Swift, C. E., O'Connor, R. T., Brown, L. E., and Dollear, F. F., *J. Am. Oil Chem. Soc.*, **71**, 1512 (1949).
25. Keeney, M., and Doan, F. J., *J. Dairy Sci.*, **34**, 713 (1951).
26. Rebello, D., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **28**, 183 (1951).
27. Golubic, C., Martin, C. J., and Daubert, B. F., *Oil and Soap*, **23**, 360 (1946).
28. Nye, W., and Spoeher, H. A., *Arch. Biochem.*, **2**, 23 (1943).
29. Farmer, E. H., *Trans. Faraday Soc.*, **42**, 228 (1946).
30. Swern, D., Scanlan, J. T., and Knight, H. B., *J. Am. Oil Chem. Soc.*, **25**, 193 (1948).
31. Sharp, D. B., Whitcomb, S. E., Patton, L. W., and Moorhead, A. D., *J. Am. Chem. Soc.*, **74**, 1802 (1952).

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## The Infrared Spectra and the Structural Relationships Between Alpha- and Beta-Eleostearic Acids and Their Maleic Anhydride Adducts

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RECENTLY Paschke, Tolberg, and Wheeler (15) have reviewed the subject of the cis, trans isomerism in the eleostearate isomers. They have pointed out that the previously proposed structures for the alpha- and beta-eleostearic acids have not been established definitely. These authors have adduced evidence from infrared spectra and chemical reactivities to show that alpha-eleostearic acid contains a cis, trans, trans conjugated triene system and that beta-eleostearic acid is the all trans isomer. Previously Morrell and co-workers (9, 11) as well as Chin (2), while investigating the maleic anhydride adducts of these two acids, reported that addition occurred across the 11 and 13 double bonds of alpha-eleostearic acid and across only the 9 and 11 double bonds of beta-eleostearic acid. Although their interpretation of these results led them to agreement regarding the cis, trans configuration of the alpha isomer, their views were divergent with regard to the beta isomer. If the beta-eleostearic acid is in fact an all trans isomer, as proposed by Paschke *et al.* (15), then two adducts would be predicted rather than only one. It is the purpose of this paper to present evidence for the existence of two maleic anhydride adducts of beta-eleostearic acid and to verify the structures of alpha- and beta-eleostearic acids through interpretation of data obtained by infrared spectroscopy as well as chemical means.

### Experimental

**Alpha- and beta-eleostearic acids.** These acids were prepared from fresh authentic samples of tung oil according to the methods described by O'Connor *et al.* (13). The spectral analysis (13) showed that the alpha-acid (m.p. 48.0°C.) had a purity of 98.6% and that the beta-acid (m.p. 71°C.) was 96.4% pure. These acids had hydrogen-iodine values (14) of 271.8 and 270.9, respectively.

**Maleinization.** Ten percent solutions of alpha- and beta-eleostearic acids in toluene were refluxed with

150% excess of maleic anhydride until the characteristic yellow color had disappeared. The reaction mixtures were then diluted with an equal volume of ethyl ether and washed with water until free of maleic anhydride. Following drying and the removal of the solvents under reduced pressure, the recovered adducts were crystallized from 90% methanol solution. The alpha-eleostearic acid-maleic anhydride adduct, m.p. 64°C., analyzed 70.26% C and 8.67% H, calculated 70.18% C and 8.57% H, and had a hydrogen-iodine value of 132.2, calculated hydrogen-iodine value, 134.1. The beta-eleostearic acid-maleic anhydride addition product, m.p. 77°C., analyzed 70.25% C and 8.59% H, and had a hydrogen-iodine value of 131.8.

**Hydrogenation of maleinated products.** Approximately 2.5% solutions of the recrystallized maleinated products in glacial acetic acid were hydrogenated at room temperature and atmospheric pressure using an excess of platinum oxide catalyst. After the absorption of the theoretical amount of hydrogen (2 moles/mole) these products were freed of catalyst and solvent in the usual manner and finally dried in vacuo over solid sodium hydroxide. The white hydrogenation products for the alpha- and beta-isomers melted at 74°C. and 58°C., respectively. Morrell and Davis report 74°C. and 63°C., respectively (9).

**Epoxidation of the maleinated products.** Preliminary experiments were conducted on the alpha- and beta-maleinated products to determine if there was a possibility of selective epoxidation of the cyclic or exocyclic double bonds. Then 3.7 grams of each of the recrystallized adducts were dissolved in 50 ml. of .4078 N perbenzoic acid-chloroform solution (approximate 10% excess based upon the epoxidation of two double bonds). After standing at 0°C. for 21 hours, titration of the excess perbenzoic acid indicated that 1.03 double bonds had been saturated. There was a white copious precipitate found in the reaction flask containing the beta-isomer, but there was no indication of an insoluble product formed in the reaction mixture containing the alpha-isomer. Infrared as well as chemical data presented elsewhere in this paper

