Derivatives of Ricinelaidic Acid. Their Infrared Spectra and Conformation of the Ricinelaidic Moiety[1]

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In continuing the study of the *trans* isomers of ricinoleic acid and its derivatives (1), we have now determined the infrared spectra and measured absorptivities in the 10.3 micron region of a series of compounds in which the functional groups of ricinelaidic acid have been systematically varied. The compounds investigated include ricinelaidic acid, 12-ketoelaidic acid, ricinelaidyl alcohol, and their respective methyl esters and acetates. This series is of particular interest because it provides a means of comparing the influence of various substituents upon the fundamental absorption pattern of ricinelaidic acid. Comparison of the relative effect of these groups upon the changes both in wavelength and magnitude of absorption in the 10.3 micron region is of additional interest. This communication presents pertinent data regarding infrared spectra and absorptivities as well as certain considerations relative to the conformation of the ricinelaidic moiety.

Experimental

Preparation of Materials

Methyl Ricinelaidate. This ester was prepared, as described previously (1), by the elaidinization of methyl ricinoleate with a relatively small quantity of a nitrite-nitric acid solution as the isomerization agent.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.02; H, 11.61; OH, 5.44; sap. equiv., 312.5. Found: C, 72.67; H, 11.72; OH, 5.71; sap. equiv., 312.6; $N^{60/D}$, 1.4468 absorptivity, (a) = 0.482 at 10.27 microns in CS_2.

Ricinelaidic Acid. Ricinelaidic acid was obtained by the saponification of methyl ricinelaidate.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.43; H, 11.48; OH, 5.69; neut. equiv., 298.4. Found: C, 72.38; H, 11.63; OH, 5.71; neut. equiv., 298.1; $N^{60/D}$, 1.4568 absorptivity, (a) = 0.558 at 10.27 microns in CS_2.

Ricinelaidyl Alcohol. Ricinelaidyl alcohol was prepared by the lithium aluminum hydride reduction of ricinelaidic acid. In a 1-liter, three-necked flask equipped with a reflux condenser, dropping funnel, and an air-driven stirrer were placed 150 ml. of dry ethyl ether and 6 g. of finely ground lithium aluminum hydride. After stirring this mixture for 1.25 hr., an ethereal solution of 29.8 g. (0.1 mole) of ricinelaidic acid was added dropwise at a rate that insured gentle refluxing. Upon completion of the addition, the stirring was continued for 1.5 hr. The excess hydride was destroyed by the dropwise addition of 15 ml. of water, followed by the decomposition of the alcoholate by addition of 250 ml. of 10% cold sulfuric acid. After separation from the ether layer, the aqueous layer was twice extracted with ether. The combined ether solutions were washed successively with water and 5% sodium carbonate until free of acid and then dried over anhydrous calcium sulfate. A portion of the crude product (19.1 g.) was crystallized from 275 ml. of pentane-acetone (1:1) at −2°C., yielding 16.3 g. of material melting at 51.9–52.6°C. Recrystallization from absolute ethanol (6 ml./g.) at −25°C. yielded 10.2 g. of ricinelaidyl alcohol, m.p. 53.0–53.4°C., which remained unchanged by further recrystallization.

Anal. Calcd. for $C_{18}H_{36}O_2$: C, 75.99; H, 12.76; OH, 11.96; I.V., 89.2. Found: C, 75.86; H, 12.63; OH, 11.92; I.V., 89.2; absorptivity, (a) = 0.570 at 10.30 microns in CS_2.

Elaidyl Alcohol. Oleyl alcohol (I.V., 94.0; OH, 6.4) was elaidinized by the same procedure as employed for methyl ricinoleate. Infrared analysis of the equilibrium mixture of the alcohols showed that it contained 72% of the *trans* isomer. The crude isomerization mixture (27 g.) was dissolved in seven volumes of pentane-acetone (5:1) and allowed to crystallize at −20°C., yielding 16.3 g. of elaidyl alcohol, m.p. 35.6–36.2°C. Two recrystallizations from four volumes of the same solvent gave a product of constant melting point, 36.5–36.9°C.

