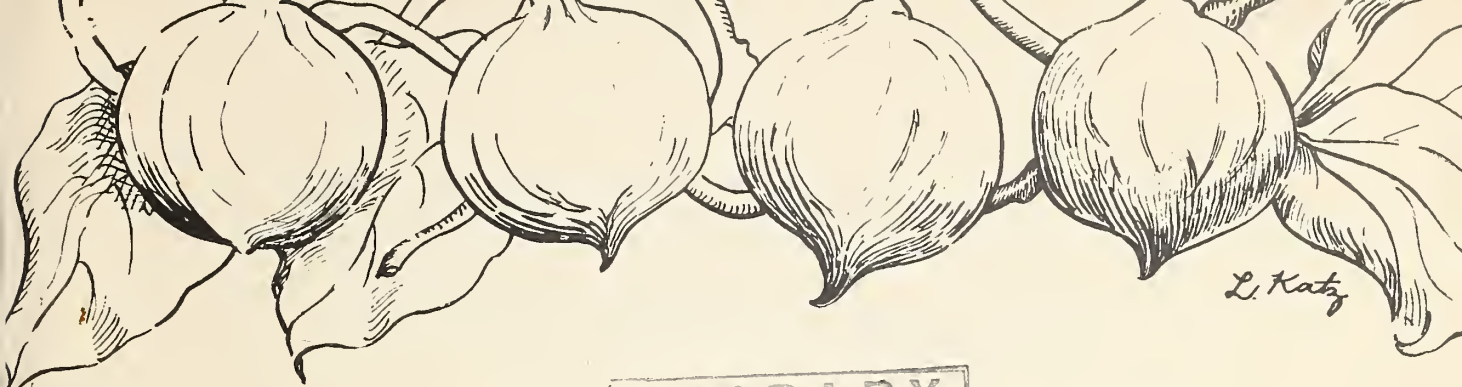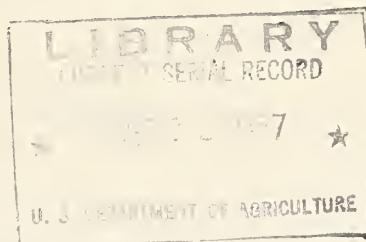# Historic, archived document

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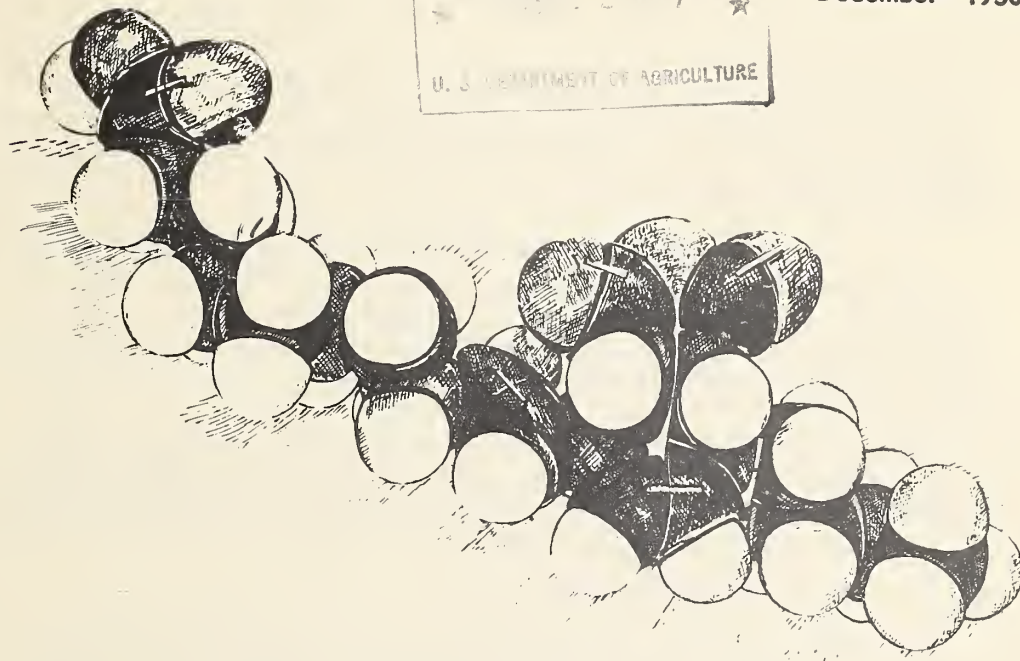
ARS-72-7
December 1956

# New tung oil derivatives

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

# SUMMARY

To extend the utilization of tung oil and improve its economic status, chemists at the Southern Regional Research Laboratory are engaged in research on the development of new chemical derivatives of the oil which may find application as specialty products.

