product therefore is predominantly a thio-ether. The C-S band, a very weak band, appears at 657 cm.$^{-1}$.

Carbonyl Absorption. Two strong bands of approximately equal intensity appear in the carbonyl region, as opposed to one in methyl stearate, in all cases where the aromatic ring contains an hydroxyl group.

Compound	Normal C=O vibration cm.$^{-1}$	Hydrogen-bonded C=O vibration cm.$^{-1}$
Methyl (o[p]-hydroxyphenyl)stearate (liquid)	1741–1735	1720–1712
Methyl (2[4]-hydroxy-4[2]-methylphenyl)stearate (liquid)	1742	1722
Methyl (2,3-dihydroxy-5[6]-t-butylphenyl)stearate (liquid)	1744–1740	1718–1713
Methyl stearate (soln.)	1750	....
Mixture of methyl stearate and phenol	1750	1730

Dilution studies were run in the carbonyl and hydroxyl regions on methyl (o[p]-hydroxyphenyl) stearate and on a mixture of methyl stearate and phenol in an effort to find an explanation for the appearance of the second carbonyl band. The mixture, in carbon tetrachloride, also produced a spectrum in which two carbonyl bands appeared, indicating that intermolecular hydrogen bonding occurs between the hydroxyl group in phenol and the carbonyl group in the ester. The second carbonyl was less intense than the ester carbonyl. The spectrum also showed free hydroxyl (3650 cm.$^{-1}$, sharp) and bonded hydroxyl (3500 cm.$^{-1}$).

When methyl (o[p]-hydroxyphenyl)stearate is diluted, the carbonyl band at 1720 cm.$^{-1}$ appears as a shoulder at a concentration of 0.010 molar. This shoulder does not disappear however at lower concentrations (0.001 molar). At higher concentrations two distinct bands appear although the second carbonyl band is smaller. In the hydroxyl region, methyl (o[p]-hydroxyphenyl)stearate in solution has a spectrum showing both free hydroxyl and bonded hydroxyl whereas in the neat liquid only the bonded hydroxyl band appears.

The ester carbonyl band in the methyl (2,3-dihydroxy-5[6]-tert.-butylphenyl)stearate spectrum is smaller than the bonded carbonyl band when the compound is prepared in sulfuric acid. The predominance of the 1,2,3,5-substituted compound was concluded from bands at 873 and 810 cm.$^{-1}$. Consistent with this are the carbonyl bands if the 1,2,3,5-substituted compound is capable of bonding and the 1,2,3,4-substituted compound is not. This is in agreement with the observation made in the C-H out-of-plane deformation vibration region. Two bands are of approximately the same intensity in the compound prepared with an ion exchange resin catalyst.

Summary

Phenols and phenyl ethers have been added to oleic acid, using both sulfuric acid and a strong acid cation exchange resin as condensing agents. By-product formation during the condensations resulted in low yields and products which were difficult to purify. Infrared spectra were used to identify the various products and to show that ring isomers form. Infrared spectra also assisted in identifying by-products and permitted differentiation between the two strong acid condensing agents.

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The Cyanoethylation and Infrared Spectra of Some Ricinoleic Acid Derivatives[1]

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THE CYANOETHYLATION of ricinoleic acid derivatives was undertaken to provide compounds from castor oil which would have potential utility, such as plasticizers or organic intermediates. According to Bruson's review (3), cyanoethylation, the addition of acrylonitrile, occurs with a variety of compounds possessing labile hydrogen atoms, such as amines, oximes, and alcohols. The esters of hydroxy acids however resisted cyanoethylation (3). Attempts in this laboratory to cyanoethylate methyl ricinoleate (methyl 12-hydroxy-9-octadecenoate) by conventional procedures were likewise unsuccessful. When potassium, sodium, or sodium methoxide was employed as the cyanoethylation catalyst, an increase in optical rotation and a decrease in hydroxyl content were observed while dissolving the catalyst in methyl ricinoleate. Very little cyanoethylation occurred while slowly adding the acrylonitrile; instead a considerable amount of polyacrylonitrile was formed, accompanied by a further increase in optical rotation and decrease in hydroxyl content. Apparently estolide formation (interesterification of the hydroxyl and carboxyl groups of ricinoleic acid) took place. When benzyl-

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trimethylammonium hydroxide (Triton B) was employed as the cyanoethylation catalyst, no increase in optical rotation or decrease in hydroxyl content was observed; however very little cyanoethylation occurred. The formation of free fatty acid neutralized the alkaline catalyst.

