

Reactions of Conjugated Fat Acids

I. Addition of Crotonic Acid Derivatives

HOWARD M. TEETER, CHARLES R. SCHOLFIELD, and JOHN C. COWAN
Northern Regional Research Laboratory,¹ Peoria, Illinois

THE recently announced (23)² catalytic method for the isomerization of vegetable oils and their derivatives furnishes raw material for the synthesis of new fat acid derivatives through the reactive conjugated system. One of the most important reactions of this system is the Diels-Alder reaction with α -, β -unsaturated carbonyl compounds.

Only a few instances of the application of the Diels-Alder reaction to conjugated fat acids and their derivatives may be cited. The practice of reacting oils and their derivatives with maleic anhydride for use in the preparation of improved drying oils and resins is perhaps the most common example. The use of maleic anhydride in the determination of diene numbers is also well known.

In these cases, it is not necessary to isolate and utilize the addition products. In fact, such products have been isolated and characterized only in the reactions of maleic anhydride with α - and β -eleostearic acids (22), α - and β -licanic acids (18), α - and β -eleostearins (21), 9,11-octadecadienoic acid (4), and three geometric isomers of 10,12-octadecadienoic acid (14).

Some attention has been given to the copolymerization of drying and semi-drying oils with styrene (1, 9, 13, 16, 26), vinyl esters (7, 10, 17), low molecular weight olefinic acids (6), acrylates (13), vinyl acetylene (15, 16), isoprene (16), undecylic acid (16), and similar compounds. Although non-conjugated oils, such as soybean or linseed oils were employed in certain of these reactions, the possibility of thermally induced conjugation under the reaction conditions employed might, in these cases, lead to reactions similar to those with conjugated oils. However, it is not known, even in the case of conjugated oils, whether the reaction products are produced by linear polymerization or by addition to the conjugated system with the formation of cyclic structures. Pure compounds have not been isolated from these reaction mixtures and have not been characterized.

The object of the present investigation was to investigate the reaction of crotonic acid derivatives with conjugated esters of fat acids, to isolate and characterize the products of reaction, and to explore the possible industrial utility of these products. The crotonic acid derivatives selected were ethyl crotonate and crotonitrile. The fat acid component was restricted essentially to conjugated linoleic acid. Methyl esters of soybean fat acids were employed, since after isomerization only the conjugated linoleic acid radicals and a small percent of conjugated linolenic acid radicals in these esters will participate in the Diels-Alder reaction. Although it is known (2) that maleic anhydride will react with non-conjugated fatty acids,

such a reaction should proceed to a negligible extent in the presence of reactive conjugated substances.

Treatment of methyl esters of soybean fat acids with a carbon-nickel catalyst, according to the directions of Radlove and Kass (23), gave a product containing 34.8% diene conjugation and 2.7% triene conjugation. In calculating weights of ethyl crotonate and crotonitrile for reaction with the conjugated esters, account was taken only of the conjugated portion of the esters, that is, 100 grams of conjugated soybean methyl esters was considered as the equivalent of 37.5 grams of conjugated methyl linoleate. Since only a small amount (2.7%) of triene conjugation was present, it was included with the diene conjugation in these calculations. For purposes of illustration, it will be assumed in writing structures in the discussion, that the conjugated isomers of linoleic acid present are the 10, 12 type.

Reaction was effected between the crotonic acid derivative and the conjugated methyl esters by heating and shaking the reactants in an autoclave for 2 to 20 hours at 150-275° C. It was advantageous to employ a 10-mole excess of the crotonic acid derivative, based upon the conjugation content of the methyl esters.

The reaction products were isolated by distillation. Unreacted crotonic acid derivative was obtained by distillation and stripping *in vacuo*; unreacted methyl esters were recovered by subsequent distillation through a fractionating column at pressures of 0.1-0.5 mm.; and the addition product was finally isolated by distillation from a small Claisen flask at pressures of about 0.1-0.3 mm. A small residue was left which probably contained polymerization products of the reactants.

Yields of addition product were good, as shown by the data in Table 1. They can be made essentially quantitative by utilizing recovered unreacted methyl esters, which still contained conjugation, in subsequent preparations.

TABLE 1.
Yields of Reaction Products.