The chief constituent of tung oil is the glyceride of *alpha*-eleostearic acid, a straight chain 18-carbon fatty acid that contains a special arrangement of alternating single and double bonds known as a conjugated triene system. *Alpha*-tung oil or its component *alpha*-eleostearic acid may be readily converted to the *beta*-isomer, which also contains a conjugated triene system.

These very active systems of double bonds react in a readily predictable fashion with a great number of different organic compounds, referred to as dienophiles, by what is known as the Diels-Alder Reaction. This particular reaction has been used to advantage in preparing new chemical derivatives of tung oil for use in the manufacture of plastics.

This paper describes the isomerization of *alpha* to *beta* tung oil, preparation and determination of the chemical structures of highly pure eleostearic acids, alcoholysis of tung oil for the production of various esters, the reactions of these materials with maleic anhydride, *beta*-propiolactone, acrylonitrile, and fumaronitrile as dienophiles, and the results obtained on testing the ester adducts as plasticizers for vinyl resins.

# NEW TUNG OIL DERIVATIVES

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## INTRODUCTION

Tung, or China wood, oil has been used for many centuries by the Chinese people in the manufacture of lacquers and waterproofing compounds. However, the culture of tung trees in the United States had its origin just 50 years ago. Since those first experimental plantings, the annual production of tung oil in this country has risen to over 40,000,000 pounds per year.

More than 80 percent of the tung oil consumed in American industries is utilized by manufacturers of protective coatings. In order to extend the utilization of tung oil and improve its economic status, this Laboratory[1] is engaged in research on the development of new chemical derivatives which may find application as specialty products.

### COMPOSITION OF TUNG OIL

Domestic tung oil is produced exclusively from tung kernels of the *fordii* species of the genus *Aleurites*. Practically all vegetable oils are glycerides, and better than 95 percent of the oil is composed of glycerine derivatives. Of this glyceride content, only about 10 percent is glycerine itself and the other 90 percent consists of fatty acid. *Fordii* oil normally contains some 78 percent of eleostearic acid in the glyceride form, together with small percentages of other fatty acid glycerides, such as oleic, linoleic, and stearic.

Two forms of tung oil are known -- the liquid, golden yellow oil designated *alpha* tung oil, and the semisolid, butterlike *beta* tung oil. The eleostearic acid portions of these oils are called *alpha*-eleostearic acid and *beta*-eleostearic acid, respectively. The exact chemical structures of these two acids have been determined, and both acids have been shown to be straight-chain $C_{18}$ fatty acids with triene unsaturation. In other words, highly reactive double bonds are located in the 9, 11, and 13 positions along the 18-carbon chains of these acids. Furthermore, such an alternating system of double and single bonds constitutes what is known as a conjugated system, which is extremely reactive in particular chemical reactions. The only difference between *alpha*-eleostearic acid and *beta*-eleostearic acid lies in the double bond located in position 9 of the carbon chain. In the case of the *alpha* acid this double bond is *cis*, and in the *beta* acid it is *trans*, while the double bonds at positions 11 and 13 are *trans* in both acids. *cis* and *trans* are merely terms describing the relative positions of hydrogen atoms around an ethylenic bond.

### ISOMERIZATION OF TUNG OIL

The tung tree elaborates only one of the so-called isomeric forms of eleostearic acid, the *alpha* form. Consequently, the eleostearic acid in fresh tung oil expressed from normal, undamaged tung kernels has the *alpha* configuration exclusively. *Beta*-eleostearic acid must be produced artificially by inducing the *cis* 9, 10 double bond of the *alpha* form of the acid to shift to a *trans* configuration.

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[1]One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Iodine, sulfur, selenium, and sunlight are variously reported to effect this *alpha* to *beta* transformation. However, it has been observed in this Laboratory that the isomerization of *alpha* to *beta*-eleostearic acid is most readily accomplished by treatment of the tung oil with a small quantity of saturated potassium iodide solution, followed by exposure to diffused daylight. In any event, the transformation from *alpha* to *beta* is easily accomplished whether the eleostearic acid is in the form of the glyceride or the free fatty acid.

