read the transmittance at the 10.36 μ maximum, convert to absorbance, and calculate the absorptivities. On the charts draw a line through the absorption peak from 10.02 μ to 10.59 μ for methyl esters (or from 10.05 μ to 10.67 μ for triglycerides). Measure the distance from the zero line of the recorder chart to the absorption peak (ab, Figure 1). Calculate the fractional transmission (bc) as the distance to the absorption peak (ab) divided by the distance to the base line (ac), convert to absorbance, and calculate the "background corrected absorptivity." Calculate the % *trans* isomer as methyl elaidate (or trielaidin) from the equation:

$$\%\ \textit{trans} \text{ as methyl elaidate (or trielaidin)} = \frac{{}^{a}\text{sample (background corrected)}}{{}^{a}\text{methyl elaidate (or trielaidin)}} \times 100$$

(background corrected)

where a = absorptivity = A/bc

A = absorbance = log 1/T

b = internal cell length in centimeters

c = concentration of solution in g./l.

NOTE 1. Prolonged breathing of CS_2 vapors is dangerous. This solvent should be handled only under conditions which provide adequate ventilation, preferably under a chemical hood.

NOTE 2. Samples of these secondary standards will be made available through the Society. Questions regarding them should be addressed to the chairman of the Spectroscopy Committee, A.O.C.S., Box 19687, New Orleans 19, La.

NOTE 3. All nomenclature and symbols used throughout this method and those suggested by the Joint Committee on Nomenclature in Applied Spectroscopy (Anal. Chem., *24*, 1349–1354 [1952]) and as adopted by the American Society for Testing Materials "Tentative Definition of Terms and Symbols Relating to Absorption Spectroscopy" (F-131-57-T).

NOTE 4. For this purpose reference is made to the American Society for Testing Materials, Committee E-13, on Absorption Spectroscopy publication, "Proposed Recommended Practices for General Techniques of Infrared Quantitative Analysis," copies of which may be obtained from A.S.T.M. Headquarters, 1916 Race street, Philadelphia 3, Pa.

Cyclization of Linolenic Acid by Alkali Isomerization[1]

C. R. SCHOLFIELD and J. C. COWAN, Northern Regional Research Laboratory,[2] Peoria, Illinois

ALTHOUGH the conjugated dienoic acids formed by alkali isomerization of linoleic acid are rather stable upon further heating with alkali, the products from linolenic acid are not. Prolonged heating of alkali-isomerized linolenic acid decreases the ultraviolet absorption in both the diene and triene regions. For example, Bradley and Richardson (1) showed that with linseed oil triene conjugation reaches a maximum and decreases during heating with NaOH in ethylene glycol, diethylene glycol, or water. Mitchell *et al.* (6) reported that in the low concentration used for analytical determinations the absorption resulting from linolenic acid at both 234 mμ and 268 mμ decreases after about 15 min. at 180°.

Kass and Burr (3) isolated pseudo-eleostearic acid (10,12,14-octadecatrienoic acid) from linseed oil isomerized with alkali. Previously unpublished work of this laboratory (4) suggested the presence of a cyclic monomer. Pseudo-eleostearic acid is however the only compound that has been obtained in a pure state from alkali-isomerized linolenic acid, and the nature of the other products has not been determined. In this paper it is shown that prolonged treatment of linolenic acid with alkaline ethylene glycol produces a large amount of cyclic monomeric material together with small amounts of dimeric and other products. The monomer is believed to be similar to the one MacDonald (5) obtained from linseed oil and to those Paschke and Wheeler (10) and Rivett (11) obtained from eleostearates by heat treatment.

Experimental

Preparation and Isomerization of Methyl Linolenate. A concentrate containing 85% of methyl linolenate was prepared from perilla oil esters by the urea complex separation procedure of Parker and Swern (9). Pure methyl linolenate was prepared from this concentrate by countercurrent distribution between acetonitrile and pentane-hexane. Details of this preparation will be described in another paper (12). The resulting product contained 100% methyl linolenate as measured by analytical alkali-isomerization. Gas chromatography indicated only a trace of impurity (<0.01%), which was probably linoleate.

