The Reaction of Beta-Propiolactone with Alpha- and Beta-Eleostearates and Plasticizer Properties of Derived Esters[1]

JOAN S. HOFFMANN, R. T. O'CONNOR, FRANK C. MAGNE, and W. G. BICKFORD,
Southern Regional Research Laboratory,[2] New Orleans, Louisiana

THE RAPID EXPANSION of the plastics industry, particularly in the field of vinyl-type resins, has increased the demand for effective plasticizing materials to the point where future availabilty of raw materials might become a matter of concern. This is especially true in view of the fact that one pound of plasticizer is required for every two pounds of certain vinyl resins, such as polyvinylchloride.

This laboratory is engaged in research on the development of new chemical derivatives of tung oil, including plasticizers, in order to extend the utilization of the oil as well as to make available a new source of raw materials.

Tung oil contains approximately 75% *alpha*-eleostearic acid, the structure of which has been shown to be 9-*cis,* 11-*trans,* 13-*trans,* octadecatrienoic acid (1, 8).

This acid may be readily converted by traces of iodine to *beta*-eleostearic acid, in which all of the double bonds have the trans-configuration (1, 8). Because of the presence of conjugated pairs of *trans*-ethylenic bonds in the triene systems these acids, particularly the *beta*-isomer, are readily modified by the Diels-Alder type of addition reaction.

Gresham *et al.* (4) recently reported that *beta*-propiolactone may be employed instead of acrylic acid as the dienophile component in Diels-Alder reactions, in which adducts of butadiene, isoprene, and cyclopentadiene were prepared. The reactions were catalyzed by potassium carbonate, which induces polymerization of *beta*-propiolactone to a polyester and assists in its pyrolysis to acrylic acid (3). This mechanism provides a means for the rapid addition of acrylic acid to conjugated dienes, thus avoiding extensive polymerization of the reactants which may occur during long reaction periods.

Beta-propiolactone has been employed in the diene synthesis with esters of α- and β-eleostearic acids, resulting in good yields of the expected addition products.

Some of the di-esters of the adducts and their hydrogenated derivatives, particularly the hydrogenated di-esters of *beta*-eleostearic acid adducts, have been found to be effective primary plasticizers for polyvinyl chloride.

Experimental

Butyl esters of alpha-tung oil fatty acids. Some 2.5 g. of freshly shaved metallic sodium were dissolved in 540 g. of *n*-butanol. To this solution were added 960 g. of *alpha*-tung oil, and the resulting mixture was heated on the steam cone for 4.5 hrs. with frequent shaking. After cooling and separation of the glycerol layer, the crude butyl esters were successively treated with two 500-ml. portions of water containing 7.5 ml. of concentrated hydrochloric acid. After water washing and drying over anhydrous sodium sulfate, the mixed butyl esters were freed from excess butanol by vacuum-stripping on the steam cone, employing a stream of carbon dioxide. Approximately 1 kg. of the mixed butyl esters was distilled through a short path colum. A fore-run of 42 g. was discarded, and a main fraction of 756 g. was collected at about 196°C./1.5-mm. pressure. This product contained 78% butyl eleostearates.

Reaction of beta-propiolactone with butyl alpha-eleostearate. The reaction mixture consisted of 642.4 g. of distilled butyl esters containing 501 g. of butyl eleostearate (1.50 moles), 112.4 g. of 97.5% pure *beta*-propiolactone[3] (1.55 moles), 0.60 g. of hydroquinone, and 1.10 g. of potassium carbonate. The reaction mixture, contained in a round bottom flask and magnetically stirred, was maintained at 200°C. for 1.5 hrs. under a blanket of carbon dioxide. In preliminary tests it was found that this temperature and time seemed to be optimum for the addition reaction.

Preparation of the di-n-butyl esters of the acrylic acid alpha-eleostearate adducts. The half-ester obtained from the above reaction was esterified directly in its reaction mixture by refluxing with 125 g. of *n*-butanol, 4.0 g. of *p*-toluenesulfonic acid catalyst, and 300 ml. of toluene. The 28 g. of water removed azeotropically indicated completion of the esterification reaction.

The reaction mixture was diluted with an equal volume of ether and washed with water (2 x 500 ml.), 5% sodium carbonate solution (3 x 500 ml.), and again with water (2 x 500 ml.). Following these operations, the excess butanol and ether were removed by vacuum-stripping with carbon dioxide on the steam cone, yielding 787 g. of the crude di-butyl esters.