## TUNG OIL ACIDS AND ESTERS

Numerous procedures have been reported in the literature for the preparation of pure *alpha*- and *beta*-eleostearic acids. Varying in their degrees of complexity, some require special apparatus for excluding oxygen, while others employ numerous washings and recrystallizations of the intermediate and final products from various solvents. Such multiple operations are not only time consuming, but by their very nature afford ample opportunity for these highly unstable acids to undergo deterioration. We have developed a simplified method involving only one recrystallization for the preparation of the pure eleostearic acids in good yields. The tung oil is saponified under mild conditions, then acidulated with dilute hydrochloric acid. The liberated acids are immediately dissolved without further treatment in 95 percent ethyl alcohol and crystallized at -20° C. The acids are recrystallized from ethanolic solution at +5° C. After vacuum drying, the white, fluffy, crystals are stored in evacuated ampoules at low temperatures. Ultraviolet absorption data obtained on these highly pure acids serve as a basis for the more accurate determination of the *alpha*- and *beta*-eleostearic acid contents of tung oil.

In preparing new chemical derivatives of tung oil, it is often more expedient to utilize various esters of the eleostearic acids instead of the fatty acids or glycerides as such. A convenient method of preparing the esters without appreciable isomerization occurring during the process is by alcoholysis. This consists of heating the glyceride with an excess of the appropriate alcohol in the presence of the corresponding sodium alcoholate. For example, in the preparation of ethyl *alpha*-tungoate, *alpha* tung oil is gently refluxed with a mixture of absolute ethyl alcohol and sodium ethylate. The sodium ethylate is prepared simply by dissolving freshly shaved metallic sodium in absolute ethyl alcohol.

## DIELS-ALDER REACTIONS

As was pointed out earlier, the conjugated system present in tung oil, its fatty acids, and its fatty esters is unique, with a chemistry all its own. This highly reactive system of double bonds reacts in a readily predictable fashion with a great number of different organic compounds by what is known as the Diels-Alder Reaction.

In order for a Diels-Alder Reaction to readily occur, there must be present in the reaction mixture a *trans, trans* diene, and a dienophile (a "diene-loving" compound). *Alpha*-eleostearic acid has a *trans, trans* conjugated system present in carbons 11-14, while *beta*-eleostearic acid has a *trans, trans* diene not only at position 11-14, but also at position 9-12. Therefore, tung oil acids and esters admirably fulfill the diene requirements for a Diels-Alder Reaction. Organic chemicals, which are suitable dienophiles, are far too numerous to list, but almost all of them have a particular type of structure, consisting of an ethylenic bond conjugated with another type of double bond, such as a carbonyl bond. A true Diels-Alder Reaction always yields a particular type of adduct, formed by *cis* addition of the dienophile to the first and last carbon atoms of the conjugated diene system (1, 4 addition). For example:

$CH_2 = CHCOOH$          $CH_3(CH_2)_3CH = CH - CH = CH - CH = CH(CH_2)_7COOH$
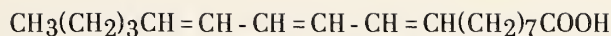
Acrylic acid                    *Alpha*-eleostearic acid
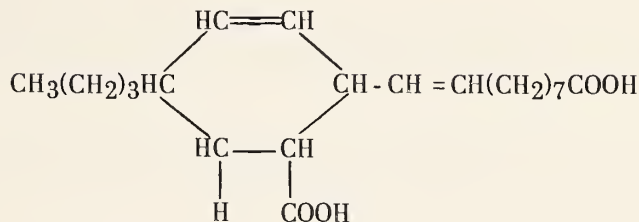


Diels-Alder Adduct

An adduct produced in this way contains a cyclohexene nucleus and one ethylenic bond out-side the nucleus referred to as an exocyclic double bond. This exocyclic double bond may be *cis* or *trans*, depending on whether *alpha-* or *beta-* eleostearic acid was employed as the reactant.

## TUNG OIL DERIVATIVES

Selection of dienophiles for reaction with the eleostearates was based principally on the probable utility of the predicted reaction products as plasticizers, biologically active agents, emulsifiers, and sticking agents, as well as their facile addition to the eleostearates without complicated side reactions such as polymerization.