A mixture of 30 g. of methyl linolenate, 30 g. of potassium hydroxide, and 125 ml. of ethylene glycol was heated for 7 hrs. at 200°C. under nitrogen. After cooling to 100°C., water was added and the reaction was refluxed for a short time. The reaction mixture was cooled and acidified with dilute H_2SO_4. The acids were dissolved in ethyl ether, washed free of H_2SO_4 with water, and dried over sodium sulfate. This procedure was repeated with another 30-g. portion of methyl linolenate, the two ether solutions were combined, and diazomethane was added to form methyl esters. After the evaporation of the solvent the yield was 55.8 g. (93%).

Fractionation of Isomerized Esters. A solution of 90 g. of urea in 300 ml. of methanol was added to the isomerized esters, and the mixture was warmed to reflux and allowed to cool to room temperature. The urea adduct was removed by filtration on a Buchner funnel and washed with ethyl ether. This ether was collected separately from the methanol filtrate. The three fractions were treated with water containing a small amount of hydrochloric acid, and the esters were recovered by extraction with ethyl ether. The ether solutions were washed with water until neutral and dried over sodium sulfate. The solvent was removed under vacuum. The weights of material recovered in the fractions were: adduct, 2.40 g.; methanol filtrate, 36.20 g.; ether wash, 14.50 g. Infrared and ultraviolet absorptions of the fractions recovered from the methanol filtrate and ether wash were quite similar, and these fractions were combined. This combined material was again treated

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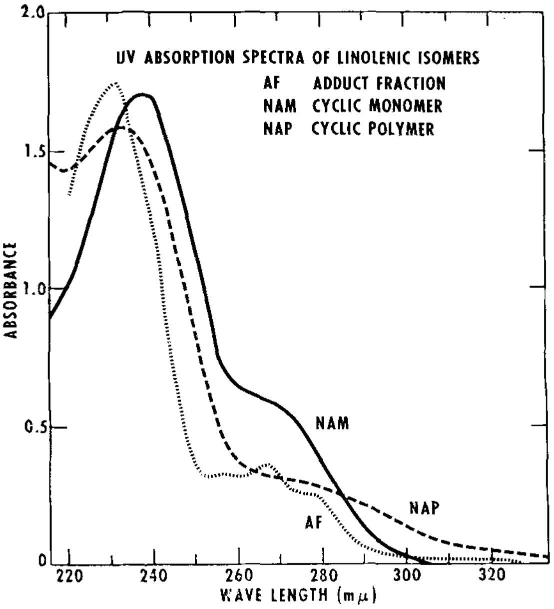

FIG. 1. Ultraviolet absorption spectra of fractions from "isomerized" linolenate: methanol solution, 1-cm. cell AF C = 0.0228 mg./ml. a_{232} = 74.5; NAM C = 0.0645 mg./ml. a_{238} = 26.4; NAP C = 0.0980 mg./ml. a_{233} = 16.2.

with urea as before, except that it was cooled to 0°C. before filtration. No additional adduct-forming material was obtained.

Nonadduct-forming material recovered from this urea treatment was distilled under vacuum through a Vigreaux column, b.p. 154°–161°, <0.1 mm. pressure. Yield of distillate from 50 g. was 40.63 g. (80.3%), and yield of residue was 6.85 g. (13.9%). After correcting for losses, the isomerized esters were estimated to contain 4.5% of urea-adduct-forming material (AF), 13.7% of nonurea-adduct-forming polymeric, nondistillable, material (NAP), and 81.8% of nonurea-adduct-forming monomeric, distillable, material (NAM). Ultraviolet absorptions of these three fractions are shown in Figure 1 with their infrared absorptions in Figure 2. Molecular weights measured by cryoscopy in benzene were 296 for NAM and 570 for NAP.

Hydrogenation of Esters. Unsaturation of the fractions was measured by determining the hydrogen uptake in ethyl acetate solution, using platinum oxide catalyst. Results calculated as iodine values were: AF 220, NAM 128, and NAP 57. The hydrogenated AF fraction melted at 36° to 37° (methyl stearate, m.p. 38°). The hydrogenated NAM was an oily liquid. A Wijs iodine value of 30 was obtained for the hydrogenated product; this value indicates that either hydrogenation was not complete or that some substitution of halogen occurred. Only 4% of the hydrogenated NAM formed an adduct with urea; therefore most of the material was of a cyclic or branched structure. Examination of the ultraviolet absorption spectrum of the hydrogenated NAM showed that the maximum at 238 mμ had disappeared. Only a general absorption, increasing at shorter wavelengths with small peaks at 265 and 272 mμ, was found.