These esters were fractionally distilled, using a short path column, and a total of 10 fractions was collected. The distillation temperatures and pressures ranged from 166°C./10 microns to 200°C./90 microns, with the main portion coming over at 183°C./15 microns. Refractive indices and saponification equivalents indicated that the unreacted mono-esters were collected in the first three fractions. Then 322 g. of a constant boiling fraction was collected.

Anal. Calculated for $C_{29}H_{50}O_4$: sap. equiv., 231.4; hydrogen-iodine value (7), 109.7. Found: sap. equiv., 233.1; hydrogen-iodine value, 111.9; acid value, 11.3.

Free dicarboxylic acids from acrylic acid—alpha-eleostearate adducts. A 92.5-g. portion (0.2 mole) of the distilled di-*n*-butyl esters of the acrylic acid—alpha-eleostearate adducts was saponified by refluxing with 500 ml. of 2 N aqueous sodium hydroxide solution. The liberated butanol was continuously removed from the refluxing solution by means of a modified Dean—Stark trap. After cooling, the alkaline solution was washed with ether for the removal of traces of butanol.

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[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

[3] *Beta*-propiolactone was obtained from the B. F. Goodrich Chemical Company, Cleveland, O.

The alkaline solution, after removal of dissolved ether, was stirred into 500 ml. of water containing 100 ml. of concentrated hydrochloric acid. Then 70 g. of liberated acids were obtained, which, after washing and drying, had a melting range of 89–94°C. These acids were taken up in 250 ml. of ether and subjected to fractional crystallization. Two crops were obtained, fraction A at 0°C. melting from 102–105°C. (13.5 g.), and fraction B at —20°C. melting from 80–85°C. (22.2 g.).

Fraction A was taken up in 80% ethanol (1:15) and fractionally crystallized at 25°C., 0°C., and —20° C. Fraction B was treated in a similar manner, and top and bottom fractions from each series having the same melting range were combined for further recrystallization. The high melting fraction (m.p. 109–110° C.) was recrystallized from 80% ethanol (1:10) at 25°C., yielding 8.6 g. of fraction C (m.p. 113°C.). This melting point remained unchanged on recrystallization from mixtures of pentane-chloroform and chloroform-dioxane.

Anal. Calculated for $C_{21}H_{34}O_4$ (m.p. 113°C.): C, 71.96; H, 9.78; neut. equiv., 175.2; hydrogen-iodine value, 144.8. Found: C, 72.01; H, 9.50; neut. equiv., 174.4; hydrogen-iodine value, 145.4.

The low melting fraction (m.p. 85–87°C.) was recrystallized from 80% ethanol (1:15) at —20°C., yielding 3.1 g. of fraction D (m.p. 85°C.). This melting point remained unchanged on recrystallization from a mixture of pentane-chloroform and from 75% methanol.

Anal. Calculated for $C_{21}H_{34}O_4$ (m.p. 85°C.): C, 71.96; H, 9.78; neut, equiv., 175.2; hydrogen-iodine value, 144.8. Found: C, 72.19; H, 9.50; neut. equiv., 174.9; hydrogen-iodine value, 145.9.

The ethereal mother liquor from which fractions A and B were obtained was evaporated to dryness. The vacuum-dried residue (34 g.) was a viscous, tacky material having some crystals dispersed throughout the mass. Repeated attempts to crystallize the material from ethanol and from pentane-chloroform solutions only resulted in the formation of a tacky, semisolid product.

Anal. Calculated for $C_{21}H_{34}O_4$: sap. equiv., 175.2; hydrogen-iodine value, 144.8; neut. equiv., 175.2. Found: sap. equiv. 174.3; hydrogen-iodine value, 137.3; neut. equiv., 202.3.

Butyl esters of beta-tung oil fatty acids. Some 1.25 g. of freshly shaved metallic sodium was dissolved in 270 g. of *n*-butanol. To this solution was added 480 g. of dry *beta*-tung oil, and the resulting mixture was heated on the steam cone 4 hrs. with frequent shaking. After cooling and separation of the glycerol layer, the crude butyl esters were treated with dilute acetic acid, then water-washed until acid free. After drying over anhydrous sodium sulfate, the mixed butyl esters were freed from excess butanol by stripping on the steam cone with carbon dioxide. Approximately 500 g. of the mixed butyl esters were distilled through a short path column. A fore-run of 50 g. was discarded, and a main fraction of 362 g. was collected at about 166°C./175 microns pressure. This product contained 75.1% butyl eleostearates.