Maleic anhydride reacts rapidly with *alpha-* and *beta-*eleostearic acids and esters, either in the melt or in solution. The *alpha-*eleostearic acid forms only one adduct, while *beta-*eleostearic acid produces two adducts with maleic anhydride. These adducts and various derivatives were used in establishing definitely the structures of the two eleostearic acids. Esterification of the maleic anhydride adducts with alcohols leads to the formation of compounds which contain three ester groups per molecule (tricarboxylic acid esters). Peracid oxidation of the adducts results in saturation of the exocyclic double bonds of the adducts with oxygen, forming oxirane derivatives. Oxygen does not attack the cyclohexene nucleus in any of the maleic anhydride adducts. Catalytic hydrogenation of the adducts results in the formation of completely saturated compounds.

*Beta-*propiolactone, in the presence of small amounts of potassium carbonate, reacts with the eleostearates to produce acrylic acid derivatives. Since acrylic acid is an unsymmetrical dieno-phile, it would be expected that a greater number of isomeric products would result from this reac-tion than from the maleic anhydride addition. Two isomeric dicarboxylic acids were isolated from the reaction of *beta-*propiolactone and *alpha-*eleostearic acid esters. Esterification of the adducts with alcohols results in the formation of diesters. Peracid oxidation of these adducts did not proceed selectively as in the case of the maleic anhydride adducts, but rather, resulted in satura-tion of both the cyclic and exocyclic double bonds. Reaction with peracids under hydroxylation conditions similarly resulted in attack at both centers of unsaturation. The adducts were catalyt-ically hydrogenated to form completely saturated compounds.

Acrylonitrile and fumaronitrile react with the eleostearates for the production of compounds which contain cyano ($C \equiv N$) groups on the cyclohexene nuclei of the adducts. The acrylonitrile adducts contain only one cyano grouping, while the fumaronitrile adducts contain two such groups per molecule. The unsymmetrical character of acrylonitrile makes possible the formation of more

isomeric compounds in the Diels-Alder Reaction than can be expected from the addition of the symmetrical fumaronitrile molecule. Also, reaction of any given dienophile with *beta*-eleostearic acid results in the production of more isomeric compounds than does an analogous reaction with *alpha*-eleostearic acid, since as was previously noted, the *beta*-acid has two reactive centers for dienophilic attack compared to the single reactive center of the *alpha*-acid. Acrylonitrile also reacts with raw tung oil via the Diels-Alder Reaction, producing nitrile derivatives of the oil itself.

The structures of the derivatives prepared in the reactions described above, together with certain of their properties, are presented in the APPENDIX.

## PLASTICIZERS

The rapid expansion of the plastics industry has greatly increased the demand for effective plasticizing materials, especially since one pound of plasticizer is required for every two pounds of certain vinyl resins.

These resins are very stiff, brittle materials; therefore, in order to prepare suitable plastics from them, chemical compounds referred to as plasticizers must be incorporated into the resins to impart flexibility and other desirable characteristics. The prime requisite for a plasticizer is that it must be compatible with the resin and not sweat or bleed out of the finished plastic.

Among the most important characteristics employed to evaluate the performance of a plasticizer are tensile strength, elongation, modulus, and brittle point of the plasticized composition. Tensile strength is the load in pounds per square inch supported by the sample at the moment of rupture. Percentage elongation is the ratio of the length of the sample at the moment of rupture to the initial length. Modulus is a measure of the ease or difficulty with which a plastic can be elongated. Modulus is reported in pounds per square inch; the lower the modulus, the greater the ease of elongation. Brittle point is a measure of the low temperature characteristics of the plasticizer -- it is the temperature at which the plastic fractures on impact.

To achieve desirable properties in the plastic, it is frequently expedient to employ a mixture of plasticizers, each of which has some particularly advantageous property. When a plasticizer is used in such a manner, it is referred to as a secondary plasticizer.

In evaluating plasticizers, it is customary to compare their properties with a reference material such as dioctyl phthalate (DOP) or tricresyl phosphate (TCP). Plasticizer data for esters of the maleic anhydride -- *beta*-eleostearic acid adducts and their derivatives are presented in Table I.

All of the adduct esters impart higher tensile strength to the vinyl resin than does DOP, and about the same elongation, although somewhat inferior moduli and brittle points.

Plastics made with vinyl chloride decompose slowly with the evolution of HCl, which induces deterioration of the plastic. The epoxy derivatives are not as good plasticizers as the other materials tested, but they would have the advantage of acting as HCl scavengers, thereby stabilizing vinyl chloride-containing plastics.

Plasticizing characteristics of diesters of the acrylic acid -- eleostearic acid adducts are summarized in Table II.