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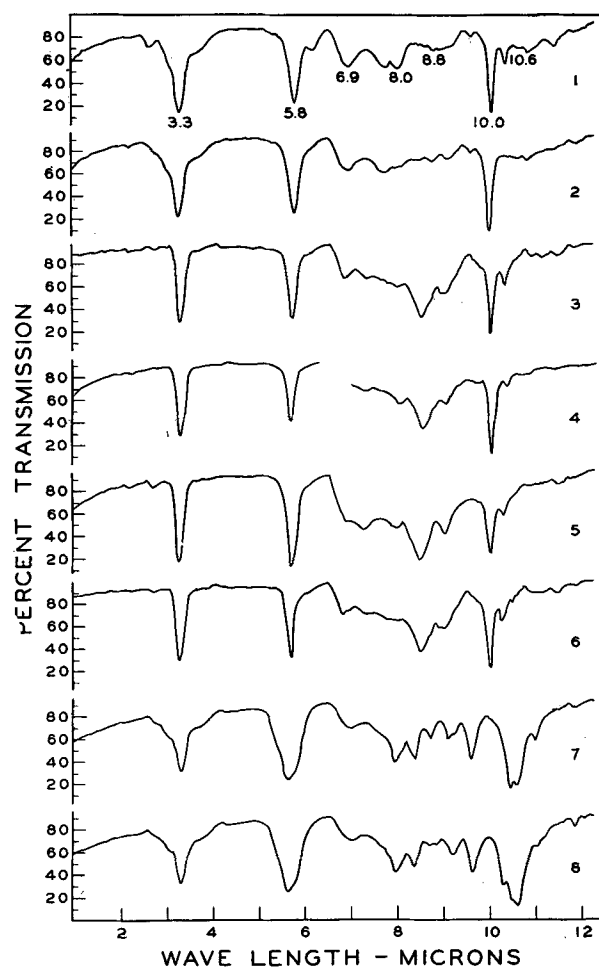
showed that the exocyclic double bond had been preferentially epoxidized.

*Selective epoxidation of the exocyclic double bond of the maleinated products.* Next 7.3 grams of each of the recrystallized adducts were dissolved in 50 ml. of .4078 N perbenzoic acid-chloroform solution and maintained at 0°C. for 41 hours. At the end of this time the reaction was 95% complete, and again it was noted that the reaction mixture containing the beta-isomer had formed a precipitate whereas none was evident in the alpha-isomer reaction mixture. The white precipitate formed in the reaction with the beta-isomer was recovered and crystallized several times from absolute methanol. A 10% yield of a compound melting at 144°C. was obtained. Subsequent recrystallization of this compound from various solvents did not result in any change in its melting point. (Calculated for  $C_{22}H_{32}O_6$ : C, 67.32%, and H, 8.22%; found, C, 67.34%, and H, 8.21%). The chloroform soluble material from the above reaction mixture was recovered from the solvent and separated from benzoic acid through crystallization from methanol. A 30% yield of this material was obtained melting at 118°C. Recrystallization of this product from chloroform did not increase its melting point. (Calculated for  $C_{22}H_{32}O_6$ : C, 67.32%, and H, 8.22%; found, C, 67.09%, and H, 8.21%). The chloroform was removed from the reaction mixture containing the epoxidized adduct of the alpha-acid. The resulting mixture containing benzoic acid was an oily viscous material, which did not crystallize from solvents such as methanol, petroleum ether, and acetone, irrespective of the temperature employed.

*Esterification of the maleinated products.* Recrystallized maleic anhydride (alpha and beta) adducts were esterified with *n*-butyl alcohol, using toluene as the solvent and *p*-toluene sulfonic acid as the catalyst. The water formed in the reaction was distilled azeotropically and continuously separated until the reaction was complete. The purified tri-*n*-butyl esters were semi-viscous and analyzed approximately 98% pure. Hydrogenation value: found, 1.95 moles hydrogen/mole of ester; calculated, 2.0 moles hydrogen/mole of ester.

*Epoxidation of the tri-butyl esters.* The tri-butyl esters of the maleinated products were epoxidized in a manner analogous to that described above. After four days the theoretical amount of oxygen had been absorbed. The chloroform solutions of the epoxides were freed from perbenzoic and excess benzoic acid by shaking for several hours with twice the theoretical amount of barium oxide in the presence of sodium sulfate. The epoxidized compounds were found to be viscous liquids. The hydrogen-iodine value for the isomer from the alpha-acid was 42.6 and for the isomer from the beta-acid, 47.3. The calculated is 43.8. These products were refluxed with a large excess of acetic acid during the course of 5 hours for the purpose of destroying the oxirane group with the attendant formation of the hydroxy-acetoxy derivative. Subsequent hydrogenation of these reaction products showed a 93% conversion of the epoxide to their respective hydroxy-acetoxy derivatives.

