

In order to obtain reproducible results from day to day, it is extremely important that the chromatographic jar be emptied once every two or three days in order to avoid contamination of the chamber with moisture. It is further necessary to prepare the impregnating solvent mixture and the heptane-methanol solution fresh before use. The ethylene glycol and the methyl alcohol should be free from moisture, other-

matographic system has been described. Whatman No. 1 filter paper was impregnated with ethylene glycol-methanol (1:4, v/v), and n-heptane saturated with methanol was used as a developing solvent. Complete separation was achieved in 3 hrs. It has been shown that the method can also be used for the separation of 2,4-dinitrophenylhydrazone derivatives of ketones.

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TABLE V

Effect of Variation in Amount of Impregnating Agent on Rf Values

Mixture of 2,4-dinitrophenyl-hydrazones	Rf values <sup>a</sup>		
	Ethylene glycol, % in methanol		
	10	20	30
Methanal.....	0.30	0.22	0.18
Ethanal.....	0.45	0.38	0.35
n-Butanal.....	0.75	0.70	0.67

<sup>a</sup> Based on averages of 3 paper strips.

wise the spots have a tendency to streak. In the separation and identification of unknown compounds, a mixture of known compounds should be run simultaneously on the same paper. The sensitivity of this chromatographic system is shown by efficient separation of compounds having close Rf values.

## Summary

A rapid method of separating the 2,4-dinitrophenylhydrazones of C<sub>1</sub> to C<sub>9</sub> aldehydes by descending chro-

## The Reaction of Methyl Vinyl Ketone with alpha- and beta-Eleostearic Acids

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IN CONTINUING the exploration of the scope of the Diels-Alder reaction of *alpha*- and *beta*-eleostearic (9,11,13-octadecatrienoic) acids (1, 2, 3), we have now investigated the suitability of methyl vinyl ketone as a dienophile for these conjugated acids. The prior literature appears to contain only a single reference to the use of methyl vinyl ketone as a dienophile for conjugated fatty acids, in which a cursory examination was made of its reaction with *trans,trans*-9,11-octadecadienoic acid (4). It seemed of interest therefore to evaluate the dienophilic activity of methyl vinyl ketone with both *alpha*- and *beta*-eleostearic acids.

This communication presents an account of the reaction of methyl vinyl ketone with the eleostearic acids as well as certain considerations regarding the structures of the resultant adducts.

## Experimental

## Starting Materials

**Methyl Vinyl Ketone.** This material, supplied by Chas. Pfizer and Company, was used without further purification.

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***beta*-Eleostearic Acid.** Pure *beta*-eleostearic acid was prepared by the low-temperature fractional crystallization of the mixed fatty acids obtained from isomerized tung oil (5). The acid, m.p. 71–72°C., had an absorptivity, (a) = 201.8 at 269.0 millimicrons in cyclohexane.

**The Methyl Esters of Tung Oil Fatty Acids.** These esters were prepared by methanolysis of *alpha*-tung oil, employing sodium methylate catalyst as described in a previous publication (6). This material, boiling range 152–155°C./5 microns, contained 82% *alpha*- and 3% *beta*-methyl eleostearates.<sup>2</sup>

**Preparation of Methyl Vinyl Ketone-Methyl *alpha*-Eleostearate Adduct.** Approximately 100 g. of the methyl esters of tung oil fatty acids (ca. 0.25 mole methyl *alpha*-eleostearate), 50 g. of methyl vinyl ketone (ca. 0.70 mole), and 100 ml. of benzene were heated at 150°C. in a 325-ml., sealed stainless steel bomb for 16 hrs. Benzene and the excess methyl vinyl ketone were removed by vacuum-stripping on a steam bath, employing a stream of carbon dioxide as a sweep gas. Approximately 130 g. of the crude product were obtained, which had only 2.7% of unreacted eleostearates. High-vacuum distillation of this

<sup>2</sup> The amount of eleostearates present was determined by the method of Hoffmann *et al.* (5).

material, employing a short path column, yielded 81 g. of the methyl vinyl ketone-methyl *alpha*-eleostearate adduct with a boiling range 171–175°C./5 microns.