Reaction of beta-propiolactone with butyl beta-eleostearate. The reaction mixture consisted of 327.7 g. of distilled butyl esters containing 246 g. of butyl *beta*-eleostearate (0.74 mole), 53.0 g. of 97.5% pure *beta*-propiolactone (0.74 mole), 0.30 g. of hydroquinone, and 0.54 g. of potassium carbonate. The reaction mixture, contained in a round bottom flask and magnetically stirred, was maintained at 200°C. for 1.5 hrs. under a blanket of carbon dioxide.

Preparation of the di-n-butyl esters of the acrylic acid-beta-eleostearate adducts. The half-ester obtained from the above reaction was esterified directly in its reaction mixture by refluxing with 63.2 g. of n-butanol, 150 ml. of toluene, and 2.6 g. of *p*-toluenesulfonic acid catalyst. The 13.4 g. of water removed azeotropically in a Dean-Stark trap indicated completion of the esterification reaction.

The reaction mixture was taken up in 300 ml. of ether and washed with water (3 x 350 ml.), 5% sodium carbonate (3 x 300 ml.), and again with water (2 x 300 ml.). The excess butanol and ether were removed by stripping with carbon dioxide on the steam cone, yielding 414 g. of the crude di-butyl esters.

These esters were fractionally distilled, using a short path column, and a total of eight fractions was collected. The constant boiling fractions (114 g.) distilled at 197°C./100 microns pressure.

Anal. Calculated for $C_{29}H_{50}O_4$: sap. equiv. 231.4; hydrogen-iodine value, 109.7. Found: sap. equiv., 237.7; hydrogen-iodine value, 112.6; acid value, 3.5.

Hydrogenation of the di-n-butyl esters of the acrylic acid adducts of alpha- and of beta-eleostearic acids. Next, 100 g. samples of each of the distilled di-n-butyl esters were hydrogenated without solvent, using 2.0 g. of 10% palladium-carbon catalyst in a Parr hydrogenation apparatus.[4] The hydrogenation was initiated at room temperature and approximately two atmospheres pressure, and the temperature was raised gradually and finally maintained at 150°C. near the end of the reaction. The reduction (100% absorption) of the *alpha*-adducts was completed in about 50 hrs. while reduction of the *beta*-adducts required only about 12 hrs. for completion. The hydrogenated products were filtered free of catalyst and found to be colorless liquids of low viscosity.

Anal. Acid value: *alpha*-adduct, 12.0; *beta*-adduct, 3.6.

Preparation of the di-ethyl esters of the acrylic acid-alpha- and beta-eleostearate adducts. The di-ethyl esters were prepared in a manner similar to that described for the preparation of the di-butyl esters. *Alpha-* and *beta*-tung oils were subjected to ethanolysis, followed by adduction with *beta*-propiolactone, and subsequent esterification of the half esters with ethanol.

The constant boiling fraction of the di-ethyl esters of the *alpha*-eleostearate-acrylic acid adducts distilled at about 180°C./145 microns.

Anal. Calculated for $C_{25}H_{42}O_4$: sap equiv., 203; hydrogen-iodine value, 124.8. Found: sap. equiv., 208; hydrogen-iodine value, 125.7; acid value, 9.9.

The constant boiling fraction of the di-ethyl esters of the *beta*-eleostearate-acrylic acid adducts distilled at 184°C./180 microns.

Anal. Calculated for $C_{25}H_{42}O_4$: sap. equiv., 203; hydrogen-iodine value, 124.8. Found: sap. equiv., 208; hydrogen-iodine value, 127.3; acid value, 0.5.

Hydrogenation of the diethyl esters of the acrylic acid adducts of alpha- and beta-eleostearic acids. The diethyl esters were hydrogenated in a manner similar

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[4] The mention of this and other commercial products does not imply endorsement or recommendation by the Department of Agriculture over others having similar properties but are mentioned as part of the exact experimental conditions used in the work being reported.

to that described for hydrogenation of the dibutyl esters. Reduction of the *alpha*-adducts was completed in about 50 hrs. while reduction of the *beta*-adducts required 31 hrs. for completion. As in the case of the dibutyl esters, it was again noted that the *beta*-isomer hydrogenated more rapidly than did the *alpha*-isomer.