It is apparent that the diesters of the acrylic acid adducts of both the *alpha-* and *beta* acids impart substantially identical characteristics to the resin with the exception of the brittle point. The butyl esters prepared from the *beta-*acid adduct are decidedly superior from the standpoint of low-temperature plasticizing characteristics.

The diethyl esters of the acrylic acid adducts of both *alpha-* and *beta-*eleostearic acid are comparable plasticizers to DOP with respect to modulus, tensile strength, and elongation. The dibutyl esters, on the other hand, are somewhat inferior in each·respect. Brittle points imparted by the *alpha-*acid derivatives are about the same as for the control DOP, while those for the *beta-*acid derivatives are somewhat better, about midway between those of DOP and di-2-ethylhexyl adipate in the case of the dibutyl ester. Volatilities of the *beta* adduct stocks run from about the same to one-half that of DOP, while those for the *alpha* adduct stocks run from about the same to twice as much. Hydrogenation results in reduced volatility for both *alpha* and *beta* derivatives, and can be expected to result in improved thermal stability, although it shows little or no consistent influence on the other plasticizing characteristics of these materials.

Primary and secondary plasticizer data on the acrylonitrile and fumaronitrile adducts of the *n*-butyl esters of *alpha-* and *beta-*eleostearic acids appear in Table III.

All of the adducts were compatible at the time of milling and molding, although at 60 days the stock plasticized with the adduct of butyl *beta-*eleostearate was bleeding, showing definite incompatibility. Both the butyl *alpha-*and butyl *beta-*eleostearate -- acrylonitrile adducts were satisfactory secondary plasticizers when incorporated with either DOP or TCP.

The screening tests show that the stocks plasticized by the fumaronitrile adducts are somewhat better in tensile strength, compatibility, and volatility than those plasticized by the acrylonitrile adducts, although the latter excell the former in modulus and brittle point. It is apparent from these results that the presence of two cyano groups on the cyclohexene nucleus of the adduct leads to greater permanence and an enhanced degree of compatibility between the plasticizer and the resin.

By incorporating the acrylonitrile adducts with DOP or TCP, it is possible to achieve either a reduction in volatility of DOP plasticized stocks or an improvement in the modulus and low-temperature performance of TCP plasticized stocks. This does not entail any sacrifice in the desirable plasticizing characteristics of DOP or TCP.

## LIST OF PUBLICATIONS

(1)  Bickford, W. G., DuPre´, E. F., Mack, C. H., and O'Connor, R. T.,  The Infrared Spectra and the Structural Relationships Between *alpha*- and *beta*-Eleostearic Acids and Their Maleic Anhydride Adducts, Jour. Amer. Oil Chemists' Soc., *30*, 376 (1953).

(2)  Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., The Reaction of *beta*-Propiolactone with *alpha*- and *beta*-Eleostearates and Plasticizer Properties of Derived Esters, Jour. Amer. Oil Chemists' Soc., *32*, 533 (1955).

(3)  Hoffmann, J. S., O'Connor, R. T., Magne, F. C., and Bickford, W. G., The Reaction of Acrylonitrile and Fumaronitrile with *alpha*- and *beta*-Eleostearates.  Plasticizer Properties of the *n*-Butyl Esters of the Adducts, Jour. Amer. Oil Chemists' Soc., *33*, 410 (1956).

(4)  Hoffmann, J. S., O'Connor, R. T., Heinzelman, D. C., and Bickford, W. G., A Simplified Method for the Preparation of *alpha*- and *beta*-Eleostearic Acids, and a Revised Spectrophotometric Procedure for their Determination, in press (Jour. Amer. Oil Chemists' Soc.)

TABLE I

Plasticizing Characteristics of Esters of the Maleic Anhydride--*Beta*-Eleostearic Acid
Adducts for Vinyl Chloride-Vinyl Acetate Copolymer