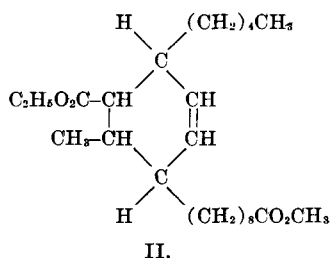
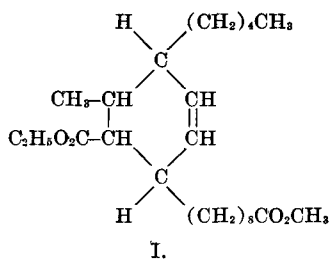
Ratio ¹	Time	Temperature	Yield
	Hours	°C.	Percent
1.50	10	185-188	20.6
1.50	20	185-188	26.4
1.50	20	190-270	51.2
10.0	10	245-260	76.5
10.0	10	240-250	65.7
10.0	20	185-188	56.1
1.50 ²	20	185-188	5.1
10.0 ²	10	244-256	24.6

¹Moles ethyl crotonate per mole of reactive soybean methyl esters.
²Non-conjugated methyl esters; assumed to contain 50% methyl linoleate.

The analytical data obtained for the addition product from ethyl crotonate and conjugated soybean methyl esters are in accord with the possible structures shown in Formulas I and II, which are further

¹One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

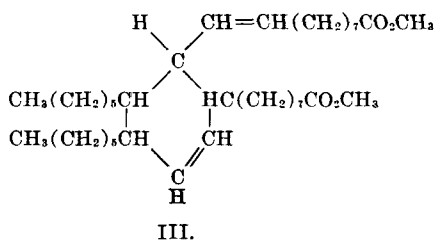
²See also the preliminary announcement by A. K. Smith and J. C. Cowan, *Soybean Digest* 5 (11): 43-44 (1945).



supported by the established structure for the maleic anhydride eleostearic acid addition product (19, 21, 24). The elementary analysis, molecular weight, and iodine value agree with the values calculated from these formulas. Hydrogenation with Adams' catalyst at room temperature and atmospheric pressures was not successful when the addition product was obtained by reaction in the steel autoclave. However, a sample obtained from a reaction run entirely in glass had a hydrogen number of 475. Beyond the fact that the hydrogen number was somewhat higher than the calculated value of 408, no evidence was found which indicated difficulty in the hydrogenation of the double bond.

This result agrees with the observation of Morrell and Davis (20) that no difference in ease of hydrogenation existed between the ring and side-chain double bonds in the maleic anhydride adducts of α - and β -eleostearic acid and α - and β -eleostearin.

On the other hand, incomplete data (5, 8, 27) on the hydrogenation of the dimer of methyl linoleate which is believed to have a structure similar to Formula III (5) indicate that under some conditions one double bond, presumably that in the side chain, is more readily hydrogenated than the other.



For purposes of comparison, ethyl crotonate and non-conjugated soybean methyl esters were reacted under the conditions employed with the conjugated esters. A product of reaction was isolated by distillation, but a much lower yield was obtained. The refractive index was higher than in the case of the compound from the conjugated esters, and the iodine number indicated a composition consisting of 64.0% of material having one double bond and 36.0% with two double bonds. The hydrogen number indicated

64.6% and 35.4% of these components, respectively.

The material having one double bond probably is the same as that derived from the conjugated esters, owing to the possibility of thermally-induced conjugation. The structure of the component containing two double bonds has not been determined. It may result from a different type of addition to non-conjugated methyl linoleate, or it may be derived from the methyl linolenate present in the soybean methyl esters.

The addition product of ethyl crotonate and conjugated methyl esters was saponified to the expected dibasic acid. In agreement with the observations of Morrell (22), difficulty in saponification of this addition product with alcoholic potassium hydroxide was found. When potassium hydroxide in ethylene glycol was employed, the dibasic acid had the correct neutralization equivalent.

The dibasic acid was polyesterified with decamethylene glycol, using *p*-toluenesulfonic acid as catalyst. The viscosity of the reaction mixture increased slowly, stopping finally after 164 hours at a value of 0.528 poises at 226° C. The polyester had a neutral equivalent of 4850. Since experiments indicated that the dibasic acid decreased both in acid number and in saponification number when heated in an inert atmosphere, polyesterification was attempted by transesterification of the ester of the dibasic acid with decamethylene glycol. A higher final viscosity, 5.30 poises, was obtained, but the equivalent weight based upon alkoxy content was 2740, a very low value. The failure to attain a high degree of reaction during polycondensation is presumably associated with steric hindrance of the acid function derived from the crotonic acid derivative.