The hydrogenated NAP fraction had a Wijs iodine value of 44. As with the NAM fraction, this may indicate either incomplete hydrogenation or substitution of halogen.

Aromatization and Oxidation. To establish the cyclic nature of the NAM, several portions were treated with N-bromosuccinimide and dehydrobrominated with dimethylaniline to give an aromatic compound. The procedure was similar to those previously used in the study of cyclic monomers from heat-treated eleostearates and linseed oil (5, 10, 11). For example, a mixture of 3.21 g. of N-bromosuccinimide and 5.21 g. of NAM in 50 ml. of carbon tetrachloride was refluxed 45 min., cooled, and filtered. The insoluble succinimide weighed 1.68 g. (theory, 1.78 g.). Titration with thiosulfate showed that it contained only 0.23% unreacted N-bromosuccinimide. After the carbon tetrachloride was evaporated, the residue was sealed in a tube with 8.5 ml. of dimethylaniline and heated 1 hr. at 130°C. The mixture was transferred to a separatory funnel that contained pentane-hexane and hydrochloric acid (10 ml. concentrated HCl diluted to 50 ml.). The pentane-hexane solution was washed six times with hydrochloric acid, then with water until neutral. It was dried over sodium sulfate, and the solvent was evaporated to yield 4.99 g. of product. This was distilled under diminished pressure from an alembic flask: from 139° to 154°, 3.71 g. distilled and from 154° to 170° (pressure, <0.1 mm.) an additional 0.54 g. of darker material distilled. The infrared and ultraviolet absorptions of the material distilling at 139° to 154° are shown in Figures 2 and 3 (dotted line). The ultraviolet absorption of the dehydrobrominated esters was found to be somewhat different for each preparation. A minimum was always found at 229 mμ. The maximum varied from 238 to 248 mμ. The absorptivity at the maximum varied from 11 to 25 and was usually greater when the maximum was at longer wavelength. The smaller peak at 271 mμ was usually found and was more pronounced when the absorptivities were low. The absorption curves seem to be of the type produced by a mixture in which several absorption peaks are

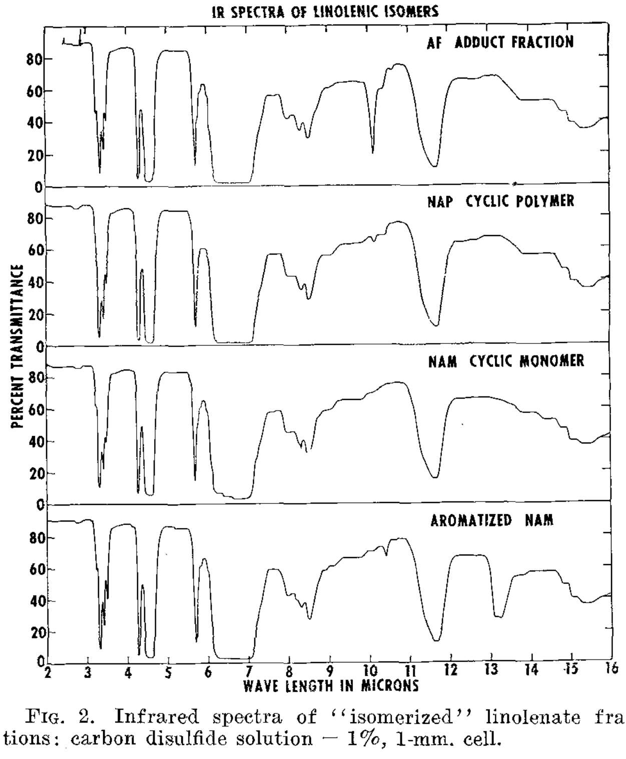

FIG. 2. Infrared spectra of "isomerized" linolenate fractions: carbon disulfide solution — 1%, 1-mm. cell.

