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BRANCHED-CHAIN FATTY ACIDS XXVI. INFRARED SPECTRA OF SOME LONG-CHAIN 2-ALKENOIC ACIDS AND THEIR BEARING ON THE STRUCTURE OF C₂₇-PHTHIENOIC ACID¹

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ABSTRACT

The infrared spectra of six long-chain 2-alkenoic acids with different types of branching near the double bond are presented and discussed. Several absorption bands are observed which do not appear in the spectra of unconjugated long-chain fatty acids. One of these is the 6.1 μ carbon-carbon double bond stretching vibration band, the intensity of which has evidently been greatly enhanced as a result of conjugation. Other new bands appear in the 10-16 μ region, some of which may prove to be analogous to those in the spectra of alkenes which characterize the arrangement of alkyl groups around the double bond. Such a relationship has not been fully demonstrated with the limited amount of data available.

Use of the 7.25 μ band intensity as an index of the number of terminal methyl groups (previously employed in branched alkanolic acids) was found to be valid for this group of alkenoic acids.

Comparison of the spectra with that of C₂₇-phtienoic acid provides additional support for previous evidence that this molecule has an α -methyl branch. There is no definite indication regarding the position of a second nearby methyl group, except that the lack of spectral conformity with 2,5-dimethyl-2-heptadecenoic acid rules out this particular structure.

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INTRODUCTION

In the course of extensive study of the branched-chain fatty acids of the tubercle bacillus, Cason and collaborators have isolated one of the principal species and shown that it is an α, β -unsaturated acid having twenty-seven carbon atoms and three branching side chains (probably methyl), one of which is on the α -carbon atom.^{2,3} This acid has been called C₂₇-phthienoic acid. Infrared spectrometry was employed to aid in establishing these structural features, and certain inferences were based on the results of a broad study of saturated branched-chain fatty acid spectra.⁴ In continuing efforts to elucidate the structure of C₂₇-phthienoic acid still further, Cason's group has synthesized several α, β -unsaturated acids with various arrangements of branching methyl groups. The properties and methods of synthesis of these acids have been described in the preceding papers.^{5,6} Their infrared absorption spectra have also been recorded, and are presented here with two purposes in view: (1) to examine the relationships between structure and spectra in this restricted class of compounds; (2) to make direct comparisons with the spectrum of C₂₇-phthienoic acid.

EXPERIMENTAL

Materials.⁷ The six synthetic acids whose spectra are shown in Figs. 2 and 3 are those of which the preparation and properties are discussed in the preceding papers of this series.^{5,6} C₂₇-phthienoic acid is also the subject of previous publications.^{2,3} Oleic acid (>99%) was obtained from the Hormel Institute, Austin, Minnesota. Stearic and elaidic acids were both recrystallized and are regarded as sufficiently pure for illustrative purposes.

Apparatus. The spectra were recorded on a Baird Associates Model B double beam spectrophotometer equipped with a sodium chloride prism. The region beyond 6.5 μ in the spectra of Figs. 2 and 3 are of liquid films between salt windows. Neither the uncertainties nor the variations in these film thicknesses are regarded as important, since quantitative measurements have only been made on the solution spectra (5.5-6.5 μ).

DISCUSSION

The main points of interest in the interpretation of the spectra (Figs. 2 and 3) are the relationships which involve the double bond, with particular reference to the effects of conjugation and the presence of alkyl branches. The spectral features of long-chain fatty acids in general have been discussed by Shreve et al.,⁸ and a more recent publication by Sinclair and collaborators⁹ includes the spectra of cis and trans-2-octadecenoic acids. Some effects of chain branching in saturated fatty acids have been reported previously from this laboratory.⁴

It is well known from the study of alkene spectra¹⁰ that structural differences among simple olefins may be manifested in one or more of three regions of infrared absorption. The first of these is the region of carbon-hydrogen bond stretching vibrations in the range from about 3.2 to 3.5 μ . Olefinic

hydrogens can be distinguished in this range, but only with better resolving power than that of the sodium chloride prism in our spectrophotometer.

Double Bond Stretching Bands.