Cyanoethylation was successful after the interfering methoxy group was converted to a morpholino group (4) or the carbomethoxy group was converted to a carbinol group. (Subsequently it was found that methyl ricinoleate could be cyanoethylated if Triton B were added dropwise to a solution of methyl ricinoleate, acrylonitrile, and dioxane. Based on infrared analysis, about 55% cyanoethylation was obtained.) Five derivatives of ricinoleic acid were cyanoethylated, namely, 4-ricinoleoylmorpholine, 4-(12-hydroxystearoyl)morpholine, 4-ricinelaidoylmorpholine, 1,12-dihydroxy-*cis*-9-octadecene, and 1,12-dihydroxyoctadecane. 1,12-Bis(β-cyanoethoxy)octadecane has previously been reported by Bruson, but it was not purified (2). 1,12-Bis(β-cyanoethoxy)-*cis*-9-octadecene was isomerized with nitrogen oxides to the *trans* isomer by the general procedure of McCutchon *et al.* (5).

The infrared spectra for all these compounds were determined. The absorptivities in the 4.44 micron region (characteristic of the C≡N group) of all the compounds and in the 10.3 micron region (characteristic of *trans* unsaturation) for the *trans* isomer were studied and used as a basis for quantitative determination of these groups.

Experimental

Materials. 4-Ricinoleoylmorpholine, 4-ricinelaidoylmorpholine, and 4-(12-hydroxystearoyl)morpholine were prepared by the general procedure of Dupuy, O'Connor, and Goldblatt (4). Commercial ricinoleyl alcohol (1,12-dihydroxy-9-octadecene) and 12-hydroxystearyl alcohol (1,12-dihydroxyoctadecane) were fractionally distilled under high vacuum. The 12-hydroxystearyl alcohol was crystallized from 15 volumes of acetone-hexane mixture (1:2) at 5°C. Eastman's practical grade of acrylonitrile and dioxane and commercial 35-40% benzyltrimethylammonium hydroxide (Triton B) in methanol were used without further purification.

4-(12-β-Cyanoethoxyoleoyl)morpholine. 4-Ricinoleoylmorpholine was cyanoethylated, employing 100% excess acrylonitrile. In a 2-liter, three-necked flask, equipped with a reflux condenser, a dropping funnel, a thermometer, and a magnetic stirrer, 368 g. of 4-ricinoleoylmorpholine (1 mole) and 368 g. of dioxane were added. Then 37 ml. of water and 37 ml. of Triton B were added, and the mixture was stirred and heated to 50°C. Two moles of acrylonitrile (106 g.) were added dropwise in about 30 min. During the addition of acrylonitrile the temperature rose from 50 to 85°C. The reaction was then continued for 3 hrs. The temperature was maintained between 60 and 70°C. The hot mixture was poured slowly into 3 liters of diethyl ether during a 15-min. period and allowed to stand for several hrs. while the polyacrylonitrile precipitated out of solution. The ethereal solution was decanted, filtered, extracted three times with 300-ml. portions of 1 *N* hydrochloric acid, and washed twice with distilled water. After the ether was evaporated from the reaction product under reduced pressure, the hydroxyl content was determined. This indicated about 60% conversion. The crude cyanoethylated product was distilled rapidly (*ca.* 200 g./hr.) under high vacuum. Distillate fractions, b.p. 248-254°C./0.02 mm., were crystallized over-night from 15 volumes of methanol at −70°C.