*Anal.* Calcd. for  $C_{23}H_{38}O_3$ : C, 76.22; H, 10.57;  $OCH_3$ , 8.56; carbonyl O, 4.42. Found: C, 76.22; H, 10.59;  $OCH_3$ , 8.44; carbonyl O, 4.34;  $n^{20/D}$ , 1.4838.

*Preparation of Methyl Vinyl Ketone-Methyl beta-Eleostearate Adduct.* An 80.6-g. sample of pure *beta*-eleostearic acid (0.29 mole), 44.2 g. of methyl vinyl ketone (0.63 mole), 100 ml. of benzene, and 0.5 g. of hydroquinone were heated at 150°C. in a 325-ml., sealed stainless steel bomb for 16 hrs. Benzene and the unreacted methyl vinyl ketone were removed by vacuum-stripping on a steam cone, employing carbon dioxide as a sweep gas. The crude product weighing 125.9 g. was dissolved in 1,000 ml. of methanol containing 5 ml. of concentrated sulfuric acid, and the solution was refluxed for 16 hrs. After removal of 500 ml. of methanol by distillation, the remaining solution was diluted with 1,000 ml. of water and extracted three times with 400-ml. portions of ether. The ether extract was washed three times with 300-ml. portions of a 5% sodium carbonate solution and three times with 300-ml. portions of water. After drying over anhydrous sodium sulfate, the ether was evaporated, and the residue (106.1 g.) was fractionally distilled under high vacuum, yielding 78.6 g. of the methyl *beta*-eleostearate adduct with a boiling range 170–173°C./5 microns.

*Anal.* Calcd. for  $C_{23}H_{38}O_3$ : C, 76.22; H, 10.57;  $OCH_3$ , 8.56; carbonyl O, 4.42. Found: C, 76.21; H, 10.60;  $OCH_3$ , 8.51; carbonyl O, 4.41;  $n^{20/D}$ , 1.4821. Absorptivity, (a) = 0.365 at 10.3 microns in  $CS_2$ .

*Hypobromite Oxidation of the Methyl Vinyl Ketone-Methyl alpha-Eleostearate Adduct.* Oxidation of the acetyl group of the adduct to a carboxyl group was effected by treatment of the sodium salt derived from the methyl vinyl ketone-methyl *alpha*-eleostearate adduct with an alkaline sodium hypobromite solution. A 2.86 N solution of sodium hypobromite was prepared by the slow addition of 28 ml. (87.5 g.) of bromine to a stirred solution of 80.0 g. of sodium hydroxide in 200 ml. of water, which was maintained at 0–10°C. A 36.5-g. sample of the adduct (0.10 mole) was saponified with 8.0 g. of sodium hydroxide in 175 ml. of water. This solution was added dropwise over a 30-min. period to 300 ml. of the sodium hypobromite solution (0.43 mole), which was rapidly stirred and maintained at 25°C. The reaction mixture was kept at 25°C. for an additional hour, after which the temperature was raised to 60°C. and the stirring continued for 2 hrs. On cooling to room temperature, the evolved bromoform was extracted with three 100-ml. portions of chloroform, and the excess sodium hypobromite (0.012 mole) was destroyed by treatment with sulfur dioxide gas. The aqueous solution was then acidified with 96 ml. of concentrated hydrochloric acid (2.5 mole), and the organic material was extracted with three 150-ml. portions of ether. The ethereal solution was repeatedly washed with 100-ml. portions of water until free of mineral acid and then dried over anhydrous sodium sulfate. On evaporation of the ether, 35.3 g. of a semisolid material was recovered, neut. equiv., 205.7. Several recrystallizations of this material from 80% ethanol at –20°C. yielded 7.0 g. of fine white crystals, m.p. 88.5–89.0°C.

*Anal.* Calcd. for  $C_{21}H_{34}O_4$ : C, 71.96; H, 9.77; neut. equiv., 175.24. Found: C, 71.70; H, 9.81; neut. equiv., 175.0.