Anal. Calcd. for $C_{18}H_{36}O$: C, 80.52; H, 13.51; I.V., 94.5. Found: C, 80.20; H, 13.25; I.V., 94.1; absorptivity, (a) = 0.612 at 10.34 microns in CS_2.

12-Ketoelaidic Acid. The 12-ketoelaidic acid employed was of commercial origin (2, 3). A 50-g. sample of the commercial product was dissolved in 350 ml. of acetone, decolorized with activated carbon, filtered, and crystallized at +5°C., yielding 38.2 g., m.p. 72.8–73.4°C. Successive crystallizations from acetone and alcohol did not change the melting point.

Anal. Calcd. for $C_{18}H_{32}O_3$: C, 72.93; H, 10.88; carbonyl O, 5.40; neut. equiv., 296.4. Found: C, 73.25; H, 10.80; carbonyl O, 5.34 neut. equiv., 295.0; absorptivity, (a) = 0.536 at 10.33 microns in CS_2.

Methyl 12-Ketoelaidate. Methyl 12-ketoelaidate was prepared by treating 14.8 g. (0.05 mole) of 12-ketoelaidic acid with 2.9 g. (0.07 mole) of diazomethane in ether. The reaction product, recovered in the usual manner, was crystallized from pentane-acetone (5:1) at −25°C. and was a colorless liquid at room temperature.

Anal. Calcd. for $C_{19}H_{34}O_3$: C, 73.50; H, 11.04; carbonyl O, 5.15; OCH_3, 9.99. Found: C, 73.07; H, 10.94; carbonyl O, 5.17; OCH_3, 9.63; $N^{30/D}$, 1.4555; absorptivity, (a) = 0.442 at 10.34 microns in CS_2.

Methyl 12-Acetoxyelaidate. Methyl ricinelaidate was acetylated by treating 31.2 g. (0.1 mole) of the ester with 160 ml. of an acetic anhydride-pyridine mixture (1:3) in a 500-ml., round-bottom flask which was fitted with a reflux condenser and thermometer. The mixture was stirred and heated to 100°C. and maintained at this temperature for 2 hrs. After cooling to 75°C., 150 ml. of water were added, and the mixture was stirred rapidly at this temperature for 15 min. It was then cooled, transferred to a separatory

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funnel, and extracted with 200 ml. of ether. The ether extract was washed four times with 250-ml. portions of 3M HCl, after which it was dried over anhydrous sodium sulfate. The recovered product was fractionally distilled, yielding a main fraction of 23.7 g., b.p. 156–157°C./30 microns.

Anal. Calcd. for $C_{21}H_{38}O_4$: C, 71.14; H, 10.80; OH, 0.0; OCH_3, 8.75; sap. equiv., 177.3; I.V., 71.6. Found: C, 70.68; H, 10.73; OH, 0.0; OCH_3 8.52; sap. equiv., 178.4; I.V., 71.6; $N^{23/D}$, 1.4530; absorptivity, (a) = 0.478 at 10.32 microns in CS_2.

12-Acetoxyelaidic Acid. Ricinelaidic acid was acetylated according to the procedure described for the methyl ester. A 16-g. sample of the material was vacuum-distilled, yielding 10.9 g. of product, b.p. 186–189° C./100 microns.

Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66; I.V., 74.5. Found: C, 69.83; H, 10.38; I.V., 74.8; $N^{26/D}$, 1.4583; absorptivity, (a) = 0.569 at 10.33 microns in CS_2.

12-Acetoxyelaidyl Acetate. Ricinelaidyl alcohol was acetylated according to the procedure described above with the exception that the ratio of acetylating reagent to diol was twice that previously employed. A 24-g. sample of the material was vacuum-distilled, yielding 14.6 g. of a product, b.p. 166–167°C./85 microns.

Anal. Calcd. for $C_{22}H_{40}O_4$: C, 71.69; H, 10.94; sap. equiv., 184.3; I.V., 68.9. Found: C, 71.54; H, 10.91; sap. equiv., 186.0; I.V., 69.0; $N^{25/D}$, 1.4508; absorptivity, (a) = 0.512 at 10.33 microns in CS_2.