| PLASTICIZER | TENSILE STRENGTH P.S.I. | 100 PERCENT MODULUS P.S.I. | ELONGATION PERCENT | BRITTLE POINT °C. | COMPATI-BILITY (DAYS) |
|---|---|---|---|---|---|
| Trimethyl ester of the maleic anhydride--*beta*-eleo-stearic acid adduct | 3360 | 1900 | 330 | - 7 | 180 + |
| Tributyl ester of the maleic anhydride--*beta*-eleo-stearic acid adduct | 3090 | 1990 | 290 | -20 | 365 + |
| Hydrogenated trimethyl ester of the maleic anhydride--*beta*-eleostearic acid adduct | 3330 | 1780 | 290 | - 7 | 365 + |
| Epoxidized trimethyl ester of the maleic anhydride--*beta*-eleostearic acid adduct | 3300 | 2400 | 270 | +11 | 365 + |
| 50-50 Blends with DOP: | | | | | |
| Trimethyl ester of the maleic anhydride--*beta*-eleo-stearic acid adduct | 3350 | 1990 | 300 | -19 | 180 + |
| Tributyl ester of the maleic anhydride--*beta*-eleostearic acid adduct | 3190 | 1880 | 310 | -27 | 365 + |
| Hydrogenated trimethyl ester of the maleic anhydride--*beta*-eleostearic acid adduct | 3270 | 1930 | 290 | -21 | 365+ |
| Control (DOP) | 3080 | 1680 | 310 | -32 | |

TABLE II

Plasticizing Characteristics of Diesters of Acrylic Acid-Eleostearic Acid Adducts
for Vinyl Chloride-Vinyl Acetate Copolymer

| PLASTICIZER | TENSILE STRENGTH P.S.I. | 100 PERCENT MODULUS P.S.I. | ELONGATION PERCENT | BRITTLE POINT °C. | VOLATILITY LOSS PERCENT | COMPATIBILITY (DAYS) |
|---|---|---|---|---|---|---|
| *Alpha*-eleostearic acid adducts: | | | | | | |
| Diethyl esters | 2900 | 1710 | 280 | -35 | 0.57 | 365 + |
| Hydrogenated diethyl esters | 2970 | 1720 | 310 | -35 | 0.16 | 365 + |
| Dibutyl esters | 2780 | 1780 | 260 | -31 | 0.72 | 365 + |
| Hydrogenated dibutyl esters | 2690 | 1890 | 240 | -29 | 0.32 | 365 + |
| *Beta*-eleostearic acid adducts: | | | | | | |
| Diethyl esters | 2990 | 1620 | 310 | -39 | 0.40 | 15 |
| Hydrogenated diethyl esters | 2960 | 1680 | 300 | -37 | 0.10 | 365 + |
| Dibutyl esters | 2800 | 1810 | 260 | -43 | 0.42 | 15 |
| Hydrogenated dibutyl esters | 2740 | 1770 | 240 | -43 | 0.14 | 365 + |
| Control DOP | 3040 | 1620 | 320 | -32 | 0.32 | |

**TABLE III**

Plasticizing Characteristics of the Adducts of Acrylonitrile and Fumaronitrile with the
Butyl Eleostearates for Vinyl Chloride-Vinyl Acetate Copolymer

| PLASTICIZER | TENSILE STRENGTH P.S.I. | 100 PERCENT MODULUS P.S.I. | ELONGATION PERCENT | BRITTLE POINT °C. | TORSION TEST °C. | COMPATABILITY (DAYS) | VOLATILITIES PERCENT LOSS |
|---|---|---|---|---|---|---|---|
| Acrylonitrile adduct of butyl *alpha*-eleostearate | a/ | 1310 | a/ | -31 | -27 | 275+ | 0.26 |
| Acrylonitrile adduct + tricresyl phosphate (50-50) | 3120 | 1630 | 290 | -15 | — | 150+ | 0.16 |
| Acrylonitrile adduct of butyl *beta*-eleostearate | 2720 | 1320 | 320 | -33 | -26 | 60 | ---- |
| Acrylonitrile adduct + DOP (50-50) | 2880 | 1460 | 300 | -31 | -28 | 150+ | 0.21 |
| Acrylonitrile adduct + tricresyl phosphate (50-50) | 3080 | 1600 | 300 | -15 | -15 | 150+ | 0.08 |
| Fumaronitrile adduct of butyl *alpha*-eleostearate | 3010 | 1780 | 310 | -9 | -9 | 335+ | 0.06 |
| Fumaronitrile adduct of butyl *beta*-eleostearate | 3070 | 1660 | 320 | -17 | -14 | 335+ | 0.09 |
| Control (DOP) | 2950 | 1600 | 310 | -33 | -24 | | 0.35 |
| Tricresyl phosphate | 3600 | 2430 | 275 | 0 | 0 | | 0.14 |

a/ Sample did not rupture at maximum extension obtainable.