*Aromatization-Oxidation of the Methyl Vinyl Ketone-Methyl alpha-Eleostearate Adduct.*<sup>3</sup> A mixture consisting of 27.1 g. of the adduct (0.075 mole) dissolved in 600 ml. of carbon tetrachloride and 133.5 g. of N-bromosuccinimide (0.75 mole) was heated at reflux for 6 hrs. The solution was cooled and allowed to stand over-night at room temperature. At this time 80.0 g. (theoret., 87.1 g.) of solid succinimide was filtered off and rinsed with fresh carbon tetrachloride. The combined filtrates were evaporated to dryness. The brominated material was dissolved in 200 ml. of N,N-diethylaniline and heated at 130°C. under a nitrogen atmosphere for 2 hrs. After cooling, the semisolid reaction mixture was dispersed in 1,000 ml. of water and extracted five times with 200-ml. portions of ether. The ether extract was washed with four 200-ml. portions of water and finally dried over anhydrous sodium sulfate. Evaporation of the solvent yielded 15.2 g. of the aromatized adduct, absorptivity, (a) = 50.52 at 265 millimicrons in ethanol. A 3.0-g. sample of this material was saponified by heating under reflux for 1 hr. with 100 ml. of water containing 3.0 g. of potassium hydroxide. During the following period of 2 hrs. 50.0 g. of powdered potassium permanganate were slowly added to this solution at a near reflux temperature. After an additional 5 hrs. of heating the excess permanganate was destroyed by the addition of 10 ml. of ethanol, and the solution was filtered while hot. The solid was extracted with two 100-ml. portions of boiling water. The combined filtrates were acidified with 40.0 ml. of concentrated hydrochloric acid, and the volume was reduced to 150 ml. by distillation. This solution was continuously extracted with ether for 24 hrs. in an efficient liquid-liquid extractor. On evaporation of the ether 0.2 g. of the oxidation product was recovered.

*Chromatography of the Oxidation Product.* Approximately 0.2-g. samples, accurately weighed, of the oxidation product and of authentic trimellitic acid were each dissolved in 5.0 ml. of distilled water. One-ml. aliquots of each of these solutions were separately chromatographed on columns prepared by the procedure described by Marvel and Rands (8), employing 20 g. of dry silicic acid, 11.5 ml. of water, and 80 ml. of chloroform. The acids were eluted with successive 100-ml. portions of chloroform solutions saturated with water containing 0, 5, 10, and 15% of *n*-butanol. The eluate was collected in 10-ml. fractions, diluted with 10 ml. of absolute ethanol, and titrated with standard 0.0255 N aqueous sodium hydroxide to the phenolphthalein end-point. The chromatograms of authentic trimellitic acid and the oxidation product each exhibited peak effluent volumes of 295 ml. Trimellitic acid was recognized in the oxidation product by the occurrence of a single major peak in a chromatogram obtained on a mixture consisting of the oxidation product and a known quantity of authentic trimellitic acid.

*Solid Isomer of the Methyl Vinyl Ketone-Methyl alpha-Eleostearate Adduct.* A 100-g. sample of the adduct was maintained at 5°C. over a period of two months, during which time 30 g. of a solid material

<sup>3</sup>The method of A. L. Clingman *et al.* (7) was modified for this aromatization procedure by increasing the amounts of N-bromosuccinimide and N,N-diethylaniline, by extending the time of reaction and by increasing the temperature of the reaction.

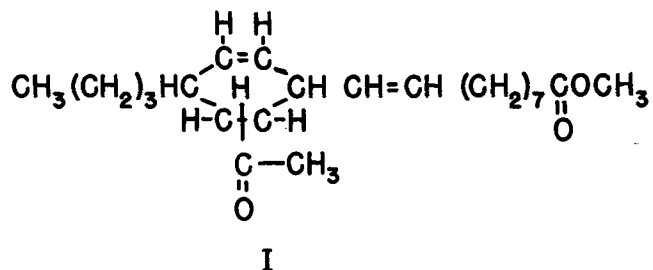
separated, m.p. 30–32°C. Several recrystallizations from petroleum ether (1 g./5 ml.) yielded 15 g. of white needle-like crystals, whose melting point remained unchanged upon further recrystallization from either ethyl ether or 95% ethanol, m.p. 36.5–37.0°C.

*Anal.* Calcd. for  $C_{23}H_{38}O_3$ : C, 76.22; H, 10.57; carbonyl O, 4.42. Found: C, 76.12; H, 10.53; carbonyl O, 4.39. This isomer gave a semicarbazone, which was recrystallized from 80% ethanol to a constant melting-point, m.p. 111.0°C.