Anal. Calcd. for $C_{25}H_{44}N_2O_3$ (420.6): C, 71.38; H, 10.54; N, 6.66; OH, 0. Found: C, 71.45; H, 10.55; N, 6.70; OH, 0; $n^{30/D}$ 1.4816; $\alpha^{25/10\text{ cm.}}$ 14.20.

4-(12-β-Cyanoethoxystearoyl)morpholine. 4-(12-Hydroxystearoyl)morpholine was cyanoethylated, employing 100% excess acrylonitrile as described above. Distillate fractions, b.p. 246-252°C./0.02 mm., were crystallized over-night from 10 volumes of acetone at −25°C. to precipitate the noncyanoethylated morpholide. After the acetone filtrate was evaporated under reduced pressure, the cyanoethylated morpholide was crystallized over-night from 15 volumes of methanol at −70°C., m.p. 35.2-36.2°C.

Anal. Calcd. for $C_{25}H_{46}N_2O_3$ (422.6): C, 71.04; H, 10.97; N, 6.63. Found: C, 70.85; H, 10.85; N, 6.55; $n^{50/D}$ 1.4684.

4-(12-β-Cyanoethoxyelaidoyl)morpholine. 4-Ricinelaidoylmorpholine was cyanoethylated by employing 100% excess acrylonitrile, as described above. Distillate fractions, b.p. 247-255°C./0.02 mm., were crystallized over-night from 3 volumes of acetone at −70°C. to precipitate the noncyanoethylated morpholide. After the acetone filtrate was evaporated under reduced pressure, the cyanoethylated morpholide was crystallized over-night from 15 volumes of methanol at −70°C.

Anal. Calcd. for $C_{25}H_{44}N_2O_3$ (420.6): C, 71.38; H, 10.54; N, 6.66. Found: C, 71.27; H, 10.51; N, 6.74; $n^{30/D}$ 1.4816; absorptivity, (a) = 0.40 at 10.33 microns in CS_2.

1-12-Bis(β-cyanoethoxy)-cis-9-octadecene. The primary and secondary hydroxyl groups of ricinoleyl alcohol were cyanoethylated by employing 100% excess acrylonitrile. One mole (284 g.) of ricinoleyl alcohol was dissolved in 284 g. of dioxane. Then 28 ml. of water and 28 ml. of Triton B were added with stirring at room temperature. Four moles (212 g.) of acrylonitrile were added dropwise in about 1 hr. During the addition of acrylonitrile the temperature rose from 25 to 70°C. The reaction was continued for 3 hrs. The temperature was maintained between 60 and 70°C. The hot mixture was poured slowly into 3 liters of diethyl ether during a 15-min. period and allowed to stand for several hrs. while the polyacrylonitrile precipitated out of solution. The ethereal solution was decanted, filtered, extracted three times with 300-ml. portions of 1 *N* hydrochloric acid, and washed twice with distilled water. After the ether was evaporated under reduced pressure from the reaction product, the hydroxyl content was determined. This indicated about 75% conversion. The crude cyanoethylated product was distilled rapidly (*ca.* 200 g./hr.) under high vacuum. Distillate fractions b.p. 228-238°C./0.02 mm., were crystallized over-night from 15 volumes of methanol at −70°C.

Anal. Calcd. for $C_{24}H_{42}N_2O_2$ (390.6): C, 73.79; H, 10.84; N, 7.17; OH, 0. Found: C, 74.20; H, 11.18; N, 7.08; OH, 0; $n^{30/D.}$ 1.4632; $\alpha^{25/10\text{ cm.}}$ 14.30.