Elaidyl Acetate. Elaidyl alcohol was acetylated in the same manner as methyl 12-acetoxyelaidate. Vacuum distillation yielded a heart cut, b.p. 147–148°C./130 microns.

Anal. Calcd. for $C_{20}H_{38}O_2$: C, 77.36; H, 12.33; I.V., 81.7. Found: C, 77.37; H, 12.21; I.V., 81.2; $N^{25/D}$, 1.4501; absorptivity, (a) = 0.530 at 10.34 microns in CS_2.

Infrared Measurements. Complete infrared absorption curves from 2 to 12 microns of all compounds investigated were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. The settings used were: resolution, 927; suppression, 3; gain, 6; response, 1; and speed, 4. All spectra were obtained in chloroform solution at concentrations of about 20 g./l. with an absorption cell 0.50 mm. in path length. Pure dry chloroform was placed in the reference beam. Absorption of chloroform was completely eliminated from the resulting spectra by this differential technique.

In addition to the complete curves, the infrared absorption of these compounds was measured in carbon disulfide solution in the 10-micron region, where the absorption maxima characteristic of C—H bending about *trans* double bonds is expected. These measurements were made with the slit width control set on manual at a width of 151 microns. The gain was set at 5, resolution at 79, response at position 1, suppression at 0; the amplifier balance was set to give a definite upscale drift to the extent that the pen would move from 50 to 100% in 50 ± 3 sec. with both light beams totally obstructed.

Discussion

TABLE I
Absorptivities of Elaidic Acid and Derivatives in Carbon Disulfide

Compound	Wave-length μ	Absorptivity[a]	Absorptivity corrected[b]	Molecular absorptivity[c]
Elaidic acid[d]	10.34	0.661	0.458	129
Methyl elaidate[d]	10.33	0.540	0.476	141
Elaidyl alcohol	10.34	0.612	0.512	137
Ricinelaidic acid	10.27	0.558	0.348	104
Methyl ricinelaidate	10.27	0.482	0.374	117
Ricinelaidyl alcohol	10.30	0.570	0.416	118
12-Ketoelaidic acid	10.33	0.536	0.367	109
Methyl 12-ketoelaidate	10.34	0.442	0.367	114
Elaidyl acetate	10.34	0.530	0.456	143
12-Acetoxyelaidic acid	10.33	0.569	0.374	127
Methyl 12-acetoxyelaidate	10.32	0.478	0.364	129
12-Acetoxyelaidyl acetate	10.33	0.512	0.397	146

[a] Average of two values obtained from measurements in CS_2 solution.
[b] Corrected by base-line technique.
[c] Based on corrected absorptivities.
[d] Authentic samples furnished by Physical Chemical Investigations of this laboratory.