The second region is near 6μ , where the carbon-carbon double bond stretching frequency is located. It is indicated in the correlation of Rasmussen¹⁰ that terminal double bonds have their absorption maxima at slightly longer wave lengths ($6.02 - 6.12 \mu$) than do internal double bonds ($5.98 - 6.03 \mu$) and that conjugation with carbonyl groups also tends to displace the peak toward longer wave lengths. The positions of the C=O and C=C stretching bands of the 2-alkenoic acids studies are given in Table I.

The carbonyl bands all lie within a small range near 5.9μ , whereas in unconjugated long-chain fatty acids (see Fig. 1) the corresponding band is found at about 5.84μ .⁸ The magnitude of the displacement associated with the conjugative effect is about the same as that observed for esters and ketones^{10,11} and for the 2-octadecenoic acids.⁹

The C=C stretching bands are all at slightly longer wave lengths than the values quoted above for internal double bonds, and this again is consistent with a conjugative effect. (For oleic and other acids in which the double bond is relatively remote from the carboxyl group, the C=C stretchings bands are very weak and not easily resolved from the strong C=O band. They are not discernible in Fig. 1.) A methyl group on either of the unsaturated carbons appears to cause a slightly larger shift. In agreement with the alkene correlation, the terminal double bond (2-methylenedodecanoic acid) has the longest wave length band.

It may be noted in Figs. 2 and 3 that at the same molar concentrations the carbonyl bands of all of these acids have approximately the same intensity (range of peak absorbance is 0.85-0.90). The C=C absorption intensities, on the other hand, vary with different arrangements of groups around the double bond.

Peak absorbance values of these bands have been included in Table I. No extension to more refined quantitative intensity measurements has been attempted. Nevertheless in comparison with the two acids which may be regarded as 1-carboxy-2-alkylethylenes, it appears that substitution of an additional methyl group on the β -carbon enhances the intensity, whereas in both cases of α -alkyl substitution the intensity is reduced. If it may be assumed that the vibrational interaction between the conjugated C=C and C=O bonds is small, then the gain in intensity by the C=C band in going from a non-conjugated to a conjugated position must be attributable mainly to its polarization by the carboxyl group. It may then be inferred that the intensity differences associated with α vs. β alkyl substitution are a reflection of the relative abilities of a hydrogen atom and an alkyl group to polarize the double bond. The net effect of a hydrogen at one end and an alkyl at the other is in one case competing with polarization by the carboxyl, and in the other case reinforcing it. This description is oversimplified, since the absorption intensity depends on the change of dipole with vibration rather than on the equilibrium dipole directly. Until absolute intensity measurements and a more detailed analysis of the factors influencing the intensity can be made, this hypothesis provides only a tentative and partial explanation of the observations.

Bands in the Range from 10 to 16 μ .

The third region in which double bond configurations may be characterized is beyond 10 μ , where the non-planar vibrations of olefinic hydrogen atoms occur. The well-established correlation of these frequencies with alkylethylene structural types^{10,12} is summarized in Table II. The bands whose maxima have been quoted to the nearest 0.05 μ are usually strong, sharp, and well defined, whereas those for the cis and trialkyl types are apt to

be broad, less intense, and less constant in position. It has been noted by other authors^{8,9} that this correlation is valid for non-conjugated fatty acids in which the double bond structure is one of the first three types listed in Table II (Their work did not include any examples with branching structures. Moreover, as may be seen in Fig. 1, the presence of a 14-15 μ band in the spectrum of oleic acid is difficult to verify). Rasmussen¹⁰ has shown that these frequencies are altered if one or more of the alkyl groups is replaced by a chlorine atom. Consequently it has not been presumed that the correlation would hold if an alkyl group were replaced by a carboxyl. Since the 2-alkenoic acids can be regarded as carboxyethylenes, it is of interest to examine their spectra with this point in mind. Fig. 4 is a chart constructed from the spectra of Figs. 2 and 3, showing the bands between 10 and 16 μ which do not occur in saturated fatty acid spectra. Heights of the solid vertical lines represent roughly the relative band intensities. Dotted lines indicate positions (or ranges) of the characteristic bands for corresponding alkylethylenes, i.e., carboxyl replaced by alkyl.