1,12-Bis-(β-cyanoethoxy)octadecane. 1,12-Dihydroxyoctadecane was cyanoethylated in dioxane solution, employing 100% excess acrylonitrile as described above except that the mixture had to be heated to 55°C. to dissolve the diol. While adding acrylonitrile,

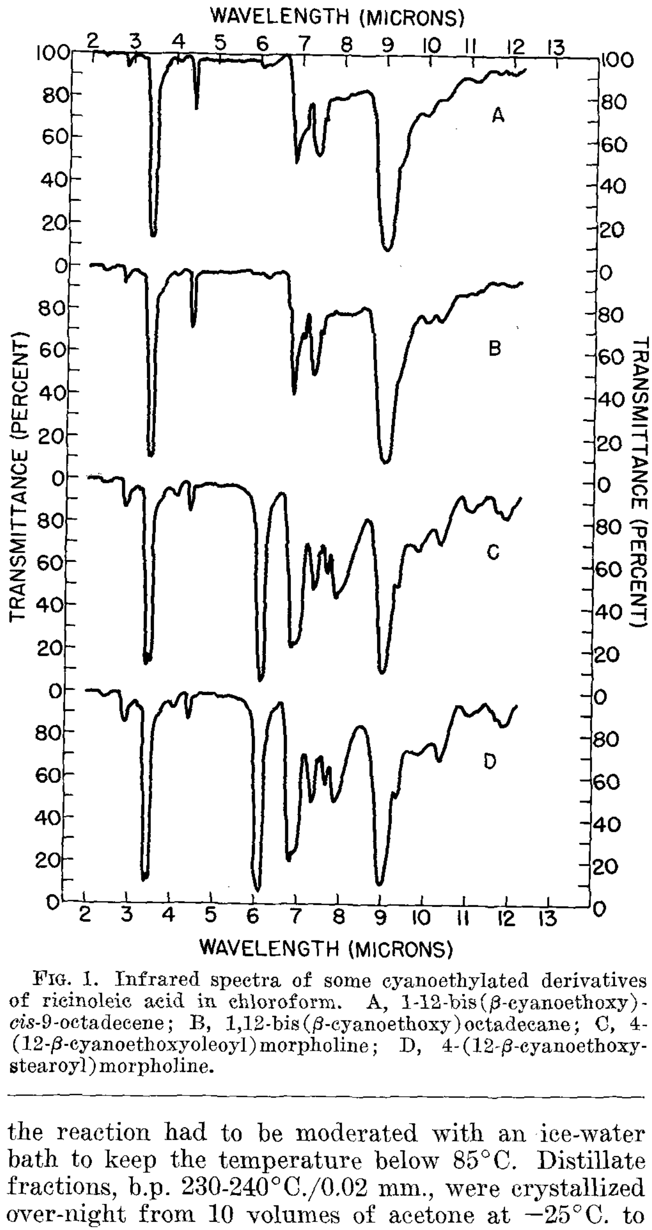

Fig. 1. Infrared spectra of some cyanoethylated derivatives of ricinoleic acid in chloroform. A, 1-12-bis(β-cyanoethoxy)-*cis*-9-octadecene; B, 1,12-bis(β-cyanoethoxy)octadecane; C, 4-(12-β-cyanoethoxyoleoyl)morpholine; D, 4-(12-β-cyanoethoxystearoyl)morpholine.

the reaction had to be moderated with an ice-water bath to keep the temperature below 85°C. Distillate fractions, b.p. 230-240°C./0.02 mm., were crystallized over-night from 10 volumes of acetone at −25°C. to precipitate the partially cyanoethylated or noncyanoethylated diol. After the acetone filtrate was evaporated under reduced pressure, the dicyanoethylated product was crystallized over-night from 20 volumes of methanol at −25°C.

Anal. Calcd. for $C_{24}H_{44}N_2O_2$ (392.6): C, 73.42; H, 11.30; N, 7.14. Found: C, 73.36; H, 11.11; N, 7.10; $n^{30/D}$ 1.4562.

1,12-Bis(β-cyanoethoxy)-trans-9-octadecene. The ethylenic bond of 1-12-bis(β-cyanoethoxy)-*cis*-9-octadecene was isomerized from *cis* to *trans* configuration by the general procedure of McCutchon *et al.* (5). To 30 g. of 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene, maintained at 60°C., were added with rapid stirring 2 ml. of 2 molar sodium nitrite solution and 1.33 ml. of 6 molar nitric acid. The heating and stirring were continued for 2 hrs. Then the reaction mixture was poured into 100 ml. of water and extracted with diethyl ether. The ethereal solution of 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene and 1,12-bis(β-cyanoethoxy)-*trans*-9-octadecene was washed with distilled water until free of acid and finally dried over sodium sulfate. Infrared analysis of the equilibrium mixture indicated about 77% *trans* isomer. The crude product was crystallized successively over-night from 3 volumes of acetone and from 10 volumes of methanol at −70°C.