*Reference compounds.* Maleic anhydride of highest analytical purity was recrystallized from chloroform; melting point, 60°C. Dimethyl maleate was prepared from the maleic anhydride by esterification in the usual way; hydrogen-iodine value, 176.1 (calculated,



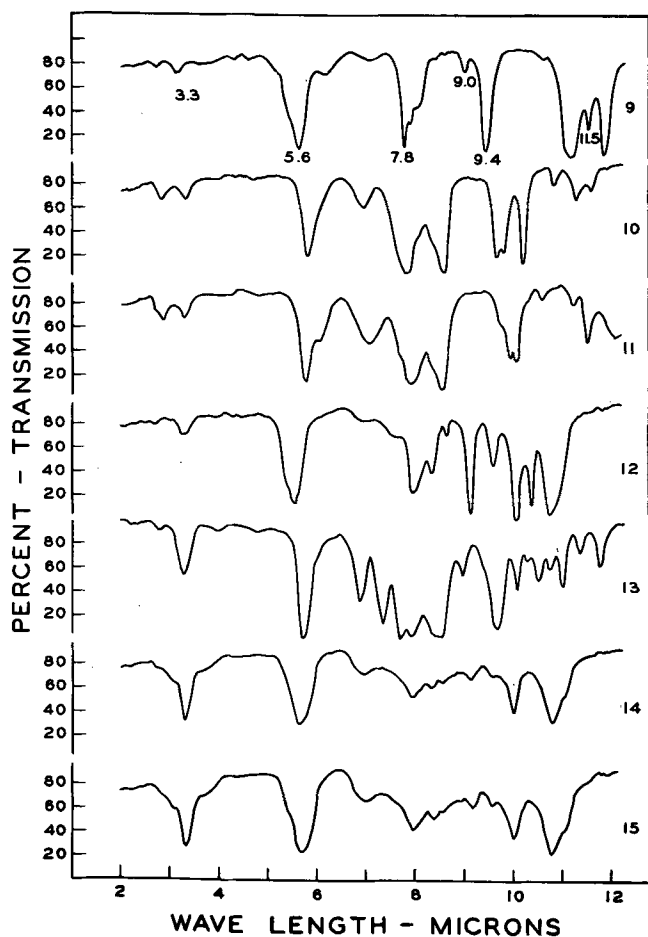
LEGEND FIG. 1

1. Alpha-oleostearic acid
2. Beta-oleostearic acid
3. Alpha-tung oil
4. Beta-tung oil
5. Oiticica oil
6. Chinese wood oil
7. Maleic anhydride—alpha-oleostearic acid adduct
8. Maleic anhydride—beta-oleostearic acid adducts  
(in chloroform except beta-tung oil in carbon disulfide)

176.1). Dimethyl fumarate was prepared from an authentic sample of fumaric acid in the usual way; melting point, 102°C., and hydrogen-iodine value, 176.6 (calculated, 176.1). The maleic anhydride adduct of butadiene was prepared in benzene solution by the method described by Flett and Gardner (4). The recrystallized product melted at 102°C. The dimethyl ester of the maleic anhydride-butadiene adduct was prepared by esterifying the above adduct with methanol; hydrogen-iodine value, 127.2 (calculated, 128.0).

*Infrared spectra.* All spectra were obtained with a model IR-2T Beckman automatic recording infrared spectrophotometer.<sup>2</sup> The instrument was housed in a room maintained at about 23.3°C. and 20% relative humidity, and its temperature was maintained constant at 25°C.  $\pm$  0.1° by water circulated from a constant temperature bath. The concentrations of the chloroform solutions were all very close to 40 g. per liter and all were measured in an 0.4 mm. rock salt cell against the pure solvent in the same cell.

<sup>2</sup>Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.



LEGEND FIG. 2

9. Maleic anhydride
10. Dimethyl fumarate
11. Dimethyl maleate
12. Maleic anhydride—butadiene adduct
13. Dimethyl ester of maleic anhydride—butadiene adduct
14. Hydrogenated maleic anhydride—alpha-eleostearic acid adduct
15. Hydrogenated maleic anhydride—beta-eleostearic acid adduct (in chloroform)

### Results and Discussion

The presence of a trans-trans conjugated pair of double bonds in the structures of both alpha- and beta-eleostearic acids can be established by consideration of maleic anhydride addition reactions and by considerations of the infrared spectra of the acids themselves. The cis, trans configuration of the third double bond can be established by interpretation and comparison of the infrared spectra of maleic anhydride addition products, their esters and their epoxy derivatives, whereby interfering absorptions are eliminated, with related "model" compounds.