The assignment of a particular band in any of these spectra as the hydrogen non-planar bending vibration is somewhat dubious. The most reliable choices are probably the bands at 10.18 and 10.15 μ in the spectra of 2-dodecenoic and 5-methyl-2-hendecenoic acids, respectively. From the method of synthesis^{5,6} these compounds are presumed to be trans, and the suggested band positions are not greatly different from the characteristic one of the trans-1,2-dialkylethylene structure (Table II). Sinclair⁹ also observed a band at 10.2 μ in the spectrum of trans-2-octadecenoic acid which was not exhibited by the cis isomer.

For 2-methylenedodecanoic acid the 10.54 μ band is the most reasonable selection, principally on the basis of intensity. This tentative choice is given some support by the appearance of strong bands at 10.6-10.7 μ (rather than 11.25 μ) in the spectra of methyl methacrylate¹³ and a number of other methacrylates¹⁴.

For the compounds which are structurally analogous to trialkylethylenes (only one remaining olefinic hydrogen) the uncertainty regarding cis - trans relationships presents an additional obstacle to fuller interpretation. Whereas the non-planar hydrogen bending bands of cis and trans -3-methyl-2-pentene appear to be at 12.2 and 12.3 μ respectively¹³, it must be assumed that the presence of a carboxyl group may have a marked effect on the corresponding vibrations in conjugated acids. It seems evident that until there are available some acids of this type which are unambiguously known to be cis or trans it will not be possible to disentangle the effects of branching and geometrical isomerism, nor to establish a meaningful correlation of the double bond absorption bands for these compounds.

Number of Branches.

It has been shown in previous work⁴ that in a saturated branched long-chain fatty acid the number of methyl groups can be determined by a suitable calibration and intensity measurement of the 7.25 μ absorption band. Measurements were made of this band in the spectra of the 2-alkenoic acids according to the procedure described elsewhere⁴ for the saturated branched-chain acids with the results shown in Table III. The values for the 2-alkenoic acids fall within the appropriate ranges, and bearing in mind the slight overlap

between the ranges for two and three methyl groups, it appears that the validity of this determination is not impaired by the presence of the double bond.

Comparison with C₂₇-Phthienoic Acid.

While no satisfactory structural correlation has been achieved for the branched 2-alkenoic acids, it is nevertheless pertinent to make certain comparisons of the available spectra with that of C₂₇-phthienoic acid. Previous chemical and spectral evidence^{2,3} has indicated that this acid has an α -methyl branch. Its spectrum has therefore been included in Fig. 3 together with those of the two synthetic acids which have α -methyl branches. All three have absorption bands at about 12.5 and 13.3 μ which do not appear in any of the other spectra (see also Fig. 4). In addition the peak absorbance of the carbon-carbon stretching band of C₂₇-phthienoic acid (when adjusted to 0.2M concentration) was found to be 0.33, in agreement with the values for α -branched acids in Table I. These observations add to the previous evidence for the α -methyl branch, and the correctness of this much of the structure seems well established.

The discrepancies among the spectra of Fig. 3 in the 10-10.5 μ range can only be taken to mean that C₂₇-phthienoic acid does not have the same overall configuration in the vicinity of the double bond as either of the two synthetic acids. Other evidence has indicated that it has two branches in addition to the α -methyl, one of which is probably on the γ - or δ -carbon. Such a branch near the double bond is also suggested by the spectra, since more remote branching would not be expected to alter the curve appreciably from that of 2-methyl-2-dodecenoic acid. The absence of a 10.1 μ band in the

spectrum of 2,5-dimethyl-2-heptadecenoic acid rules out at least one isomeric form of this structure. The available spectra do not provide any basis for a choice from among the other most likely structures.

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Table I

<u>2-Alkenoic Acid</u>	<u>$\lambda_{C=O}(\mu)$</u>	<u>$\lambda_{C=C}(\mu)$</u>	<u>Intensity^a of C=C band</u>
2-dodecenoic acid	5.90	6.05	0.39
5-methyl-2-hendecenoic acid	5.87	6.05	0.39
2-methylenedodecanoic acid	5.89	6.13	0.29
3-methyl-2-nonenic acid	5.90	6.10	0.63
2-methyl-2-dodecenoic acid	5.91	6.08	0.33
2,5-dimethyl-2-heptadecenoic acid	5.90	6.09	0.32

(a) Intensity is expressed as the peak absorbance of the band for a 0.2M solution in chloroform in a 0.1 mm cell.