*Anal.* Calcd. for  $C_{24}H_{41}N_3O_3$ : C, 68.75; H, 9.78; N, 10.02. Found: C, 68.71; H, 9.71; N, 9.98.

### Discussion

It is well known that under mild conditions the Diels-Alder reaction of conjugated fatty acids proceeds with the formation of substituted cyclohexene compounds by the addition of the dienophile across *trans,trans*-ethylenic bonds only (9, 10). Thus the expected product from the reaction of methyl vinyl ketone with *alpha*-eleostearic (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic) acid would consist of two positional isomers, 10-[5(6)-acetyl-4-*n*-butyl-2-cyclohexene-1-yl]-*cis*-9-decenoic acid (I), differing only in the position of the acetyl group on the ring. Since there



are two positions open for dienophilic attack in the *beta*-eleostearic (*trans*-9, *trans*-11, *trans*-13-octadecatrienoic) acid, it follows that four positional isomers would result from the addition of methyl vinyl ketone to this acid.

It was found that both *alpha*- and *beta*-eleostearates react smoothly with methyl vinyl ketone under the conditions described above, producing nearly quantitative yields of adducts as judged by the disappearance of the triene conjugation in the reaction mixtures. In early experiments hydroquinone was employed as a stabilizer during the reaction of methyl *alpha*-eleostearate. However its use was discontinued in later experiments because the adducts formed in its presence showed considerable absorption at 10.3 microns, indicating the presence of an isolated *trans*-ethylenic bond. Apparently hydroquinone at elevated temperatures may act as an isomerization catalyst for the conversion of eleostearates from the *alpha* to the *beta* form. Since these reactions were carried out at higher temperatures and pressures than those usually employed in the addition of fatty acids, evidence was desired concerning the constitution of the resulting compounds. To obtain this information, the methyl vinyl ketone-methyl *alpha*-eleostearate adduct was subjected to quantitative hydrogenation, aromatization-oxidation, hypobromite oxidation, and fractional crystallization.

Quantitative hydrogenation experiments were per-

formed on the adducts to determine the amount of unsaturation present. When palladium-carbon was employed as a catalyst, it was observed that the theoretical amount of hydrogen required for the complete saturation of the two expected ethylenic bonds was absorbed. In an experiment employing Adam's catalyst sufficient hydrogen was absorbed to reduce the carbonyl group to a secondary alcohol as well as to saturate the ethylenic linkages. It has been observed previously (11) that carbonyl compounds can be readily reduced to alcohols by the use of Adam's catalyst.

Preliminary studies showed that the methyl vinyl ketone-methyl *alpha*-eleostearate adduct is remarkably resistant to dehydrogenation or disproportionation under conditions which produce both results in the maleic anhydride-*beta*-eleostearic acid adduct. The action of palladium-carbon catalyst on the latter adduct in xylene resulted in the loss of the exocyclic *trans*-ethylenic bond with attendant aromatization and disproportionation (12, 13). However, under identical conditions as well as without a solvent at 210°C., the methyl vinyl ketone-methyl *alpha*-eleostearate adduct was entirely unaffected, as indicated by infrared and ultraviolet spectra. Aromatization was finally achieved, establishing the presence of a 6-membered unsaturated ring in the original adduct, by the bromination-dehydrobromination procedure as well as by the use of palladium-carbon catalyst with nitrobenzene as a hydrogen acceptor (14). Since the permanganate oxidation of the aromatized adduct resulted in the formation of trimellitic acid (1,2,4-tricarboxybenzene), it follows that the unsaturated ring of the original adduct contained three substituents in the positions required by the structure of the expected Diels-Alder adduct.

The presence of an acetyl group in the adduct has been confirmed by the selective oxidation of this moiety to a carboxyl group employing the alkaline hypobromite oxidation procedure. This type of oxidation is known to convert unsaturated methyl ketones to the corresponding acids (15). Fractional crystallization of the mixed acids obtained by the oxidation of the adduct yielded a product which appeared to be identical with the mixture of isomers of the acrylic acid adduct obtained previously from the reaction of propiolactone with *alpha*-eleostearic acid (1).