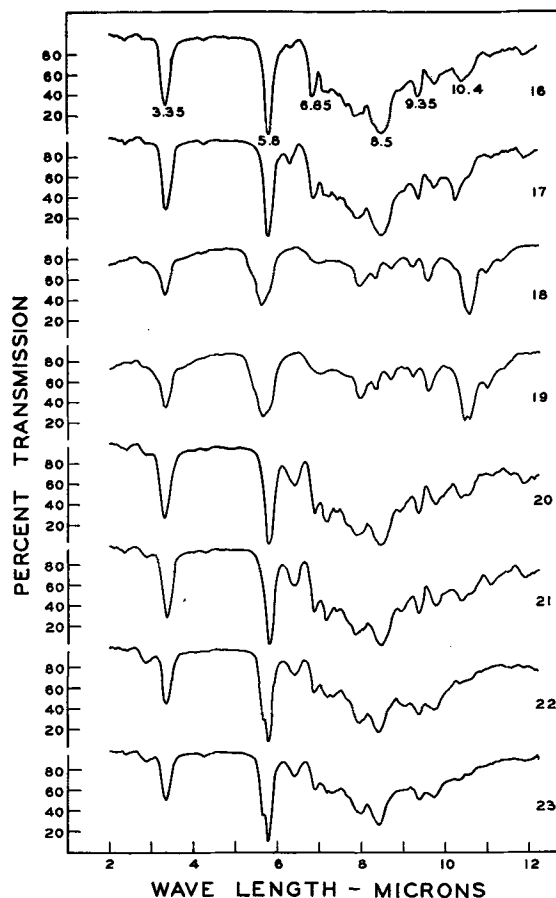
Infrared spectra of chloroform solutions of alpha- and beta-eleostearic acids, of oils containing eleostearins, and of several maleic anhydride and epoxy derivatives, are shown in Figures I, II, and III. In these figures are included spectra of selected "model" compounds of known molecular configuration. These spectra are used to clarify some of the interpretations of the infrared spectra of maleic anhydride adducts of the alpha- and beta-eleostearic acids and of their derivatives.

In the "group frequency" region of the infrared spectra, between 2 and 9 microns, the spectra of the eleostearic acids and of oils containing them, exhibit

some half dozen prominent bands resembling those found in the spectra of saturated fatty acids and esters. From previous studies (12) these bands can be readily correlated with the vibrating groups which give rise to them; 3.30 microns (0.88),<sup>3</sup> C—H stretching vibration; 5.70-5.80 microns (0.66), C=O stretching vibration; 6.95 microns (0.27), C—H bending vibration; and 7.75, 8.00, and 8.80 microns (0.28), (0.28), and (0.16), C—O stretching vibrations. The values cited are from the spectra of alpha-eleostearic acid. Corresponding values from the spectra of beta-eleostearic acid are essentially identical while those from the spectra of the oils are compatible with their glyceride content.

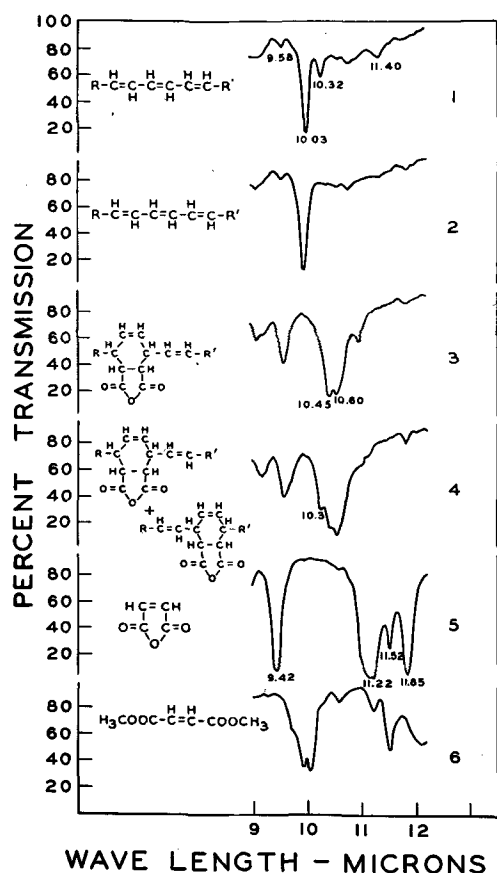
In the "fingerprint" region of the infrared spectra included in these studies, from 9 microns to 12 microns, absorption maxima are more dependent upon the entire molecule as a vibrating unit, and differences indicative of cis- and trans-configuration may be expected. In spectra of mono-unsaturated com-

<sup>3</sup>Wavelength positions are those of band maxima. Values in parentheses are absorptivities. All spectroscopic nomenclature used throughout this paper is in conformity with the "Suggested Nomenclature in Applied Spectroscopy" (17).