Table II^a

<u>Alkyl-substituted Ethylene</u>	<u>Characteristic wave length (μ)</u>
RCH = CH ₂	10.05, 10.95
RCH = CHR' (<u>trans</u>)	10.35
RCH = CHR' (<u>cis</u>)	14-15
RR'C = CH ₂	11.25
RR'C = CHR''	11.5-12.5

(a) These are essentially the values given in Ref. 10. Other authors give slightly different limits to the ranges for cis and trisubstituted types.

Table III

Intensity measurements of 7.25 μ absorption band. 0.1M solutions in CCl_4 ; 0.5 mm cell; estimated baselines (see Ref. 4).

<u>Number of Methyl Groups</u>	<u>Absorbance Range Found in Saturated Branched-chain Acids</u>	<u>2-Alkenoic acid</u>	<u>Absorbance of 7.25 μ Band</u>
1	0.03-0.05	2-dodecenoic	0.05
		2-methylene-dodecanoic	0.06
2	0.10-0.17	3-methyl-2-nonenoic	0.11
		2-methyl-2-dodecenoic	0.10
		5-methyl-2-hendecenoic	0.14
3	0.15-0.21	2,5-dimethyl-2-heptadecenoic	0.17

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FIGURE CAPTIONS

Fig. 1 Infrared absorption spectra of some non-conjugated fatty acids.

Fig. 2 Infrared absorption spectra of some α, β -unsaturated fatty acids.

5.5-6.5 μ : 0.2M in CHCl_3 ; 0.1 mm cell.

6.5-16 μ : liquid films: upper two curves, 0.025 mm spacer; lower two curves, no spacer.

Fig. 3 Infrared absorption spectra of some α, β -unsaturated fatty acids having α -methyl branches.

Upper two curves: 5.5-6.5 μ , 0.2M in CHCl_3 , 0.1 mm cell; 6.5-16 μ , liquid films, 0.025 mm spacer.

C_{27} -phthienoic acid: 5.5-6.5 μ , 0.25M in CHCl_3 , 0.1 mm cell; 7-16 μ , 50 gm/l in CS_2 , 0.9 mm cell.

Fig. 4 Line diagram of the spectra of Figs. 2 and 3 (omitting 10.7 and 13.8 μ bands).

Solid lines represent absorption bands.

Dotted lines show positions of characteristic absorption by same structure when COOH is replaced by alkyl.

A 2-dodecenoic acid) $\text{HO}_2\text{CCH}=\text{CHR}(\text{trans})$
 B 5-methyl-2-hendecenoic acid)

C 2-methylenedodecanoic acid $\text{HO}_2\text{CCR}=\text{CH}_2$

D 3-methyl-2-nonenic acid $\text{HO}_2\text{CCH}=\text{CRR}'$

E 2-methyl-2-dodecenoic acid) $\text{HO}_2\text{CCR}=\text{CHR}'$

F 2,5-dimethyl-2-heptadecenoic acid)