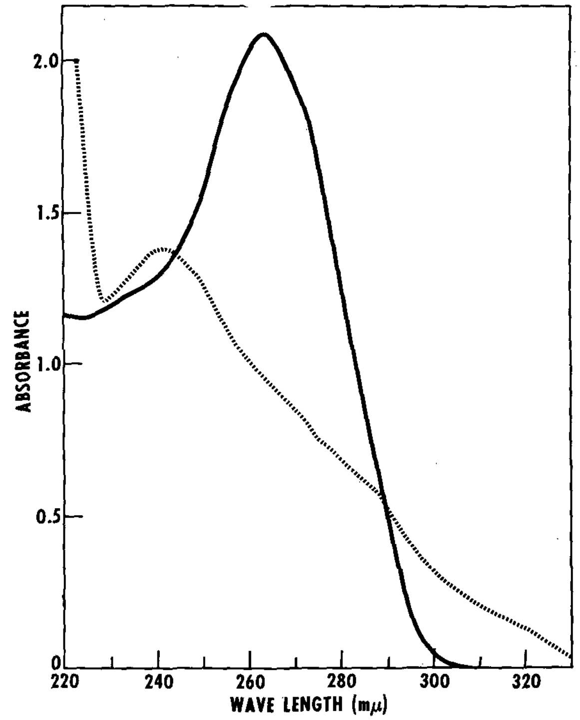

FIG. 3. Ultraviolet absorption spectrum of aromatized NAM: methanol solution, 1-cm. cell (dotted line) C = 0.1264 mg./ml. a_{242} = 11.6. Ultraviolet absorption spectrum of fraction obtained from NAM by countercurrent distribution between 2*N* $AgNO_3$ in 90% methanol and pentane-hexane (solid line). Methanol solution, 1-cm. cell C = 0.1116 mg./ml. a_{264} = 18.6.

superimposed upon a general absorption increasing at shorter wavelengths.

A 1.62-g. sample of aromatized material was refluxed with 3.48 g. of NaOH in 50 ml. of water, and 20 g. of $KMnO_4$ were added in several portions. The permanganate color remaining in the supernatant liquid was destroyed by adding ethyl alcohol. The reaction was made acid with hydrochloric acid, and sulfur dioxide was passed in to react with the manganese dioxide. The solution was saturated with NaCl and extracted six times with ethyl ether. The ether solution was dried over Na_2SO_4 and evaporated to give 0.69 g. of residue. This residue was extracted with pentane-hexane to remove 0.08 g. of an oily material and leave 0.60 g. of a brown powder. The powder was sublimed twice, giving 0.29 g. of sublimate. The ultraviolet absorption spectrum of this sublimate in 1*N* HCl was quite similar to that of pure phthalic anhydride. However the absorptivity at 275 mμ was lower, indicating 80% phthalic anhydride in the sublimate. Thus the phthalic anhydride recovered from the oxidation represented 28% of the theoretical yield, assuming starting material to be all aromatic. After recrystallizing the sublimate twice from benzene, a yield of 74 mg. of material was obtained, m.p. 128° to 131° (phthalic anhydride m.p. 130.8).

Fractionation of NAM. The NAM could be separated both by countercurrent distribution and by gas chromatography into fractions having different ultraviolet absorption spectra. Although the NAM was not completely separated into pure components, these techniques did demonstrate its heterogeneity.

The most complete separation was obtained by countercurrent distribution between pentane-hexane and 2*N* $AgNO_3$ in 90% methanol, a system similar to that studied by Nichols (7). With this system approximately 20% of the monomer can be obtained in a fraction with partition coefficient of 2.2. This material had a maximum absorptivity at 264 mμ of 18.6. Its ultraviolet absorption is shown in Figure 3 (solid line). The remainder of the monomer was found in a single peak with a partition coefficient of 7.3. The ultraviolet absorption in general resembles that of the original NAM. However there are marked differences both in absorptivity and in the shape of the ultraviolet absorption curves among the different tubes from this peak. If the NAP is not previously removed by distillation of the NAM, it passes through the countercurrent distribution apparatus rapidly with a partition coefficient of about 40.