LEGEND FIG. 3

16. Tributyl ester of maleic anhydride—alpha-eleostearic acid adduct
17. Tributyl ester of maleic anhydride—beta-eleostearic acid adducts
18. Mono-epoxide of maleic anhydride—beta-eleostearic acid adduct (m.p. 144°C.)
19. Mono-epoxide of maleic anhydride—beta-eleostearic acid adduct (m.p. 118°C.)
20. Mono-epoxide of tributyl ester of maleic anhydride—alpha-eleostearic acid adduct
21. Mono-epoxide of tributyl ester of maleic anhydride—beta-eleostearic acid adducts
22. Tributyl ester of hydroxy-acetoxy maleic anhydride—alpha-eleostearic acid adduct
23. Tributyl ester of hydroxy-acetoxy maleic anhydride—beta-eleostearic acid adducts (in chloroform)



LEGEND FIG. 4

1. Alpha-eleostearic acid
  2. Beta-eleostearic acid
  3. Maleic anhydride—alpha-eleostearic acid adduct
  4. Maleic anhydride—beta-eleostearic acid adducts
  5. Maleic anhydride
  6. Dimethyl maleate  
(in chloroform)
- R =  $\text{CH}_2(\text{CH}_2)_3-$  and R' =  $-(\text{CH}_2)_7\text{COOH}$

pounds, appearance of a band with maximum at 10.3 microns, assigned to a C—H deformation vibration about a trans C=C group (7, 16, 18), would establish the presence of a trans C=C group. In polyunsaturated compounds evidence is accumulating that the absorption of isolated trans double bonds is additive, but conjugated systems exhibit bands with maxima at appreciably different wavelengths (6). In the spectra of both alpha- and beta- eleostearic acids the most prominent band in this region is at 10.03 microns (Figure IV, 1 and 2), arising from conjugated carbon-carbon double bonds. Further Jackson *et al.* show that a band at about 10.03 microns is characteristic of a trans-trans conjugated system. It is evident therefore that both alpha- and beta-eleostearic acids contain a conjugated trans-trans pair.

Von Mikusch (20) and also Alder and Vogt (1) have demonstrated that trans-trans conjugated dienes readily react with maleic anhydride at temperatures below 100°C. whereas cis-cis and cis-trans conjugated dienes do not. On the bases of these and other observations Paschke, Tolberg, and Wheeler have concluded that both alpha- and beta-eleostearic acids contain a pair of conjugated trans-trans acyclic double bonds. Observations made in this laboratory, identical with Paschke *et al.*, support and confirm this conclusion.

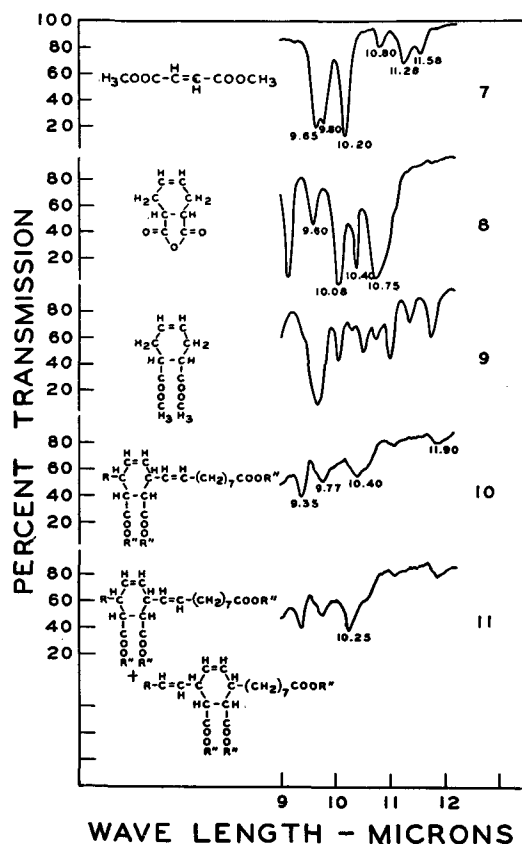
Maleinization reactions and infrared spectra have established that a trans-trans conjugated pair does in

fact occur in both alpha- and beta-eleostearic acids. Therefore the only problems which remain to confirm the complete cis-trans configuration of the two acids are definitely to establish the position of the trans-trans pair along the molecular chain and to prove the cis- or trans-configuration of the remaining unsaturated bond. Morrell and Davis (10) through ozonolysis of the maleic anhydride adduct of alpha eleostearic acid have established the position of the trans-trans pair along the molecular chain for this acid and hence the position of the remaining cis double bond to be at the 9,10 position. However the evidence is inconclusive with respect to the beta isomer (2, 11). The infrared spectra of the maleic anhydride reaction product with both alpha- and beta-eleostearic acids might be expected to supply an answer to this second problem. These adducts are non-conjugated dienes with one of the double bonds a cis bond in a ring structure. The other unsaturated bond, which did not take part in the addition of the maleic anhydride, appears in a side chain and should, if trans, exhibit the well established band with maximum at 10.3 microns. If this third unsaturated bond is cis, no maximum should appear at 10.3 microns. Study of the spectra of the two adducts of the eleostearic acids in this region (Figure IV, 3 and 4) reveals very intense bands with maxima at 10.45 and 10.60 microns, which interfere with the C=H bending band at 10.3 microns. It is very significant however that in the spectra of the maleic anhydride adduct of the beta-eleostearic acid a very pronounced shoulder is exhibited on the short wavelength side of the 10.45 and 10.60 micron band, at about 10.3 microns. No similar shoulder is observed in the spectra of the adduct with the alpha-eleostearic acid. Examination of the spectra of the hydrogenated adducts of both alpha- and beta-eleostearic acids (Figure II, 14 and 15) shows that neither exhibits a shoulder at 10.3 microns. This may be interpreted as evidence that this absorption at 10.3 microns in the spectra of the adduct of beta-eleostearic acid arises from a double bond and at this wavelength must be attributed to a C—H bending about a trans C=C. Thus the infrared spectra indicates that the third double bond in beta-eleostearic acid is trans while in alpha-eleostearic acid it is cis.