Anal. Calcd. for $C_{24}H_{42}N_2O_2$ (390.6): C, 73.79; H, 10.84; N, 7.17. Found: C, 73.93; H, 10.73; N, 7.11; $n^{30/D}$ 1.4622; absorptivity, (a) = 0.40 at 10.32 microns in CS_2.

Spectrophotometric Determinations. Complete infrared absorption curves from 2 to 12 microns of all compounds investigated were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. Settings used were: resolution, 927; suppression, 3; gain, 5; response, 1; and speed, 0.5 micron/min. The spectra of all compounds except the *trans* isomers were obtained both in chloroform and carbon tetrachloride solutions at about 30 g./l. with a 0.48-mm. absorption cell. The spectra of the *trans* isomers were obtained only in chloroform solution. Pure dry chloroform or carbon tetrachloride was placed in the reference beam.

In addition, the absorption of the *trans* isomers was measured in carbon disulfide solution at about the 10 micron region where the absorption maxima characteristic of C—H bending about the *trans* double bond is expected. These measurements were made with the following settings: suppression, 0; gain, 5; response, 1; speed, 0.5 cm.$^{-1}$/sec.; slit manual, 151 microns; and filter in place.

Results and Discussion

Preparation of Compounds. The addition of water (10% by weight based on the morpholide or carbinol) to the cyanoethylation mixture retarded the formation of polyacrylonitrile. A lower water-content was not very effective; a higher water-content produced excessive amounts of bis(β-cyanoethyl) ether. Benzyltrimethylammonium hydroxide was employed as the cyanoethylation catalyst because it readily dissolved in the morpholide and carbinol solutions, and it was just as effective as other catalysts examined, namely, potassium, sodium, and sodium methoxide. Several hours of agitation at fairly high temperatures were necessary to dissolve them.

Cyanoethylation was carried out between 25 and 85°C. by adding dropwise 100% excess acrylonitrile to the reaction mixture. A greater excess of acrylonitrile increased the extent of cyanoethylation but also increased the polymerization of acrylonitrile. The minimum temperature suitable for cyanoethylation

TABLE I

Absorption Bands in the Infrared Spectra of Cyanoethylated Products of Some Ricinoleic Acid Derivatives in Chloroform

Functional group	Wavelength position of maxima (microns)[a]					
	A	B	C	D	E	F
Unassigned	2.86	2.86	2.91	2.91	2.85	2.90
C—H stretching	3.44	3.44	3.44	3.44	3.44	3.44
C—H stretching	3.50	3.50	3.51	3.51	3.50	3.50
C≡N stretching	4.44	4.44	4.44	4.44	4.44	4.44
C=O stretching (amide)	......	......	6.14	6.14	......	6.13
C—H deformation	6.85	6.85	6.86	6.86	6.85	6.86
C—H deformation	7.08	7.08	7.00	7.00	7.08	6.97
C—H deformation	7.41	7.34	7.36	7.35	7.36	7.36
C—H deformation	7.54	7.55	7.52	7.54	7.54	7.54
C—N stretching	......	......	7.70	7.69	......	7.69
C—O stretching	......	......	7.90	7.90	......	7.89
C—O—C stretching	9.05	9.06	9.04	9.01	9.05	9.02
C—O, C—N stretching	......	......	9.37	9.36	...	9.37
C—H deformation	......	......	......	......	10.31	10.33
Morpholino ring moiety	......	......	10.41	10.40	......	10.33
Unassigned	......	......	11.05	11.05	......	11.03
Unassigned			11.95	11.93	......	11.90