Countercurrent distribution of NAM between acetonitrile and pentane-hexane was less successful. Only one broad band with a partition coefficient of 3.1 was obtained. However a small amount of material with ultraviolet absorption similar to that in Figure 4 was obtained (a_{272} = 17.2) in the first fractions of this band to emerge from the instrument. Other tubes differed among themselves in a manner similar to that found in the distribution between pentane-hexane and methanolic silver nitrate.

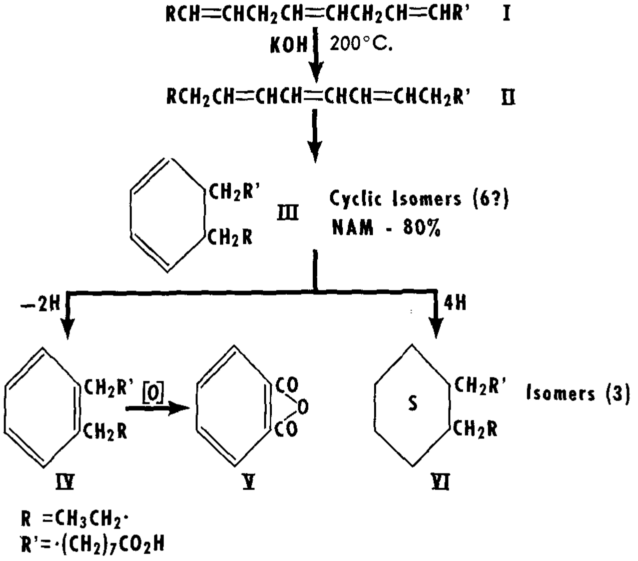

FIG. 4. Suggested structures for some intermediates and products from linolenic acid.

The NAM could also be fractionated by gas chromatography by using Resoflex 296 on Celite at 204°. At least seven incompletely separated components appeared to be present. The eluent gas was collected in methanol in eight fractions, and the ultraviolet absorption was measured. These fractions differed among themselves much as those obtained by countercurrent distribution did. One fraction representing 10% of the eluate was again quite similar to Figure 4. The NAM was eluted rather slowly; most of it passed through the column more slowly than linolenate. By contrast hydrogenated NAM gave three incompletely separated bands, which were eluted more rapidly than methyl linolenate.

Discussion

Alkali isomerization of linolenic acid (I) yields a mixture of products. Under the conditions described about 80% of NAM is formed. This NAM is a complex mixture as shown by countercurrent distribution and gas chromatography. It has not been completely fractionated, and the number and structure of its components are not known. The reactions shown in Figure 4 give suggested structures for some of the intermediates and products obtained by alkali isomerization of linolenic acid and subsequent treatment of the products. Roman numerals given in this discussion refer to Figure 4.

The first step in the reaction is probably the formation of triene conjugation (II), followed by the formation of a cyclohexadiene structure (III) as suggested for eleostearate by Paschke (10). This cyclohexadiene may rearrange to a number of conjugated diene structures as listed by Rivett (11). It is also possible that the cyclic structure may act as a hydrogen donor and disproportionate to give some aromatic compounds (IV). Slansky has reported formation of stearic acid during alkali isomerization of linseed oil (13).

If the NAM is formed from a triene-conjugated intermediate (II), it would be expected to resemble the cyclic monomers formed from eleostearate. Although the cyclic monomers formed by heating methyl eleostearate (10, 11) and linseed oil (5) have been converted to aromatic compounds and oxidized to phthalic acid, they differ among themselves in their ultraviolet and infrared absorption. Our NAM resembles the monomer described by Paschke more closely than it does the others.

As indicated in Figure 1, the AF still had some triene conjugation as shown by the three peaks in the triene region. This conjugation corresponds to only about 7% of conjugated linolenate. In addition, it had a maximum absorption in the diene region equivalent to about 60% of *trans,trans*-conjugated esters. This diene may be formed by a shift of the middle double bond in linolenic acid, producing diene conjugation and leaving two methylene groups between the conjugated system and the remaining double bond or by a shift of only one of the other double bonds to produce a conjugated diene system. It may also be caused by partial hydrogenation with the cyclic compounds acting as hydrogen donor and acceptor. This explanation is supported by the hydrogen-iodine value of 220 for AF, which indicates that some unsaturation has been lost. Because of the small amount of material, no further fractionation was attempted.