Preparation of the di-2-ethylhexyl esters of the acrylic acid-alpha-eleostearate adducts. The di-2-ethylhexyl esters were prepared by esterification of the corresponding free dicarboxylic acids in toluene solution, using 2-ethylhexanol and *p*-toluenesulfonic acid catalyst. The liberated water was removed by means of a Dean-Stark trap. The esters were worked up in the usual manner and finally bleached with a mixture of carbon and clay.

Anal. Calculated for $C_{37}H_{66}O_4$: hydrogen-iodine value, 88.3. Found: hydrogen-iodine value, 89.3; acid value, 0.7.

Infrared spectra. All spectra were obtained with a Model 21–Perkin and Elmer Double Beam Automatically Recording Infrared Spectrophotometer.[4] Samples were measured in chloroform solutions against pure chloroform in the comparison beam. The concentration of the *beta*-propiolactone solution was 23.90 g. per liter. The concentrations of all other solutions ranged from 30 to 40 g. per liter. The slit and gain programming, Resolution Dial 915, Response 2, Gain 7, Speed 4, and Suppressed 2, was used in obtaining all curves.

Plasticizer screening. The esters were compounded for testing purposes according to the following basic formulation:

Resin (polyvinyl-chloride-polyvinyl-acetate copolymers Vinylite VYDR)	63.5%
Plasticizer	35.0%
Stearic acid	0.5%
Basic lead carbonate	1.0%

These formulations were milled and molded at 310°F. The detailed procedures followed in these operations as well as the preparation of the test specimen and the various tests have been previously described (5).

Results and Discussion

Infrared Spectra and Reaction Mechanism. The spectra of *alpha*- and *beta*-tung oils (1) are characterized by four very strong bands: the C—H stretching vibration at about 3.33 microns, a C—O stretching of the glyceride at about 8.55 microns, the C—H deformation about a *trans-trans* conjugated system at 10.04 microns, and a band at about 5.75 microns, arising from the C═O stretching of the ester group. *Beta*-propiolactone (Figure 1A) exhibits the C—H stretching bands between 3.35 and 3.45 microns. In addition, this molecule exhibits very intense, characteristic bands with maxima at 5.4 to 5.5 microns, arising from C═O stretching on the four-membered lactone ring; at about 9.0 microns, assigned to a C—O stretching band; and at 10.94 and 11.40 microns, due to four-membered oxygen ring vibrations.

The spectra of the reaction mixtures before heating (Figures 1B and 1D) exhibit all these bands characteristic of the butyl eleostearate and *beta*-propiolactone. After heating (Figures 1C and 1E), the formation of an adduct is indicated by complete disappearance of the 10.04 micron band characteristic of the conjugated unsaturation of the tung oils, and of the 5.4–5.5 micron, 9.0 micron, and 10.9 and 11.4 micron bands characteristic of the lactone ring moiety of *beta*-propiolactone.