Infrared Spectra. The 12 compounds whose infrared spectra have been investigated are listed in column 1 of Table I. The complete infrared spectra in the rock salt region of elaidic and ricinelaidic acids, and their methyl esters, as well as the spectrum of elaidyl alcohol, have been published and discussed previously (1, 4, 5, 6, 7). To the best of our knowledge the spectra of the remaining compounds have not been reported heretofore; these are presented in Figure 1. Other than the changes observed in the position and intensity of the C—H bending band in the 10-micron region, discussed in detail below, these spectra resemble those of the parent compounds although modified by bands due to the additional functional groups. The spectrum of ricinelaidyl alcohol resembles very closely that of elaidyl alcohol except that, at the concentration employed, the ricinelaidyl alcohol exhibits two bands arising from O—H stretching at 2.78 and 2.90 microns whereas the elaidyl alcohol has only a single band at 2.70 microns (6). The spectrum of 12-ketoelaidic acid is almost identical with that of elaidic acid. The strong band at 5.83 microns is due to the unresolved bands arising from the C=O stretching of the carboxyl group, 5.80–5.88 microns, and the keto group, 5.80–5.85 microns (8). However in methyl 12-ketoelaidate the band arising from the ester C=O stretching, 5.75 microns (8), and the keto group, 5.80–5.85 microns, appears as a double-peaked maximum exhibiting some resolution of these two bands. A single C=O stretching at 5.78 microns, characteristic of the ester group, appears in the spectrum of elaidyl acetate. This spectrum is differentiated from keto derivatives by the increased intensity of the C—H bending bands at 6.86 and 7.33 microns and the appearance of the strong C—O stretching bands at 7.95 and 9.78 microns. A broad band is found in the spectrum of the 12-acetoxyelaidic acid between 5.75 and 5.85 microns, arising from unresolved absorption of the C=O stretching of the acid and the ester groups. The spectrum of methyl 12-acetoxyelaidate reveals only a single sharper band of the C=O of the ester group. The spectra of both of these compounds show strong C—H bending bands at 6.84 and 7.26 microns and strong C—O stretching bands at 7.95 and 9.80 microns. The methyl group is indicated in the spectrum of 12-acetoxyelaidic acid by the shoulder at 6.96 microns. This has developed into a weak but sharp band in methyl 12-acetoxyelaidate. The spectrum of 12-acetoxyelaidyl acetate shows no evidence for a methyl group at 6.96 microns and is characterized by a single C=O stretching band at 5.80 microns, intense bands arising from C—H