[a] A, 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene; B, 1,12-bis(β-cyanoethoxy)octadecane; C, 4-(12-β-cyanoethoxyoleoyl)morpholine; D, 4-(12-β-cyanoethoxystearoyl)morpholine; E, 1,12-bis(β-cyanoethoxy)-*trans*-9-octadecene; F, 4-(12-β-cyanoethoxyelaidoyl)morpholine.

was used as high temperatures cause excessive polymerization of acrylonitrile. Since the cyanoethylation of the primary and secondary hydroxyl groups and the polymerization of acrylonitrile are exothermic reactions, the temperature of the reaction mixture rose rapidly even though the acrylonitrile was added dropwise.

Acrylonitrile was added to the reaction mixture of ricinoleyl alcohol (1,12-dihydroxy-9-octadecene) at room temperature, as ricinoleyl alcohol, Triton B, and water are miscible in dioxane and the primary hydroxyl group is readily cyanoethylated at room temperature. The exothermic reactions cause a temperature rise sufficient to enhance the cyanoethylation of the secondary hydroxyl group. Before acrylonitrile was added to the reaction mixture of 1,12-dihydroxyoctadecane, it had to be heated to 55° C. to dissolve the diol. During the addition of acrylonitrile the reaction temperature had to be moderated. The reaction mixture of 4-ricinoleoylmorpholine was heated to 50°C. before acrylonitrile was added to promote cyanoethylation of the secondary hydroxyl group. The reaction mixture of 4-(12-hydroxystearoyl)-morpholine was heated to 50°C. before acrylonitrile was added to promote solubility of the morpholide and cyanoethylation of the secondary hydroxyl group. In all cases the reaction was continued for 3 hrs. after the addition of acrylonitrile, and the temperature was maintained between 60 and 70°C. to obtain maximum conversion, *ca.* 60% for the secondary hydroxyl group and *ca.* 90% for the primary hydroxyl group.

Any polyacrylonitrile formed during the reaction was readily separated from the reaction product by pouring slowly the hot cyanoethylated mixture during a 15-min. period into 3 volumes of diethyl ether. Most of the polyacrylonitrile precipitated out of the ethereal solution within several hrs. The catalyst was removed by extracting the ethereal solution three times with excess 1 *N* hydrochloric acid. The crude cyanoethylated product was purified by rapid distillation under high vacuum to prevent decomposition. Very little decomposition occurred when the material was distilled rapidly, *ca.* 200 g./hr.; but considerable decomposition occurred when the material was distilled slowly, *ca.* 50 g./hr. or less. Distillate fractions of 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene, 4-(12-β-cyanoethoxyoleoyl)morpholine and 4-(12-β-cyanoethoxystearoyl)morpholine which contained at least 80, 85, and 90%, respectively, of cyanoethylated material were crystallized over-night from 15 volumes of methanol at −70°C.

Distillate fractions of 1,12-bis(β-cyanoethoxy)octadecane which contained at least 95% cyanoethylated material readily crystallized over-night from 20 volumes of methanol at −25°C. Distillate fractions of 1,12-bis(β-cyanoethoxy)octadecane which contained at least 80% cyanoethylated material were purified by first crystallizing out most of the partially cyanoethylated and noncyanoethylated diol from 10 volumes of acetone at −25°C.

1,12-Bis(β-cyanoethoxy)-*trans*-9-octadecene was easily prepared by isomerizing 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene with a sodium nitrite-nitric acid catalyst. The maximum conversion, *ca.* 77% *trans* isomer, was obtained within 2 hrs. Then the *trans* isomer was purified from the equilibrium mixture by successive crystallization over-night from 3 volumes of acetone and from 10 volumes of methanol at −70°C.