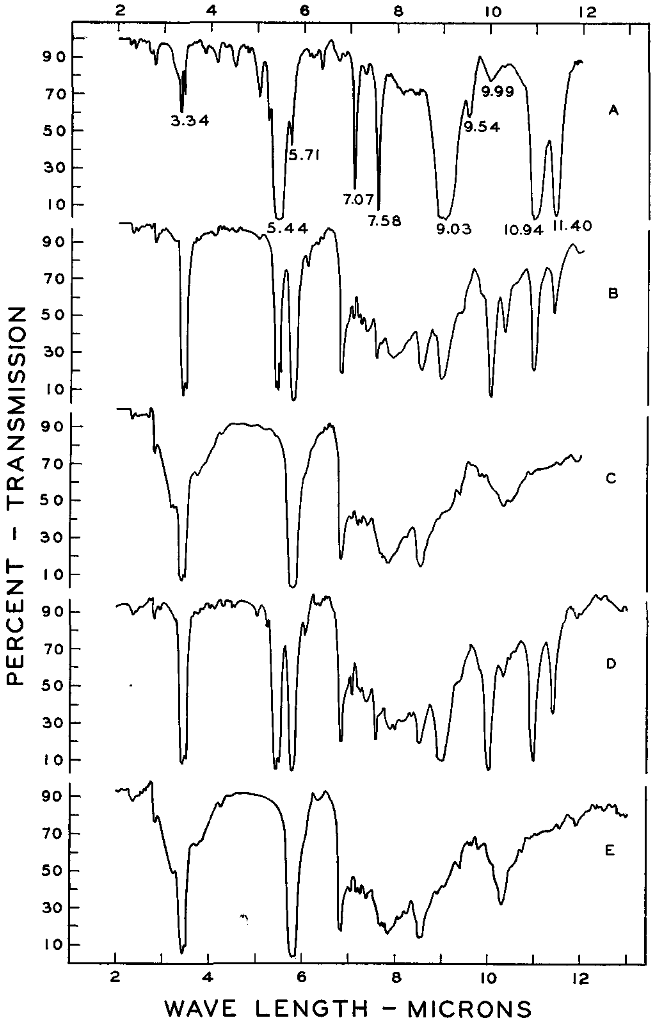


FIG. 1

A. *Beta*-propiolactone.

B. Reaction mixture butyl esters of *alpha*-tung oil acids and *beta*-propiolactone before heating.

C. Reaction mixture butyl esters of *alpha*-tung oil acids and *beta*-propiolactone after heating.

D. Reaction mixture butyl esters of *beta*-tung oil acids and *beta*-propiolactone before heating.

E. Reaction mixture butyl esters of *beta*-tung oil acids and *beta*-propiolactone after heating.

The infrared spectra of the distilled diethyl and di-n-butyl esters of the acrylic acid—*alpha*-eleostearate adducts (Figures 2A and 3A) and of the distilled diethyl and di-n-butyl esters of the acrylic acid—*beta*-eleostearate adducts (Figures 2B and 3B), like those of the reaction mixtures after heating, exhibit none of the bands characteristic of the unreacted tung oil or *beta*-propiolactone. As shown in Figures 2B and 3B, the spectra of the *beta*-eleostearate adducts reveal a sharp strong band with maximum at 10.32 microns, characteristic of the isolated *trans* bond. The spectra of the *alpha*-eleostearate adducts (Figures 2A and 3A) exhibit only a very weak band at this wavelength, indicating only slight *alpha* to *beta* isomerization. Analysis of the butyl esters of the *alpha*-tung oil fatty acids by means of ultraviolet absorption (6) indicated about 5% *beta*-isomer. The corresponding ethyl esters contained only 0.5% *beta*-isomer. The presence of the band at 10.32 microns in the spectra