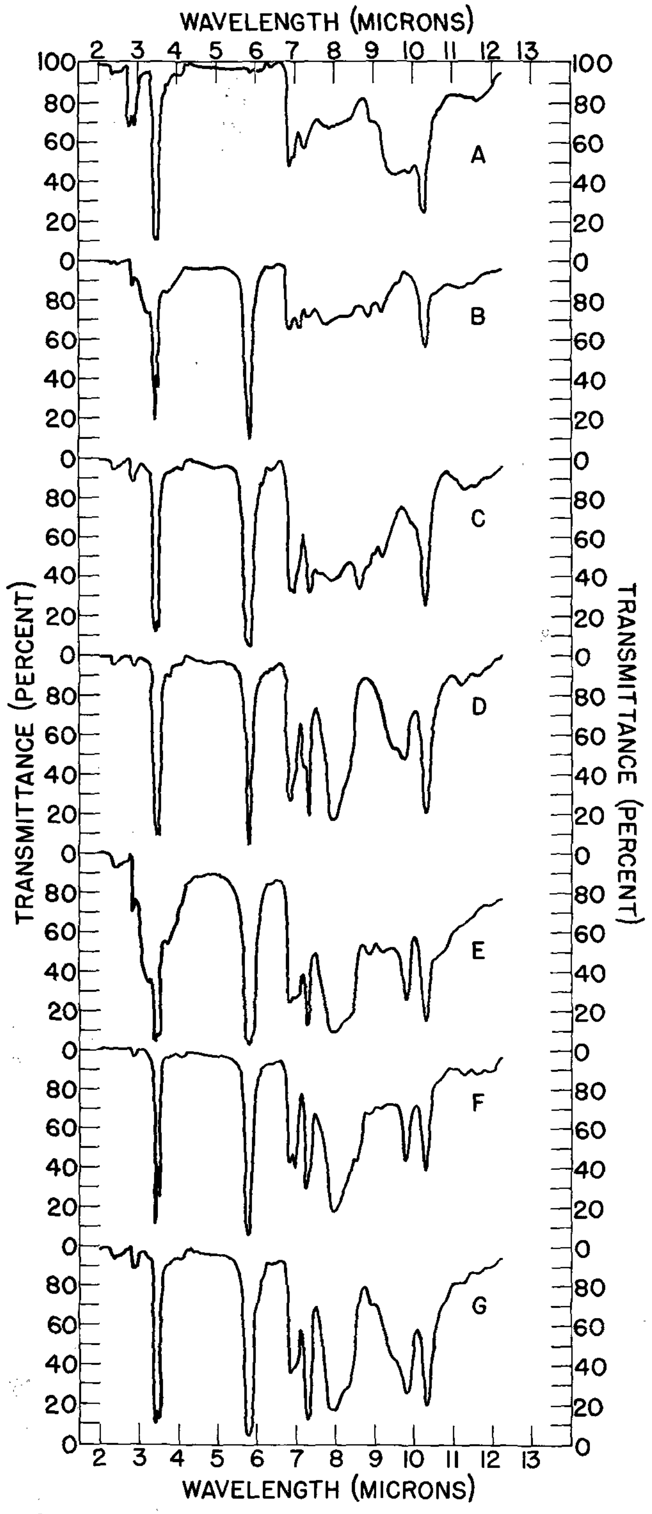

FIG. 1. Infrared spectra of derivatives of elaidic acid in chloroform. A. ricinelaidyl alcohol; B. 12-ketoelaidic acid: C. methyl 12-ketoelaidate; D. elaidyl acetate; E. 12-acetoxyelaidic acid; F. methyl 12-acetoxyelaidate; G. 12-acetoxyelaidyl acetate.

bendings at 7.30 and 7.85 microns, and from C—O stretchings at 7.96 and 9.85 microns.

Calculation of Absorptivity in the 10-Micron Region. From the tracings of the C—H bending bands in the 10-micron region, obtained in carbon disulfide solution, the wavelength positions and absorptivities of this band for elaidic acid and 11 derivatives have been measured. These are presented in Table I. The total absorptivities, given in column 3 of Table I, reflect contributions from other bands in the spectra. For comparison of intensities integrated absorptivities were considered, but these are difficult to obtain with accuracy owing to the strong 10.6 micron band on the long wavelength side of the C—H bending band in the spectra of the acids and owing to the band about 9.8 microns on the short wavelength side in the spectra of the acetates and acetoxy compounds. Absorptivities corrected by the well-known base-line technique (9, 10, 11) are given in column 4 of Table I. In this application of the base-line technique a straight line was drawn on the charts from each side of the strong C—H bending band. The positions on each side of the band were arbitrarily selected for the different groups of derivatives as follows: acids, 10.13 and 10.67 microns; esters, 10.02 and 10.59 microns; and alcohols, 10.10 and 10.60 microns. The distances from the zero line of the recorder chart to the absorption peak and to the base line along the vertical line through the absorption peak were measured. The fractional transmission was calculated as the distance to the absorption peak divided by the distance to the base line. This corrected transmittance was converted to absorbance, and the absorptivity, calculated in the usual way, is the "background-corrected absorptivity" of column 4 of Table I.

The values of the absorptivities for elaidic acid, methyl elaidate, and elaidyl alcohol are considerably higher than those reported by earlier workers. It is believed that these higher values result partially from the higher resolution of the instrument when operated as described above and partially from the fact that these particular compounds were very highly purified. These values represent the best obtained for these compounds and have been checked from compounds prepared in other laboratories. They are the values for the primary standards which, it is contemplated, will be used to establish an official A.O.C.S. method for the determination of *trans* isomers.

Substituent Effects on Absorptivity in the 10.3 Micron Region. Absorption in the 10.3 micron region has been assigned to a C—H out-of-plane bending about an internal *trans* ethylenic bond (12). It may be presumed *a priori* that the characteristics of this vibration will be influenced by the electron density at the double bond. That band intensities can be affected by changes in electron density produced by inductive effects of substituents has been demonstrated in *meta*-substituted benzonitriles (13). It was found that the intensity of the C≡N stretching vibration could be correlated with Hammett's σ-values; the band intensity decreases with the increasing electron-attracting capacity of the substituent. Although it was not possible in the present investigation to evaluate absolute band intensities in the 10.3 micron region owing to indeterminate contributions of —OH deformation and C—O stretching vibrations, it is nevertheless of interest to intercompare molecular absorptivities associated with variations in the substituents. These data are presented in Table I. The changes in molecular absorptivity and wavelength associated with variation of the internal substituents may be attributed to electronic and steric effects. It is also probable that these effects are responsible for the changes associated with a terminal substituent; however the mechanism operating in the latter case is rather obscure. The probable relationship existing between electron density at the double bond and the characteristics of the 10.3 micron absorption may be deduced from a consideration of 12-ketoelaidic acid. It is evident that the introduction of a carbonyl oxygen atom into elaidic acid or its methyl ester in the *beta*-position with respect to the ethylenic bond results in a decreased molecular absorptivity. Since the carbonyl oxygen is strongly electron-withdrawing, it follows that the electron density at the double bond is diminished with a corresponding reduction in the basicity of the π-electrons. The π-orbital lies above and below the ethylenic plane, precisely in the locality in which the C—H out-of-plane bending must occur. It could be expected therefore that the characteristics of the C—H bending vibration would be influenced by the basicity existing at the double bond because the hydrogen is relatively poorly screened.