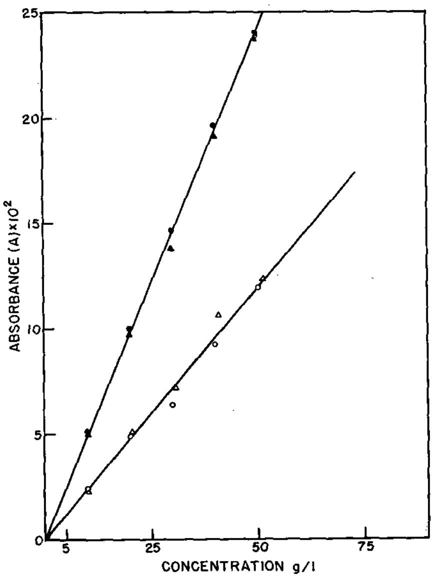

FIG. 2. Relationship between the absorbance of the $C\equiv N$ group and the concentration of cyanoethylated ricinoleic acid derivatives. ▲, 1,12-bis(β-cyanoethoxy)-*cis*-9-octadecene; ●, 1,12-bis(β-cyanoethoxy)octadecane; △, 4-(12-β-cyanoethoxyoleoyl)morpholine; ○, 4-(12-β-cyanoethoxystearoyl)morpholine.

4-(12-β-Cyanoethoxyoleoyl)morpholine was easily isomerized to 4-(12-β-cyanoethoxyelaidoyl)morpholine with a sodium nitrite-nitric acid catalyst. The maximum conversion, *ca.* 75% *trans* isomer, was obtained within 2 hrs. However purification of the *trans* isomer from the equilibrium mixture was not too successful. The *trans* isomer was only concentrated by successive crystallizations over-night from 10 volumes of ethyl acetate, from 5 volumes of acetone, and from 10 volumes of methanol at −70°C. Maximum absorptivity at 10.33 microns in carbon disulfide was only 0.37.

4-(12-β-Cyanoethoxyelaidoyl)morpholine was easily prepared by cyanoethylating 4-ricinelaidoylmorpholine, followed by distillation of the cyanoethylated product. Suitable fractions were crystallized overnight from 3 volumes of acetone to precipitate the noncyanoethylated morpholide at −70°C. 4-(12-β-cyanoethoxyelaidoyl)morpholine was obtained by evaporating the acetone filtrate and crystallizing the residue over-night from 15 volumes of methanol at −70°C. Maximum absorptivity at 10.33 microns in carbon disulfide was 0.40.

Infrared Spectra. Spectra in chloroform are shown in Figure 1. With the few rather significant differences mentioned below, the spectra in carbon tetrachloride very closely resemble those in chloroform. Wavelength positions of absorption maxima for all bands with absorptivities of *ca.* 0.05 or more with their most probable assignments for the six compounds investigated are given in Table I. From previously reported investigations of long-chain compounds and from recent discussions of the spectra of morpholides of ricinoleic acid (4), correlations of the bands which appear in these spectra with vibrational groups giving rise to them can be made with considerable degree of certainty.

The band with maxima at 2.86 to 2.91 microns, found in the chloroform solution spectra of all compounds, is interesting. This is the position of absorption commonly assigned to a stretching of the O—H or N—H group, neither of which is found in these molecules. This sharp band with low intensity in chloroform spectra does not appear at all in carbon tetrachloride spectra. This may be interpreted as indicating that the band arises from some interaction of these compounds with the chloroform. The double bond is not involved in this interaction as it appears with equal intensity in the spectra of the saturated and unsaturated compounds. The band of the monocyanoethylated morpholides has twice the intensity of the dicyanoethylated diols. Therefore it cannot arise from the interaction with the C≡N group. This might be explained by hydrogen bridging between the chloroform and nonbonding electron pairs of the solute.

The C—H stretching bands in the 3.44 and 3.5 micron regions exhibit an interesting difference between the chloroform solution spectra and the carbon tetrachloride solution spectra. In carbon tetrachloride the 3.44 micron band in all compounds is more intense than the 3.5 micron band whereas in chloroform the 3.5 micron band in most compounds is slightly more intense than the 3.44 micron band.