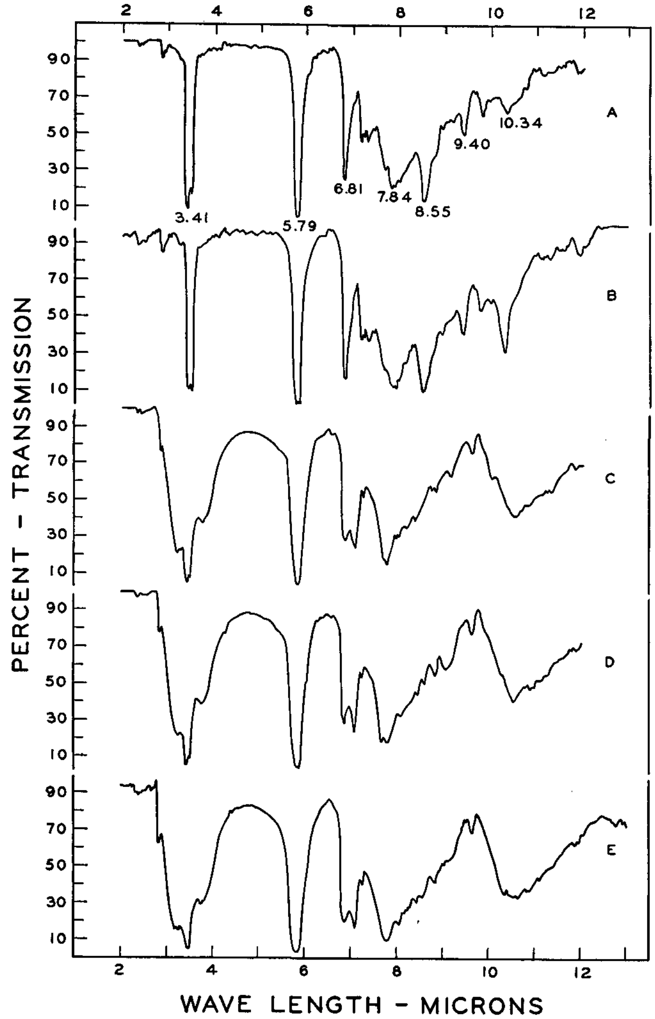


FIG. 2

A. Di-n-butyl esters of the acrylic acid—*alpha*-eleostearic acid adducts.

B. Di-n-butyl esters of the acrylic acid—*beta*-eleostearic acid adducts.

C. Acrylic acid—*alpha*-eleostearic acid adduct (m.p. 85°C.).

D. Acrylic acid—*alpha*-eleostearic acid adduct (m.p. 113°C.).

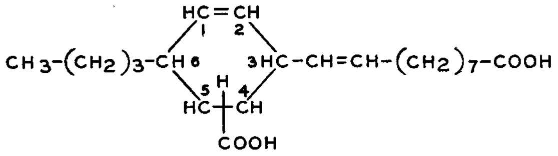
E. Non-crystallizable dicarboxylic acid adducts.

of the *beta*-eleostearate adducts and not in that of the *alpha*-eleostearate adducts is consistent with the known structures of these two eleostearic acids (1, 8).

The spectra of the di-n-butyl esters of the acrylic acid-eleostearate adducts (Figures 2A and 2B) exhibit bands with maxima at 9.40, 9.80, 11.08–11.18, and 11.50 microns, not found in the spectra of the compounds before reaction. The spectra of the diethyl esters reveal comparable bands with maxima at 9.10, 9.70, 11.00–11.10, and 11.60 microns. The spectra of cyclohexene exhibits four strong bands with maxima at 9.64, 9.92, 10.90–11.06, and 11.41 microns, arising from C—H deformations about the ring or from symmetrical "breathing" vibrations of the entire ring (1). The bands at about 9.40 microns and 9.80 microns and at about 9.10 and 9.70 microns in the spectra of the adducts are very strong and can probably be assigned to C—H deformation vibrations about the highly substituted cyclohexene ring. The bands at about 11.0 and 11.5–11.6 microns are considerably weaker and may be "breathing" vibrations of this highly substituted ring.

The spectra of the completely hydrogenated diethyl esters of the acrylic acid-eleostearic acid adducts are shown in Figures 3C and 3D. The spectra are almost identical with those of the adducts before hydrogenation. The very weak bands at about 6.00 microns (C=C stretching) in the spectra of both adducts have completely disappeared in the spectra of the hydrogenated samples. The strong band in the spectra of the *beta*-eleostearate adduct at 10.32 microns (C—H bending about a C=C) has, also as expected, completely disappeared in the spectra of the hydrogenated product.

In the light of a) the known structures of *alpha*- and *beta*-eleostearates and the infrared spectra of their maleic anhydride adducts (1, 8), b) the generally accepted fact that Diels-Alder reactions more readily attack a *trans-trans* conjugated pair than a *cis-trans* conjugated pair (1, 8), and c) the above discussions of the infrared spectra, it can be concluded that Diels-Alder adducts are formed between *beta*-propiolactone and *alpha*- and *beta*-eleostearic acids and that the most probable configuration of the *alpha*-eleostearic acid adduct is:

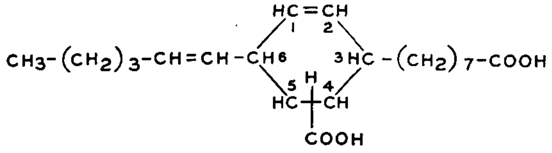


$$\begin{array}{c} \mathrm{HC{=}CH} \\ \mathrm{CH_3{-}(CH_2)_3{-}CH^{6}} \quad \mathrm{{}^{3}HC{-}CH{=}CH{-}(CH_2)_7{-}COOH} \\ \mathrm{HC{-}CH} \\ \mathrm{COOH} \end{array}$$

The carboxyl group on the cyclohexene ring may be attached to either the No. 4 or No. 5 carbon atom. The exocyclic double bond is *cis*, as shown by the absence of a strong band in the infrared spectra of the adduct at 10.32 microns. This is consistent with the known structure of eleostearic acid.

Bruson and Niederhauser (2) report a similar configuration for an acid melting at 110°C., which was isolated from an isomeric mixture of acids obtained from the reaction of ethyl acrylate with tung oil.