The occurrence of the two positional isomers in the reaction product of methyl vinyl ketone-methyl *alpha*-eleostearate was demonstrated by the separation of the adduct into solid and liquid fractions. The solid product appears to be a pure isomer, as indicated by chemical analyses and the constancy of its melting point. Presumably the liquid fraction obtained contains a high concentration of the other positional isomer.

On the basis of the above observations and considerations, carried out on *alpha*-eleostearate adduct, it may be concluded that methyl vinyl ketone reacts with the eleostearates to yield normal Diels-Alder addition products.

### Summary

Methyl vinyl ketone was found to be an active dienophile for the modification of the eleostearate

moiety of tung oil by means of the Diels-Alder reaction. Moderate quantities of methyl vinyl ketone-methyl *alpha*- and methyl *beta*-eleostearate adducts have been prepared in good yields. A portion of the former material has been subjected to aromatization and selective oxidation in establishing a proof that the reaction proceeds by the Diels-Alder addition. A sample of the methyl vinyl ketone-methyl *alpha*-eleostearate adduct has been fractionally crystallized and one of its two positional isomers isolated in pure form. A semicarbazone derivative of this isomer has also been prepared.

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## An Extrapolation Procedure for Determining Solubilities of Mixtures

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**D**IFFERENCES in solubility form the basis for the resolution of many complex mixtures of chemical compounds into simpler ones. In some cases the solubility characteristics of the substances present are so different that the desired separation can be achieved by exhaustive extraction with an appropriate solvent. Methods for the determination of fat in cereals and of volatile oils in spices are well-known examples. In other cases however the constituents of the mixture have such similar solubility characteristics that exhaustive extraction results in the dissolution of the entire mixture. Clear-cut separations are not obtainable, and it is impossible to establish a value for the percentage of the more soluble fraction without resorting to purely arbitrary criteria for the amounts of solvent and sample used. The percentages of natural waxes which will dissolve in a certain solvent have been determined in this manner (1, 2).

The solubilities of natural waxes also have been expressed in terms of the grams of wax which will dissolve in 100 g. of the solvent (3). Although satisfactory for pure compounds, this expression of solubility is rather indefinite when applied to a mixture whose composition is changed during extraction. The solution in apparent equilibrium with undissolved wax may or may not be saturated with respect to every constituent of the mixture. The solubility thus obtained will be dependent upon the original amount of wax used.

The present paper describes a method which permits the calculation of the total amount of the more soluble fraction of a mixture from the amounts of material dissolved in each of several successive extractions.

An accurately weighed sample of the mixture is successively extracted with equal volumes of solvent to obtain a series of fractions. Following removal

of the solvent by evaporation, each of the fractions is weighed. The total weight extracted,  $w$ , is then plotted against the number of extractions,  $n$ . The resulting curve is a section of a hyperbola, the shape of which has been determined by the solubility of the more soluble fraction of the mixture. The equation describing this curve is

$$w = \frac{n}{A + Bn} \quad (1)$$

where  $A$  and  $B$  are constants. Rearrangement of this equation shows that a straight line should be obtained by plotting  $n/w$  vs.  $n$ . The constant,  $B$ , is the slope of the line while  $A$  is its intercept on the  $n/w$  axis.

$$n/w = A + Bn \quad (2)$$

Multiplying through by  $w/n$  gives

$$1 = \frac{Aw}{n} + Bw \quad (3)$$

To determine the amount of the more soluble fraction present in the mixture, let the number of extractions approach infinity. The first term on the right-hand side of equation (3) approaches zero, and the maximum value of  $w$  equals  $1/B$ . The amount of the more soluble fraction in the mixture is equal to the reciprocal of the slope of the linear graph.

#### Experimental

The solubility of sugar cane wax in ethanol was determined at 50°C. The extractor, designed to operate at constant temperature, is shown in Figure 1. It consists of a 250-ml. boiling flask fitted with a filter tube and a reflux condenser. The tube extends to within 1 mm. of the bottom of the flask, and the end is packed with a glass wool plug. Joints connecting the filter tube assembly to the flask and the condenser are made secure by springs.