The 4.44 micron band, assigned to the C≡N stretching, is sharp both in chloroform and in carbon tetrachloride solutions, but its intensity in chloroform is about 67% greater than in carbon tetrachloride. The cyanoethylated morpholides in chloroform have absorptivities of about 0.05 whereas in carbon tetrachloride their absorptivities are about 0.03. The dicyanoethylated diols in chloroform have absorptivities of about 0.10 whereas in carbon tetrachloride their absorptivities are about 0.06. It may be postulated that this increased intensity arises from an interaction between the nitrile group and chloroform. This is in agreement with the findings of T. L. Brown (1) that hydrogen-bonding solvents, such as chloroform, interact with the carbonyl group of a compound resulting in greater absorption. The important conclusion is that, for a quantitative analysis of the nitrile group, measurements in chloroform result in greater sensitivity. As shown in Figure 2, for both types of compounds it follows the Beer-Lambert Law over a wide range of concentrations. The cyanoethylation reaction and the purification of the cyanoethylated product could readily be followed by infrared analyses.

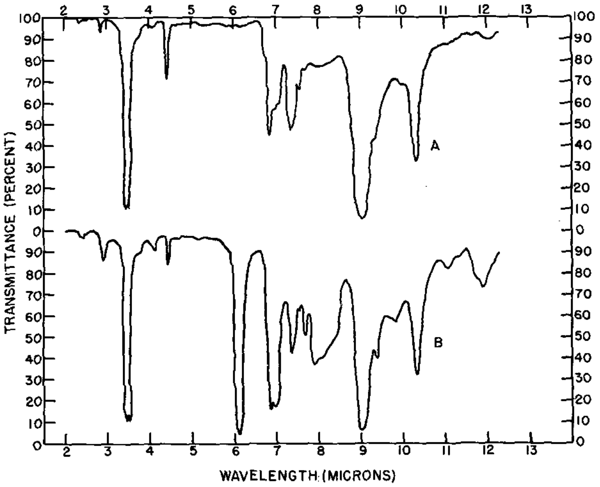

FIG. 3. Infrared spectra of some cyanoethylated derivatives of ricinelaidic acid in chloroform. A, 1,12-bis(β-cyanoethoxy)-*trans*-9-octadecene; B, 4-(12-β-cyanoethoxyelaidoyl)morpholine.

The very intense band of the C=O stretching of the amide group at 6.14 micron readily differentiates the cyanoethylated product of the morpholides from those of the alcohols. The morpholides are further differentiated by their C—O and C—N stretchings at 7.70, 7.90, and 9.37 microns and by the band assigned to the morpholino ring moiety at 10.40-10.41 microns (4). All compounds are characterized by the intense band at 0.01-9.06 microns assigned to a C—O—C stretching.

The infrared spectra of 1,12-bis(β-cyanoethoxy)-*trans*-9-octadecene and 4-(12-β-cyanoethoxyelaidoyl)-morpholine are given in Figure 3. The only significant difference in the spectra of these *trans* isomers is the appearance of the intense *trans* band at 10.32 microns arising from a C—H deformation about the *trans* C=C.

Summary

Five ricinoleic acid derivatives have been cyanoethylated with acrylonitrile, namely, 4-ricinoleoylmorpholine, 4-ricinelaidoylmorpholine, 4-(12-hydroxystearoyl)morpholine, 1,12-dihydroxy-9-octadecene and 1,12-dihydroxyoctadecane, using benzyltrimethylammonium hydroxide as a cyanoethylation catalyst and water to retard the polymerization of acrylonitrile. Any polyacrylonitrile formed was readily precipitated out of an ethereal solution. Purification of the cyanoethylated products was accomplished by washing out the catalyst, rapid distillation under high vacuum, and crystallizations from methanol. In addition, 1,12-bis(β-cyanoethoxy)-9-octadecene was isomerized from *cis* to *trans* form and crystallized successively from acetone and methanol. The infrared spectra of these compounds have been determined. It was found that the characteristic absorption for the nitrile group at 4.44 microns is about 67% greater in chloroform than in carbon tetrachloride and that it obeys Beer's law over a wide range of concentrations, thus permitting convenient infrared analysis of this type of compound. Some properties of these compounds are described.

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