The intense bands at 10.45 and 10.60 microns in the spectra of the maleic anhydride adducts of alpha- and of beta-eleostearic acids probably arise from ring vibrations of the cyclohexene or the maleic anhydride ring, or from both. Maleic anhydride exhibits four strong bands in this region (Figure IV, 5); 9.45 microns (1.24); 11.22 microns (1.68); 11.52 microns (0.66); and 11.87 microns (1.32); comparable to the four strong bands exhibited by cyclohexane 9.63 (6),<sup>4</sup> 9.86 (4), 11.05 (9), and 11.60 (10), and by cyclohexene 9.64 (7), 9.92 (4), 10.90-11.06 (8), and 11.41 (9). That these intense bands in the spectra of maleic anhydride are due to the ring structure is demonstrated by comparison with the spectra of dimethyl maleate or dimethyl fumarate, where the ring is broken and only weak bands (intensities less than 0.5) are observed (Figure IV, 6 and Figure V, 7).

The intense bands in the spectra of maleic anhydride would not interfere with the identification of

<sup>4</sup>Data for cyclohexane and cyclohexene are taken from the A. P. I. library of infrared curves. Wavelengths are positions of maxima, values in parentheses are relative intensities (on a scale of 0-10, 10 = most intense).



LEGEND FIG. 5

7. Dimethyl fumarate
  8. Maleic anhydride-butadiene adduct
  9. Dimethyl ester of maleic anhydride-butadiene adduct
  10. Tributyl ester of maleic anhydride-alpha-eleostearic acid adduct
  11. Tributyl ester of maleic anhydride-beta-eleostearic acid adducts (in chloroform)
- $R = \text{CH}_3(\text{CH}_2)_6-$ ;  $R' = -(\text{CH}_2)_7\text{COOH}$ ; and  $R'' = \text{CH}_3(\text{CH}_2)_6-$

the C—H bending bands with maximum at 10.3 microns. However in the spectra of the maleic anhydride addition products with butadiene (Figure V, 8) the four strong bands appear but at considerably different wavelength positions: 9.60 (0.41), 10.08 (2.0), 10.40 (1.06), and 10.75 (1.44). These bands resemble rather closely the prominent bands in this region exhibited by the spectra of the maleic anhydride adducts of both alpha- and beta-eleostearic acids. The band with maximum at 10.40 microns, comparable to the band with maximum at 10.45 microns in the spectra of the eleostearic acid adducts, interferes with the C—H bending band at 10.3 microns. That these bands also arise from ring vibrations can be demonstrated by comparison of the spectra of the dimethyl ester of the maleic anhydride adduct of butadiene (Figure V, 9), which exhibits no strong bands in this region. The spectra of the heavily substituted cyclohexene ring does not exhibit the symmetrical "breathing" vibrations which appear in the spectra of unsubstituted cyclohexene.

It is to be expected from the foregoing observations that opening of the anhydride ring present in the adducts of alpha- and beta-eleostearic acids by means of esterification would result in the disappearance of the strong interfering bands at 10.45 and 10.60 microns. Both of the eleostearic acid adducts were converted to the corresponding tri-*n*-butyl esters

and spectra of each obtained. Examination of these spectra (Figure V, 10 and 11) reveals a pronounced 10.3 micron band in the spectra of the tri-butyl ester of the maleic anhydride adduct from beta-eleostearic acid and no trace of a corresponding band in the spectra of the ester from the adduct from alpha-eleostearic acid. Thus infrared spectra establishes the fact that alpha-eleostearic acid has one cis and two trans double bonds while the beta-isomer has three trans bonds.

Feuge *et al.* (3) have shown that isolated trans double bonds have an absorptivity in chloroform solution of approximately 0.4, at 10.36 microns. From the infrared spectra of alpha- and beta-eleostearic acids (Figure IV, 1 and 2) the absorptivities have been calculated to be 0.8 for the alpha isomer and 1.2 for the beta isomer at 10.01 microns. On the basis of simple additive absorption of the trans double bond it may be concluded that the alpha eleostearic acid has two trans double bonds and beta eleostearic acid, three trans double bonds.