*APPENDIX*

Diels-Alder Products of *Alpha-* and *Beta*-Eleostearates

$R_1$ ⌐— $R_2$ ⌐—

$$CH_3-(CH_2)_3-C=C-C=C-C=C-(CH_2)_7-COOH$$
$$\quad\quad\;\; H\;\; H\quad H\; H$$

*Alpha*-Eleostearic Acid

$R_3$ ⌐— $R_4$ ⌐—

$$CH_3-(CH_2)_3-C=C-C=C-C=C-(CH_2)_7-COOH$$
$$\quad\quad\quad H\quad\; H\; H\quad H\; H$$

*Beta*-Eleostearic Acid

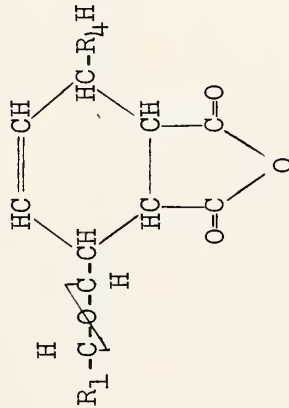| Adduct | Structure | Comments |
|---|---|---|
| 1. Maleic anhydride —— *alpha*-eleostearic acid adduct. |  | M. P. 64°C. H-I values, C and H determinations in agreement with theory. |
| 2. Compound #1 hydrogenated. | #1 with cyclic and exocyclic double bonds saturated. | M. P. 74°C. |
| 3. Maleic anhydride ——*beta*-eleostearic acid adducts. | Mixture of: Structure #1 (with *trans* exocyclic bond) and  | M. P. 77°C. H-I values, C and H determinations in agreement with theory. |

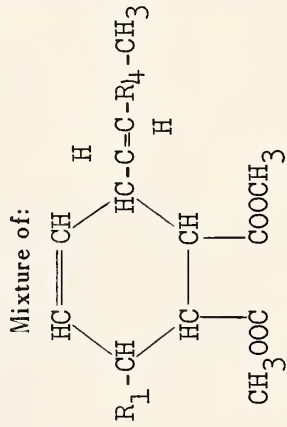| | | |
|---|---|---|
| 4. Compound #3 hydrogenated. | #'s 3, with cyclic *and* exocyclic double bonds saturated. | M. P. 58°C. |
| 5. Mono-epoxide of maleic anhydride-*beta*-eleostearic acid adduct. | Mixture of:<br><br>and | M. P. 144°C. |
| 6. Trimethyl ester of maleic anhydride-*beta*-eleostearic acid adducts. | Mixture of:<br><br>and | M.P. 118°C. |

| | | |
|---|---|---|
| 7. Compound #6 hydrogenated. | #'s 6, with cyclic *and* exocyclic double bonds saturated. | |
| 8. Compound #6, mono-epoxide. | #'s 6, with oxirane groups as in #'s 5. | |
| 9. Tributyl esters of maleic anhydride *beta*-eleostearic acid adducts. | See structures for #6, with appropriate ester groups. | Product - a viscous liquid. H-I value 47.3 (theory 43.8). |
| 10. Tributyl esters of maleic anhydride-*alpha*-eleostearic acid adduct. | | Product - a viscous liquid. H-I value 42.6 (theory 43.8). |
| 11. Compound #9 mono-epoxide. | #'s 9, with oxirane groups as in #'s 5. | |
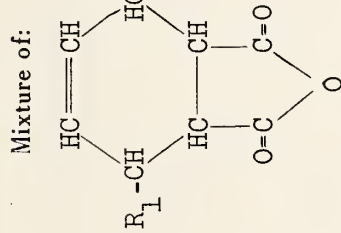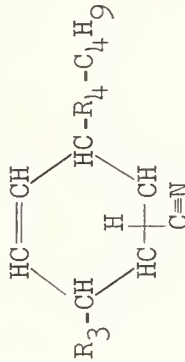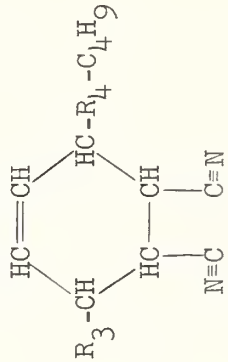
Structure for #7:

$$HC = CH \quad\quad HC - R_4 - CH_3$$
$$R_3 - CH \quad\quad HC - CH - COOCH_3$$
$$CH_3OOC$$