The absorption curve for NAM is quite similar in shape to that reported by Paschke, but it has a higher absorptivity at the maximum. The maximum absorption is at 238 mμ with a shoulder extending to higher wavelengths. The NAM contains a number of substances with different ultraviolet absorption characteristics. It contains about 20% of material with a maximum absorption at 264 mμ as shown in Figure 3 (solid line). Although 1,3-cyclohexadiene itself has a maximum absorption at 256 mμ (2), Rivett (11) predicts that the 1,2-disubstituted 3,5-cyclohexadiene (III), which should be the first product of ring formation, will absorb near 270 mμ. Other conjugated cyclohexadiene derivatives will absorb at shorter wavelengths. Such absorption would also be predicted from the values found for conjugated terpene hydrocarbons by O'Connor and Goldblatt (8) The absorption curve for NAP resembles that for NAM, but its maximum is at shorter wavelength.

The infrared spectrum of the AF fraction has a band at 10.15 μ corresponding to *trans,trans* conjugation. In the spectrum of NAM no bands are present in the 10 μ region corresponding to *trans,trans* or *cis,trans* conjugation This is additional evidence for the existence of a ring structure.

As previously stated, the ultraviolet absorption of the aromatic material (IV) prepared by dehydrobromination seems to indicate a mixture of materials. Although this mixture undoubtedly reflects the complexity of the NAM, it is also true that Ziegler (14) was unable to isolate any definite product on treating 1,3-cyclohexadiene with N-bromosuccinimide. Our ultraviolet absorption curves are quite similar to those reported both by Paschke and MacDonald. This similarity is also found in the infrared region. A band similar to the one at 13.1 to 13.3 μ, which is characteristic of ortho-disubstituted benzenes, was found by both in their aromatized monomers.

The failure of the hydrogenated NAM (VI) to form an urea adduct must be caused either by the presence of a ring or branched chain in the molecule, and the formation of an aromatic compound which can be oxidized and converted to phthalic anhydride (V) shows that at least a large part of the NAM must contain a 6-carbon ring.

Summary

Methyl linolenate was isomerized by heating in an alkaline ethylene glycol solution for 7 hrs. at 200°. Methyl esters of the isomerized acids were treated with urea in methanol, and the nonurea-adduct-forming fraction was distilled. The isomerized esters consisted of 81.8% of nonurea-adduct-forming monomeric distillate (NAM), 13.7% nonurea-adduct-forming polymeric nondistillable material, and 4.5% of urea adduct-former.

The NAM has a maximum absorption in the ultraviolet region at 238 mμ. Ultraviolet absorption extends into the region associated with triene conjugation, but the characteristic structure of triene absorption is absent. Infrared absorption bands in the 10 μ region ordinarily found with *trans,trans* or *cis,trans* are absent. The NAM is shown to contain a cyclic monomer by treatment with N-bromosuccinimide, followed by dehydrobromination with dimethylaniline. The resultant product was oxidized to phthalic acid with permanganate.

The NAM was separated both by countercurrent distribution and by gas chromatography into fractions having different ultraviolet absorption spectra. However complete fractionation of the mixture into its pure components has not yet been achieved.

Acknowledgment

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Castor Oil-Derived Plasticizers. Some Nitrogen-Containing Derivatives as Plasticizers for Vinyl Chloride-Vinyl Acetate Copolymer and Cellulose Acetate Resins

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ALTHOUGH simple esters of ricinoleic acid are not compatible with polyvinyl chloride, some of their acyl and aroyl derivatives are satisfactory plasticizers; furthermore the diacetate of ricinoleyl alcohol is an excellent low-temperature plasticizer (5, 7). Since the acyl, carbonyl, morpholino, cyanoethyl ether, and some ester groups are good plasticizing functional groups (1, 2, 5, 7), prior work in this laboratory was directed toward the preparation of compounds, from methyl ricinoleate, possessing some of these groups, in extending the scope of suitable derivatives of ricinoleic acid as primary plasticizers (3, 4).