Conformation of the Beta-Hydroxy-ene System. Substitution of a hydroxyl group into elaidic acid, methyl elaidate, or elaidyl alcohol in the *beta*-position with respect to the ethylenic bond results in a lowering of molecular absorptivity as well as a shift in the absorption maximum to a shorter wavelength. The alteration in electron density at the double bond cannot be attributed to an inductive effect owing to the small negative value of the substituent constant for the hydroxyl group. The origin of this alteration can be traced to the disposition of the hydroxyl group with respect to the ethylenic bond. In this connection it is of interest that chloro-acetone has been shown to exist in two rotational isomeric forms (14). The form in which the carbonyl absorption has been shifted to a lower wavelength than that of acetone has been assigned a conformation in which the halogen and acyl oxygen atoms are in close proximity. On the other hand, monochloro-acetaldehyde exhibits a single carbonyl absorption and is thus presumed to exist in only one rotational isomeric form (14). It is significant that each of the compounds containing the *beta*-hydroxy-ene system shows a single absorption maximum in the 10.3 micron region and that this maximum occurs 0.04 to 0.07 micron lower than the analogous band for elaidic acid. It is of equal importance that acetylation of these compounds produces an increase in absorptivity as well as a shift in the absorption maximum to approximately 10.33 microns, the region in which the elaidic type compounds show absorption maxima. On the basis of these considerations, it appears probable that the ricinelaidic moiety exists principally in a single rotational isomeric form, in which the hydroxyl group lies above the ethylenic plane with its hydrogen oriented toward the double bond (Figure 2). Reference to scale models shows that in this conformation the hydroxyl group is constrained owing to the steric requirements of the ethylenic hydrogen atoms and further that the system would be stabilized by intramolecular hydrogen bonding between the hydroxyl group and the π-electrons of the double bond. Further support for this latter viewpoint is to be found in the observations that intramolecular hydrogen bonding occurs between unlikely groups as in 2-allyl phenol (15) and 3-butenol (16), also that the entropy losses attending the formation of the intramolecular hydrogen bond are much lower than those of the intermolecular hydrogen bond (17).

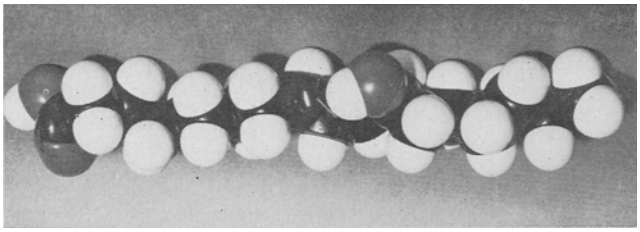

FIG. 2. Model of ricinelaidic acid showing the conformation of the *beta*-hydroxy-ene system.

Summary

The infrared spectra and absorptivities in the 10.3 micron region have been determined for a series of compounds in which the functional groups of ricinelaidic acid were varied systematically. The compounds investigated included ricinelaidic acid, 12-ketoelaidic acid, ricinelaidyl alcohol, and their respective methyl esters and acetates. The influence of the internal substituents on the fundamental absorption pattern of ricinelaidic acid was determined. Observed decreases in molecular absorptivities and shifts in position of maximum absorption are related to the electron-withdrawing character of relevant substituents and to hydrogen bonding in the *beta*-hydroxy-ene system. The conformation of this system is discussed.

Acknowledgments

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