Structure for #10:

$$HC = CH \quad\quad HC - R_2 - C_4H_9$$
$$R_1 - CH \quad\quad HC - CH - COOC_4H_9$$
$$C_4H_9OOC$$

| # | Description | Structure | Notes |
|---|---|---|---|
| 12. | Compound #10 mono-epoxide. | #10, with exocyclic cis bond epoxidized. | |
| 13. | Free dicarboxylic acids from the *beta*-propiolactone-*alpha*-eleostearate adducts. | Mixture of: $R_1$-CH / HC=CH / HC-CH with HC-$R_2$H, CH-COOH, H *and* $R_1$-CH / HC=CH / HC-CH$_2$ with HC-$R_2$H, CH-COOH | Two forms of white, fluffy crystals - one melting at 113°C., and the other at 85°C. Neut. equiv., H-I value, C & H determinations very close to theory. |
| 14. | Diethyl esters of the *alpha*-eleostearic acid--*beta*-propiolactone adduct. | $R_1$-CH / HC=CH / HC-CH with HC-$R_2$-$C_2H_5$, CH-$COOC_2H_5$, H | B. P. 180°/145 microns. H-I values and sap. equiv. in agreement with theory. |
| 15. | Compound #14 hydrogenated. | $R_1$-CH / HC-CH (H,H) / HC-CH with HC-(CH$_2$)$_9$-$COOC_2H_5$, CH-$COOC_2H_5$, H | |

| # | Compound | Reference / Structure | Properties |
|---|----------|----------------------|------------|
| 16. | Dibutyl esters of the *alpha*-eleostearic acid-*beta*-propiolactone adduct. | See #14, with appropriate ester groups. | B. P. 183°/15 microns. H-I value and sap. equiv. in agreement with theory. |
| 17. | Compound #16 hydrogenated. | See #15. | |
| 18. | Diethyl esters of the *beta*-eleostearic acid-*beta*-propiolactone adducts. | Mixture of: [structure] and Structure #14 | B. P. 184°/180 microns. H-I values and sap. equiv. in agreement with theory. |
| 19. | Compound #18 hydrogenated. | See # 15. | |
| 20. | Dibutyl esters of the *beta*-eleostearic acid-*beta*-propiolactone adducts. | See #18. | B. P. 197°/100 microns. H-I value and sap. equiv. in agreement with theory. |
| 21. | Compound #20 hydrogenated. | See #17. | |

| No. | Structure | Notes |
|---|---|---|
| 22. Diepoxide of the diethyl esters of the *beta*-propiolactone-*alpha*-eleostearic acid adduct. | $R_1-CH$ $HC-CH$ (epoxide O), $HC-CH-CH-R_4-C_2H_5$, $HC-CH$ $COOC_2H_5$ (epoxide O) | Non-crystallizable material. |
| 23. Tetrahydroxy derivative of the diethyl esters of the *beta*-propiolactone-*alpha*-eleostearic acid adduct. | $R_1-CH$ $OH$ $OH$ $HC-CH$ $HC-CH-CH-R_4-C_2H_5$ $OH$ $OH$ $HC-CH$ $COOC_2H_5$ | Non-crystallizable material. |
| 24. Acrylonitrile adduct of butyl *alpha*-eleostearate. | $HC=CH$ $HC-R_2-C_4H_9$ $R_1-CH$ $HC-CH$ $H$ $C=N$ | Boiling range 183-188°/60-70 microns. |
| 25. Fumaronitrile adduct of butyl *alpha*-eleostearate. | $HC=CH$ $HC-R_2-C_4H_9$ $R_1-CH$ $HC-CH$ $N=C$ $C=N$ | Boiling range 217-226°/90-230 microns. |

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| 26. Acrylonitrile adduct of butyl *beta*-eleostearate. | Mixture of:<br><br>HC=CH   HC-R$_4$-C$_4$H$_9$<br>R$_3$-CH   HC—CH<br>   H—CH C≡N<br><br>and Structure #24 (with *trans* exocyclic bond). | Boiling range 184-190°/70-75 microns. |
| 27. Fumaronitrile adduct of butyl *beta*-eleostearate. | Mixture of:<br><br>HC=CH   HC-R$_4$-C$_4$H$_9$<br>R$_3$-CH   HC—CH<br>   N≡C—CH C≡N<br><br>and Structure #25 (with *trans* exocyclic bond). | Boiling range 224-234°/200-450 microns. |
| 28. Acrylonitrile adduct of *alpha*-tung oil. | Glyceride structure similar to #24. | . |