As *beta*-eleostearic acid has two possible *trans-trans* conjugated pairs of ethylenic bonds, like maleic anhydride, the *beta*-propiolactone may add acrosss the 9, 10 and 11, 12 pair or across the 11, 12 and 13, 14 pair. The adducts will therefore very probably be mixtures of the above structure and:



$$\begin{array}{c} \mathrm{HC{=}CH} \\ \mathrm{CH_3{-}(CH_2)_3{-}CH{=}CH{-}CH^{6}} \quad \mathrm{{}^{3}HC{-}(CH_2)_7{-}COOH} \\ \mathrm{HC{-}CH} \\ \mathrm{COOH} \end{array}$$

with the exocyclic double bond a *trans* bond, consistent with the known structure of *beta*-eleostearic acid and with the observed spectra of the *beta*-eleostearic acid-acrylic acid adducts. Again the carboxyl group on the cyclohexene ring may be attached to either the carbon atom No. 4 or No. 5.

In Figures 2C and 2D are shown the infrared spectra of the free dicarboxylic acids obtained from the di-n-butyl esters of the acrylic acid—*alpha*-eleostearate adducts. Two free dicarboxylic acids were obtained from the acrylic acid — *alpha*-eleostearate adducts, one melting at 85°C. and the other at 113° C. A reasonable postulation for the appearance of two acid adducts is that one is represented by the first configuration with the carboxyl on the No. 4

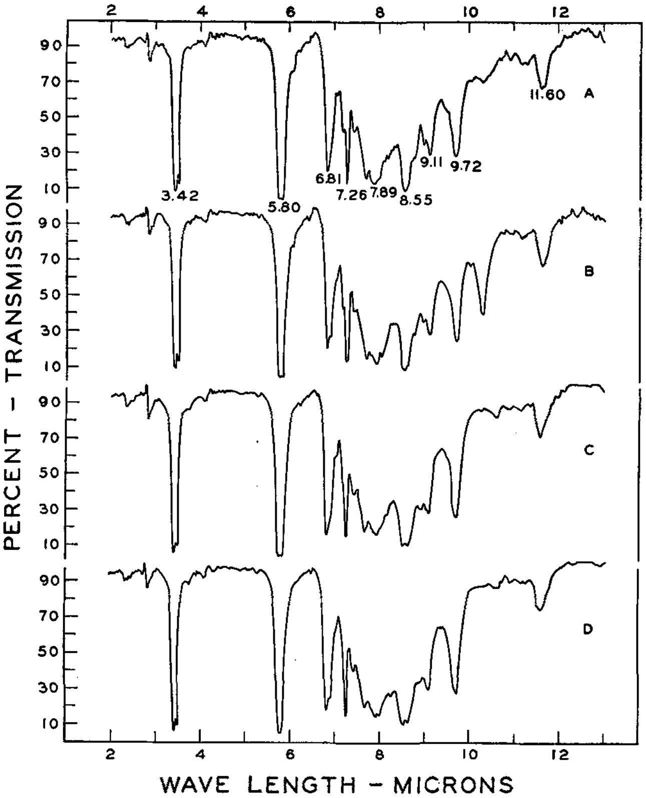


Fig. 3

A. Diethyl esters of the acrylic acid—*alpha*-eleostearic acid adducts.

B. Diethyl esters of the acrylic acid—*beta*-eleostearic acid adducts.

C. Hydrogenated diethyl esters of the acrylic acid—*alpha*-eleostearic acid adducts.

D. Hydrogenated diethyl esters of the acrylic acid—*beta*-eleostearic acid adducts.

position, the other by the same formula with the carboxyl group on the No. 5 carbon atom. The infrared spectra of these two compounds (Figs. 2C and 2D) are nearly identical, consistent with this postulation, as substitution of the COOH group on either the No. 4 or No. 5 position would not be expected to greatly influence the infrared absorption spectra.

Figure 2E represents the spectra of a third acid fraction which is non-crystallizable but which analyzes correctly for the first configuration with the correct "saponification equivalent" for this compound. However neither the hydrogen iodine value nor the neutral equivalent are in agreement with this configuration. The infrared spectra of this fraction very closely resembles those of the two free carboxylic acid adducts and affords no clue to explain the anomalous hydrogen-iodine value or neutral equivalent.

Plasticizer tests. The results of the plasticizer screening tests are reported in Table I. It is apparent that the di-esters 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, di-2-ethylhexyl phthalate (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, but it shows little or no consistent influence on the other plasticizing characteristics of these materials.