A polyamide was prepared from the dibasic acid and ethylene diamine. In the one experiment performed, the product had an acidic neutral equivalent of 918 and a basic neutral equivalent of 1280. In the absence of steric hindrance, neutral equivalents of 3000-4000 have been obtained (11) for polyamides prepared in a similar manner.

TABLE 2
Compatibility of Ethyl Crotonate Addition Product
With Resins¹

Resin	Solvent	Ratio		
		1:1	3:1	9:1
Nitrocellulose	Ethyl acetate	C	C	C
Cellulose acetate	Acetone	C	C	C
Cellulose acetate-butyrate	Acetone	C	I	C
Polyvinyl chloride-acetate	50% methyl ethyl ketone; 50% dioxane	C	C ²
Ethyl cellulose	80% ethanol; 20% toluene	C	C	C
Polymethyl methacrylate	Acetone	C	C	C
Polystyrene	Toluene	C	C	C
Ester gum	Toluene	C	C	C
Modified rosin maleic	Toluene	C	C	C

¹C—compatible; I—incompatible.

²Resin did not dissolve in volume of solvent employed.

In order to evaluate the possible industrial value of these materials, the compatibility of the addition product with conjugated esters was determined with a number of synthetic resins. The results, given in Table 2, indicate possible value of the product as a plasticizer. Because of its insolubility in many resin solvents, and the limited amount of material available, the decamethylene glycol polyester was tested for compatibility only with ester gum and a modified 9:1

rosin-maleic-type resin. Other compounds mentioned were not tested, nor were the advantages and limitations of any substance as a plasticizer determined.

The addition product from crotononitrile and conjugated soybean methyl esters, after reduction of the nitrile group to a primary amino group, should be of value either as an intermediate or as a primary source of polyamides derived by self-condensation. It was found that reduction with platinum catalyst in ethanol solution proceeded with great difficulty. At room temperature and 50 pounds pressure, hydrogenation was very slow, stopping entirely after 45 hours, even after addition of several portions of fresh catalyst. Most of the hydrogen uptake represents saturation of the carbon-carbon double bond in the compound. When hydrogenation was continued with Raney nickel at 2,000 pounds pressure, 4 hours' treatment at 150° C. and 11 hours at 200°, with addition of several portions of fresh catalyst, gave a product having a neutralization equivalent of 568 upon titration with hydrochloric acid.

Partition of this product between petroleum ether and dilute hydrochloric acid resulted in isolation of a substance having a neutral equivalent of 507. The calculated neutral equivalent for the primary amine is 367.6. The method of isolation of this material indicates that it is a mixture of primary and secondary amines.

Experimental

Ethyl crotonate was prepared by esterification of crotonic acid with ethanol using sulfuric acid as a catalyst and an azeotropic distillation technique with carbon tetrachloride entrainer. The yield averaged 81%; b.p. 123-133° C.

Crotononitrile was prepared by distillation of crotonamide (25) with phosphorous pentoxide according to a procedure applied to maleamide by Blomquist and Winslow (3). The product boiled at 119-120° (12). The yield was 52%.

Soybean methyl esters were prepared by transesterification of alkali-refined soybean oil, and after distillation, they were conjugated by heating for 6 hours at 170° C. with a nickel-carbon catalyst according to the directions of Radlove and Kass (23). The product contained 34.8% diene conjugation and 2.7% triene conjugation.

Hydrogen numbers were determined by hydrogenation in ethanol solution using a platinum oxide catalyst. The results were calculated in terms of the weight of material absorbing 1 mole of hydrogen.

Addition of Ethyl Crotonate to Conjugated Soybean Methyl Esters. Sixty grams of the conjugated methyl esters were mixed with 86.0 grams of ethyl crotonate giving a ratio of 10 moles of ethyl crotonate per mole of conjugated methyl linoleate present in the methyl esters, and the mixture was sealed in a steel autoclave. After heating and shaking at 245-260° C. for 10 hours, the reaction mixture was cooled, transferred to a still equipped with a concentric tube fractionating column, and distilled *in vacuo*. After recovery of unreacted ethyl crotonate, 42.4 grams of unreacted methyl esters was collected. The residue was transferred to a short-path pot-still, and by distillation at 0.5 mm. pressure 23.9 grams of the addition product boiling at 207-217° C. was isolated. The yield was 76.5%. Yields under other conditions of time and temperature are given in Table 1.