It is the object of this communication to report the screening of some of these derivatives of ricinoleic acid (12-hydroxy-9-octadecenoic acid, the principal component of castor oil) as primary plasticizers for vinyl chloride-vinyl acetate copolymer resin. The plasticizing efficiency of

4-ricinoleoylmorpholine,
4-(12-hydroxystearoyl)morpholine,
4-(12-acetoxyoleoyl)morpholine,
4-(12-acetoxystearoyl)morpholine,
4-(12-β-cyanoethoxyoleoyl)morpholine,
4-(12-β-cyanoethoxystearoyl)morpholine,
1,12-bis(β-cyanoethoxy)-9-octadecene, and
1,12-bis(β-cyanoethoxy)octadecane

were intercompared with DOP, di(2-ethylhexyl) phthalate. Their compatibilities with cellulose acetate were also evaluated.

Experimental

The following nitrogen-containing derivatives of ricinoleic acid were prepared in pure form according to the general procedure described previously by Dupuy *et al.* (3, 4).

4-Ricinoleoylmorpholine. Methyl ricinoleate was refluxed with 100% excess of morpholine for a 36-hr. period, at a temperature just sufficient to liberate the methanol evolved from the reaction mixture but not enough to distill off the morpholine. After the excess morpholine was distilled under reduced pressure, 4-ricinoleoylmorpholine was isolated by rapid, vacuum distillation, b.p. 243–246°C./0.2 mm.

Anal. Calcd. for $C_{22}H_{41}NO_3$: C, 71.88; H, 11.24; N, 3.81; OH, 4.63. Found: C, 71.47; H, 11.02; N, 3.80; OH, 4.68; $n^{25/D}$ 1.4891; $\alpha^{25/10\,cm.}$ 4.27.

4-(12-Hydroxystearoyl)morpholine. The morpholide of methyl 12-hydroxystearate was prepared as described above; b.p. 245–249°C./0.25 mm. Crystallizations from petroleum ether, Skellysolve B, gave a product of constant melting point, 52.5–53.0°C.

Anal. Calcd. for $C_{22}H_{43}NO_3$: C, 71.49; H, 11.73; N, 3.79; OH, 4.60. Found: C, 71.53; H, 11.79; N, 3.75; OH, 4.59.

4-(12-Acetoxyoleoyl)morpholine. 4-Ricinoleoylmorpholine was refluxed with an equal weight of acetic anhydride for 2 hrs. After the excess acetic anhydride and acetic acid were distilled under reduced pressure, 4-(12-acetoxyoleoyl)morpholine was isolated by rapid, vacuum distillation, b.p. 230–234°C./0.2 mm.

Anal. Calcd. for $C_{24}H_{43}NO_4$: C, 70.37; H, 10.58; N, 3.42. Found: C, 69.99; H, 10.53; N, 3.24; $n^{25/D}$ 1.4789; $\alpha^{25/10\,cm.}$ 20.02.

4-(12-Acetoxystearoyl)morpholine. 4-(12-Hydroxystearoyl)morpholine was acetylated as described above. The 4-(12-acetoxystearoyl)morpholine was distilled at 234–235°C./0.2 mm.

Anal. Calcd. for $C_{24}H_{45}NO_4$: C, 70.03; H, 11.02; N, 3.40. Found: C, 69.62; H, 11.17; N, 3.24; $n^{25/D}$ 1.4709.

4-(12-β-Cyanoethoxyoleoyl)morpholine. The cyanoethylated derivative of 4-ricinoleoylmorpholine was prepared in the following manner. The morpholide was dissolved in an equal weight of dioxane; then water (10% by weight) and benzyltrimethylammonium hydroxide (10% by weight of a 40% methanol solution) were added. This reaction mixture was stirred and heated to 50°C.; then 100% excess of acrylonitrile was added dropwise. The exothermic reaction was moderated with an ice-water bath when the reaction temperature rose above 85°C. After all the acrylonitrile was added, the reaction was continued for 3 hrs. and the temperature was maintained between 60 and 70°C. The hot mixture was poured slowly into 3 volumes of diethyl ether to precipitate

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