Shreve *et al.* (19) have shown that, in the spectra of epoxy compounds, a band with maximum at 11.2 microns is exhibited if the oxirane ring is derived from an internal mono-unsaturated compound having the trans configuration at the double bond, *i.e.*, elaidic acid. The corresponding cis configuration, *i.e.*, oleic acid, gives rise, in the spectra of the epoxy derivative, to a weak band at 12.0 microns only. These correlations afford an opportunity to confirm the cis-trans structure of the exocyclic double bond in the spectra of the maleic anhydride adducts of alpha- and beta-eleostearic acids.

In view of the above considerations the maleic anhydride adducts of alpha- and beta-eleostearic acids were selectively epoxidized. The chemical evidence obtained showed that only one gram atom of oxygen was absorbed per mole of adduct irrespective of the amount of oxygen available even though there were two double bonds present in the molecule. This indicates that only one of the two double bonds was being attacked. While it was found impossible to crystallize the epoxide of the maleic anhydride adduct of alpha eleostearic acid, there were obtained two crystalline mono-epoxides of the beta-isomer. The infrared spectra of these two beta-mono-epoxides showed that the exocyclic double bond had selectively been saturated. Reference to Figure VI, 12 and 13, shows that the characteristic trans absorption at 10.3 microns was no longer present but that a new absorption band appeared at 11.0 microns indicative of a trans epoxide. The fact that two trans epoxides were isolated from the beta-isomer is further strong evidence for the trans, trans, trans configuration since two maleic anhydride adducts for beta-eleostearic acid would be predicted, one involving the 9,11 pair of double bonds with the exocyclic double bond at 13 and the other involving the 11,13 pair of double bonds with the exocyclic double bond at the 9 position.<sup>5</sup> In the interest of exact comparison between the epoxides of the alpha- and beta-adducts with a reference to the cis-trans configuration of the exocyclic bonds, it was found expedient to prepare the tri-butyl esters of the adducts prior to epoxidation. This was necessitated by the fact that the epoxide of the maleinated

<sup>5</sup>Recent investigations of this point through application of ozonolysis and chromatographic separation of the fission products (8) yielded evidence for the presence of the expected valeric and azelaic acids (5).

alpha-acid could not be isolated in a pure form, and hence no direct comparison between the epoxy maleinated alpha- and beta-acids was possible. The spectra for these compounds are also shown in Figure VI, 14 and 15. The spectra of the epoxy compound from the alpha-oleostearic acid derivative exhibits a weak maximum at 12.0 microns and no band at 11.0 microns, verifying the fact that the exocyclic double bond was cis prior to epoxidation. The spectra of the compound from the beta-oleostearic acid derivatives reveal pronounced bands at 11.0 microns and no bands at 10.3 or 12.0 microns, verifying the fact that the epoxidation had attacked a trans exocyclic double bond. These data again confirm the presence of cis-, trans-, trans- (or trans-, trans-, cis-) double bonds in alpha-oleostearic acid and of trans-, trans-, trans-double bonds in beta-oleostearic acid. The postulation of Shreve *et al.* that the bands with maxima at 11.0 microns and 12.0 microns arise from vibrations of the oxirane ring (19) can be further verified by examination of the spectra of acetylated epoxy derivatives of the maleic anhydride adducts of the tri-butyl esters of alpha- and of beta-oleostearic acids, Figure VI, 16 and 17. In these compounds the oxirane rings have been broken and their spectra exhibit no bands with maxima at 11.0 or 12.0 microns.

### Summary

The cis, trans, and positional configuration of alpha- and beta-oleostearic acids have been investigated. The maleic anhydride adducts of alpha- and beta-oleostearic acids were prepared and subjected to hydrogenation, selective epoxidation, and esterification. Two epoxy derivatives of the maleinated beta-oleostearic acid were isolated and characterized. Infrared spectra of these maleic anhydride adducts and their various derivatives have been measured in the rock salt region, 2-12 microns. These infrared data together with chemical evidence have been used to confirm the structure of alpha-oleostearic acid as 9-cis, 11-trans, 13-trans octadecatrienoic acid and beta-oleostearic acid as 9-trans, 11-trans, 13-trans octadecatrienoic acid.