The product was a liquid having $d_{30}^{30} = 0.9480$ and $n_D^{30} = 1.4651$. *Anal.* Calcd. for $C_{25}H_{44}O_4$ (Structure I or II) C, 73.5; H, 10.78; I.V., 62.0; M.W., 408. Found C, 73.8; H, 10.84; I.V., 64.6; M.W., 427 (cryoscopic in benzene).

When hydrogenation in ethanol solution with a platinum oxide catalyst was attempted at room temperature and atmospheric pressure, no hydrogen was taken up.

A similar preparation of the addition product was conducted in glass apparatus. The resulting product had an iodine value of 69.9 and a hydrogen number of 475 which corresponds to an iodine value of 53.4.

Addition of Ethyl Crotonate to Non-conjugated Soybean Methyl Esters. An experiment was conducted under the conditions just described using 50.0 grams of non-conjugated soybean methyl esters (assumed to contain 50% methyl linoleate) and 96.3 grams of ethyl crotonate. A yield of 6.4 grams of addition product (24.6% based on methyl linoleate content) was isolated by distillation. Yields under several conditions are given in Table 1. It had n_D^{30} , 1.4704; I.V., 84.7; M.W., 416; and hydrogen number, 332.

Calculated values for $C_{25}H_{44}O_4$ (Structure I or II): I.V., 62.0; hydrogen number, 408; for $C_{25}H_{44}O_4$ (Structure IV): I.V., 124.0; hydrogen number, 204. Calculations made from either the observed iodine value or hydrogen number indicate the presence of approximately 64% of material having one double bond and 36% of material having two double bonds.

Addition of Crotononitrile to Conjugated Soybean Methyl Esters. To 72.7 grams of conjugated methyl esters were added 62.3 grams of crotononitrile, and the mixture was heated and shaken in an autoclave for 10 hours at 240-250° C. By distillation at 0.55-0.8 mm., 43.9 grams of unreacted methyl esters was recovered, and by distillation at 0.10-0.14 mm., 21 grams (62.5%) of an addition product, having $n_D^{30} = 1.4749$ and $d_{30}^{30} = 0.9488$, was obtained.

Anal. Calcd. for $C_{23}H_{39}O_2N$: C, 76.5; H, 10.79; N, 3.88; I.V., 70.4. Found: C, 76.5; H, 10.77; N, 4.06; I.V., 72.3.

Dibasic Acid. A 33.2-gram sample of the addition product of ethyl crotonate and conjugated soybean methyl esters was refluxed for 3.5 hours with a solution composed of 17.5 grams of potassium hydroxide in 90 ml. of ethanol. There was isolated 26.9 grams of dibasic acid having a neutral equivalent of 192. Resaponification by refluxing with a solution of potassium hydroxide in ethylene glycol of the same concentration gave 24.7 grams of acids having a neutral equivalent of 185.8. The calculated neutral equivalent for $C_{20}H_{36}(COOH)_2$ is 183.

Effect of Heat on Dibasic Acid. A sample of the dibasic acid was heated for 66 hours at 226° C. under purified nitrogen. Before heating, the acid number was 299.0. After heating, the acid number was 258.0 and the saponification number was 289.4.

Polyesterification of the Dibasic Acid. Polyesterifications were conducted under atmospheric pressure at 226-227° C. in the apparatus described by Cowan and Wheeler (8). Oxygen-free nitrogen was bubbled through the reactants, and heat was supplied by refluxing technical undecanol (b.p. 223-228° C.).

In the first experiment 21.41 grams of dibasic acid was polyesterified directly with 10.0 grams of decamethylene glycol and 43 milligrams of *p*-toluene sul-

fonic acid as catalyst. After 164 hours at 224° C., the neutral equivalent was 4850, and the viscosity at 226° was 0.528 poise.

In the second experiment, 22.4 g. of the dibasic acid ester was transesterified with 9.6 grams of decamethylene glycol and 0.47 gram of the zinc salt of the dibasic acid as catalyst. After 165 hours at reaction temperature, the viscosity at 226° C. was 0.334 poise, and the alkoxy content was 2.01% calculated as methoxyl. After addition of 0.25 gram of decamethylene glycol (to replace losses) and 0.3 gram of sodium methoxide, and heating for 282 hours longer, the viscosity at 227° C. was 5.30 poises, and the alkoxy content was 1.13% calculated as methoxyl. The methoxyl values correspond to equivalents of 1540 and 2740, respectively, if one alkoxy group per molecule is assumed.