The data available are insufficient to establish definite trends in compatibility. However, the unhydrogenated *alpha*-derivative is much better than either the corresponding *beta*-derivative or the hydrogenated *alpha*-derivative. On the other hand, hydrogenation has resulted in an improvement of the *beta*-derivative. There seems to be little promise of any success with higher esters in view of the gross incompatibility of the di-2-ethylhexyl ester tested. While the compatibilities observed for many of these adducts are not all that would be desired, they show marked improvement over the original unadducted butyl eleostearate esters. Blends with DOP may be warranted for those adduct esters which excel in low-temperature characteristics.

Any explanation as to why the *beta*-derived plasticizers impart more satisfactory brittle points will at best be inconclusive since the adduct products of either the *alpha*- or *beta*-eleostearic acids are complex mixtures. However, since the *beta*-adduct presumably

TABLE I

Plasticizing Characteristics of Diesters of Acrylic Acid—Eleostearic Acid Adducts

Plasticizer	Tensile Strength P.S.I.	100% Modulus P.S.I.	Elongation %	Brittle Point °C.	Volatility Loss[a] %	Compatibility (days)[b]
alpha-Eleostearic Acid Adducts:						
Diethyl Esters	2900	1710	280	—35	0.57	113+
Hydrogenated Diethyl Esters	2970	1720	310	—35	0.16	113+
Dibutyl Esters	2780	1780	260	—31	0.72	263+
Hydrogenated Dibutyl Esters	2690	1890	240	—29	0.32	15
Di-2-Ethylhexyl Esters		Incompatible on Mill				
beta-Eleostearic Acid Adducts:						
Diethyl Esters	2990	1620	310	—39	0.40	15
Hydrogenated Diethyl Esters	2960	1680	300	—37	0.10	113+
Dibutyl Esters	2800	1810	260	—43	0.42	15
Hydrogenated Dibutyl Esters	2740	1770	240	—43	0.14	196+
Control DOP	3040	1620	320	—32	0.32	

[a] Activated carbon test ASTM D 1203–52T.

[b] + indicates no exudation during time specified.

consists of four isomers, two of which are not likely to be found in adducts of the *alpha*-acid, it would seem probable that the better performance of the *beta*-derived compounds results from the presence of these two additional isomers.

Summary

Beta-propiolactone has been employed as the dienophile component in the Diels-Alder reaction with *alpha*- and *beta*-eleostearates, yielding acrylic acid adducts. Catalytic amounts of potassium carbonate were used to induce polymerization of *beta*-propiolactone to a polyester and to assist in its pyrolysis to acrylic acid.

The ethyl and *n*-butyl esters of the mixed fatty acids of *alpha*- and of *beta*-tung oil, containing about 75% eleostearates, were reacted with the theoretical amount of *beta*-propiolactone at 200°C. for a period of 1.5 hrs. Spectral analyses indicated nearly quantitative conversion of the reactants to the expected Diels-Alder products.

The acrylic acid adducts were esterified in their reaction mixtures with the appropriate alcohols to produce the corresponding di-esters. These esters were purified by means of high vacuum distillation.

Fractional crystallization of the free acids obtained by saponification of the di-butyl esters of the *alpha*-eleostearic acid adducts yielded two isomeric dicarboxylic acids, melting at 113°C. and 85°C. These isomers differ only in the position of the carboxyl group on the cyclohexene nucleus of the adduct.

The di-ethyl and di-butyl esters of both the *alpha*- and *beta*-eleostearic acid adducts and their hydrogenated derivatives have been intercompared as primary plasticizers for vinyl type resins. The hydrogenated di-esters of the *beta*-eleostearic acid adducts were found to be the most effective.

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Letter to the Editor

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In two current articles (1, 2) it has been claimed that diacetylenic compounds could not be prepared by dehydrobromination of tetrabromostearic acids. The reason was attributed to some side reactions caused by sodamide on diacetylenic substances in liquid ammonia (2).

It would be interesting for Journal readers to know that the dehydrobromination of tetrabromostearic acid has been previously studied, revealing a number of difficulties (3). Our recent investigations (4) have adduced evidences for the stepwise ionic mechanism of polymerization reactions involved in this dehydrobromination of polybromides. Polymerization possibly occurs in steps, prior to formation of acetylenic derivatives.

Other studies on acetylenic compounds (5) may throw light on side reactions that may be caused by sodamide in liquid ammonia and offer suggestions for future investigations.

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N. A. Khan
Department of Physiology
University of Minnesota
Minneapolis, Minn.