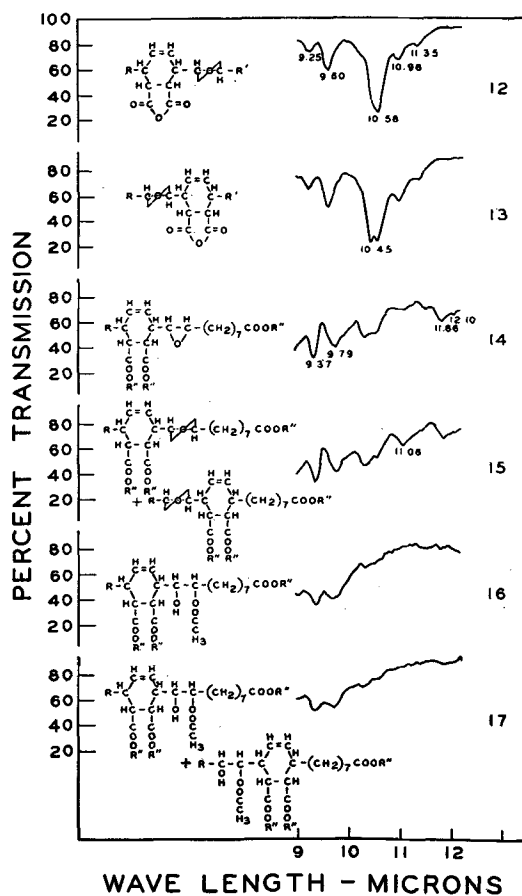
Complete infrared spectra are presented for authentic samples of alpha- and beta-tung oil, China wood oil, oiticica oil, and alpha- and beta-oleostearic acids. Infrared absorption curves are presented, including the maleic anhydride adducts of alpha- and beta-oleostearic acids, various derivatives of these adducts and the following reference compounds: maleic anhydride, dimethyl maleate, dimethyl fumarate, the butadiene-maleic anhydride adduct and its dimethyl ester.

### Acknowledgments

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### REFERENCES

1. Alder, K., and Vogt, W., *Ann.* 571, 137-52 (1951).
2. Chin, C., *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 53, 333 (1950); *Pette u. Seifen*, 53, 102 (1951).
3. Feuge, R. O., Pepper, M. B., O'Connor, R. T., and Field, E. T., *J. Am. Oil Chem. Soc.*, 28, 420-426 (1951).
4. Flett, L. H., and Gardner, W. H., "Maleic Anhydride Derivatives," John Wiley and Sons, New York (1952), pp. 12-13.



LEGEND FIG. 6

12. Mono-epoxide of maleic anhydride—beta oleostearic acid adduct (m.p. 144°C.)
  13. Mono-epoxide of maleic anhydride—beta-oleostearic acid adduct (m.p. 118°C.)
  14. Mono-epoxide of tributyl ester of maleic anhydride—alpha-oleostearic acid adduct
  15. Mono-epoxide of tributyl ester of maleic anhydride—beta oleostearic acid adducts
  16. Tributyl ester of hydroxy-acetoxy maleic anhydride—alpha-oleostearic acid adduct
  17. Tributyl ester of hydroxy-acetoxy maleic anhydride—beta-oleostearic acid adducts (in chloroform)
- R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>-; R' = -(CH<sub>2</sub>)<sub>7</sub>COOH; and R'' = CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>-

5. Haverkamp Begemann, P., Keppler, J. G., and Boekenoogen, H. A., *Rec. trav. chim.*, 69, 447 (1950).
6. Jackson, J. E., Paschke, R. F., Tolberg, W., Boyd, H. M., and Wheeler, D. H., *J. Am. Oil Chem. Soc.*, 29, 229-234 (1952).
7. Lemon, H. W., Kirby, E. M., and Knapp, R. M., *Can. J. of Tech.*, 29, 523-539 (1951).
8. Marvel, C. S., and Rands, R. D. Jr., *J. Am. Chem. Soc.*, 72, 2642 (1950).
9. Morrell, R. S., and Davis, W. R., *Trans. Faraday Soc.*, 32, 209-19 (1936).
10. Morrell, R. S., and Davis, W. R., *J. Soc. Chem. Ind.*, 55, 261-5T (1936).
11. Morrell, R. S., and Samuels, H., *J. Chem. Soc.*, 1932, 2251-54.
12. O'Connor, R. T., Field, E. T., and Singleton, W. S., *J. Am. Oil Chem. Soc.*, 28, 154-160 (1951).
13. O'Connor, R. T., Heinzelman, D. C., Freeman, A. F., and Pack, F. C., *Ind. Eng. Chem.*, 17, 467 (1945).
14. Pack, F. C., Planck, R. W., and Dollear, F. G., *J. Am. Oil Chem. Soc.*, 29, 227-228 (1952).
15. Paschke, R. F., Tolberg, W., and Wheeler, D. H., *J. Am. Oil Chem. Soc.*, 30, 97 (1953).
16. Rasmussen, R. S., Brattain, R. R., and Zucco, P. S., *J. Chem. Phys.*, 15, 135-140 (1947).
17. Report No. 6 of the Joint Committee on Nomenclature in Applied Spectroscopy, established by the Society for Applied Spectroscopy and the American Society for Testing Materials, *Anal. Chem.*, 24, 1349-1354 (1952).
18. Sheppard, N., and Sutherland, G. B. B. M., *Proc. Roy. Soc. (London)*, A 196, 195-216 (1949).
19. Shreve, O. D., Heether, M. R., Knight, H. B., and Swern, D., *Anal. Chem.*, 23, 277-282 (1951).
20. von Mikusch, J. D., *Angew. Chem.*, 62, 475-480 (1950).

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