Polyamide of Ethylene Diamine and Dibasic Acid. In the apparatus of Cowan and Wheeler (8), 16.0 grams of the dibasic acid was reacted with 2.89 grams of an aqueous solution containing 91.3% of ethylene diamine. In this experiment, conducted at atmospheric pressure, carbon dioxide was used for the inert atmosphere. After 18 hours at 195° C., heat being supplied by boiling ethylene glycol, titration of free carboxyl and amino groups gave neutral equivalents of 918 and 1280, respectively. Attempts to continue the reaction failed, because of the occurrence of oxidation or decomposition.

Hydrogenation of Addition Product of Crotonitrile and Conjugated Soybean Methyl Esters. A solution of 43.3 (0.11 mole) grams of the addition product in 120 ml. of ethanol was reduced in a Parr apparatus with 0.2 gram platinum oxide catalyst. After 27 hours (0.15 gram fresh catalyst added after 18 hours) 0.12 mole of hydrogen had been taken up. Fresh catalyst (0.1 gram) was then added, but only 0.056 mole of hydrogen was taken up during the next 18 hours, and no change was observed during the last 4 hours of this period. Since leakage amounted to 0.0006 mole per hour, the total hydrogen absorbed was 0.14 mole. Titration of a sample of the product with hydrochloric acid gave a neutral equivalent of 24,600.

One-half of the alcoholic solution of this product was shaken in a steel bomb under a hydrogen pressure of 1,975 pounds with 1 gram of Raney nickel, but no reduction occurred. The temperature was raised to 150° C., and after 4 hours, the neutralization equivalent was 693. After 4 more hours at 200° C. and 1,910 pounds, the neutralization equivalent was 562. One gram of fresh catalyst was added, and reduction was continued for 5 hours at 200° C. and 1,900 pounds. The product had a neutralization equivalent of 568. All pressures were measured at 25° C.

Partition of Reduced Product. A Skellysolve F solution of 14.1 grams of the reduced addition product was shaken with dilute hydrochloric acid, and the acid layer was separated and extracted with Skellysolve F. The combined Skellysolve F solutions were dried and evaporated, yielding 1.9 grams of a material having a neutralization equivalent of 6130. The acid solution was made basic and extracted with Skellysolve F and ether. The extract was washed until neutral, dried and evaporated, giving 10.9 grams of a material having a neutral equivalent of 507.

Compatibility of Products With Resins. For each resin tested, three solutions were prepared containing 0.25, 0.75, and 2.25 grams of resin in 10 ml. of an

appropriate solvent. To each solution was added, as a plasticizer, 0.25 gram of the addition product of ethyl crotonate and conjugated soybean methyl esters. In this way, ratios of 1:1, 3:1, and 9:1, with respect to resin and plasticizer, were obtained. Films were cast on glass with a 3-mil filmograph in each case, and after drying they were inspected for indications of incompatibility, such as cloudiness, blushing, and spewing or film discontinuities. The results are shown in Table 2.

The decamethylene glycol polyester was not soluble in the solvents mentioned in Table 2 with the exception of toluene. Compatibility of the polyester was therefore determined only with ester gum and the modified rosin maleic resin. With ester gum compatibility was found in all three ratios, while with the other resin compatibility was observed only in the 9:1 ratio of resin to plasticizer.

Summary

1. Addition products of ethyl crotonate and crotonitrile with conjugated methyl linoleate, derived from soybean methyl esters conjugated with a nickel-carbon catalyst, were prepared.

2. The addition product of ethyl crotonate and non-conjugated methyl linoleate was prepared and compared with that from conjugated methyl linoleate.

3. The addition product of ethyl crotonate and conjugated methyl linoleate was saponified to a dibasic acid which was used to prepare a decamethylene glycol polyester and an ethylene diamine polyamide.

4. The compatibility of the addition product of ethyl crotonate and conjugated methyl linoleate with various synthetic resins was determined.

Acknowledgment

The authors are grateful to C. H. Van Etten and Ruth M. Johnson of the Analytical and Physical Chemistry Division for the microanalyses and spectrophotometric determinations of conjugation. They also appreciate the services of June Bramlet in performing the compatibility experiments.

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