G C_{27} -phthienoic acid

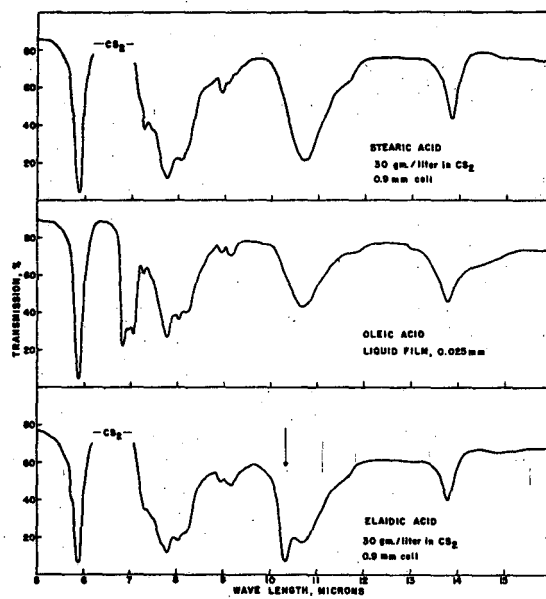


Fig. 1

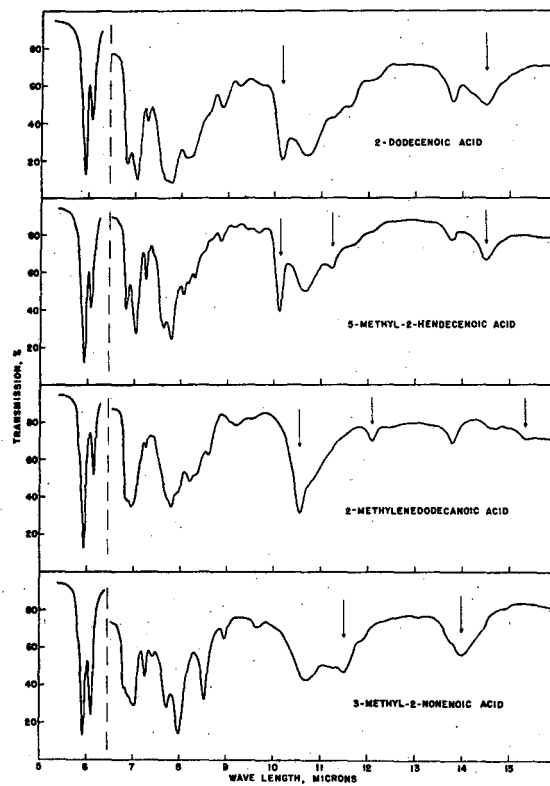


Fig. 2

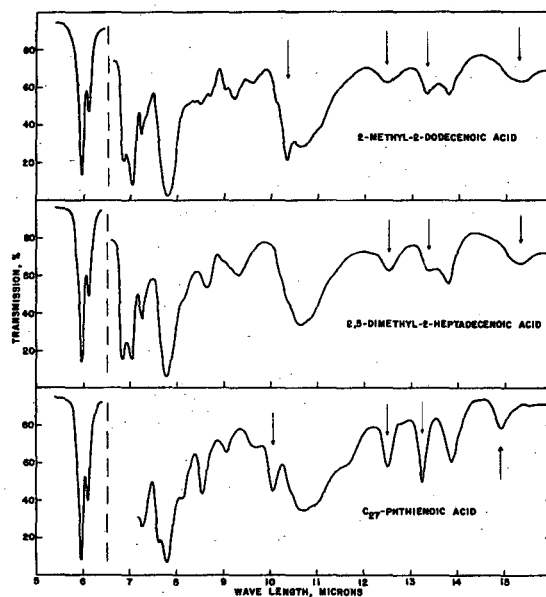


Fig. 3

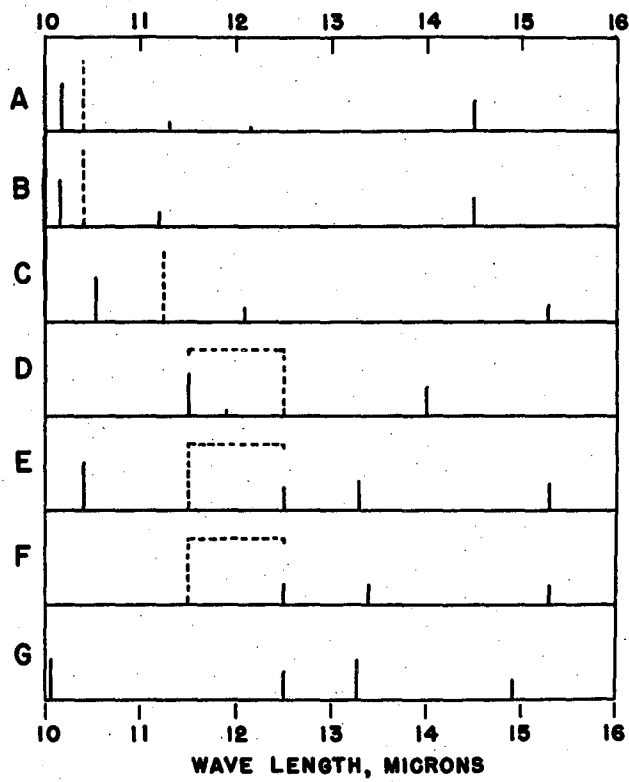


Fig. 4