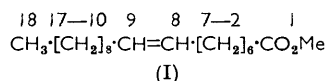


Infrared and Raman Studies of Some Monounsaturated Olefinic and Acetylenic Fatty Acids and their Derivatives

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The Raman spectra (800—3200 cm^{-1}) of carbon tetrachloride solutions of the 15 isomeric methyl *cis*-octadecenoates, the 15 isomeric *trans*-octadecenoic acids, methyl octadec-17-enoate, and of the 16 isomeric octadecynoic acids have been obtained. Provided that the double bond is not conjugated with the carbonyl group, and does not occur in the terminal position, the double-bond vibration gives rise to a strong Raman band at $1656 \pm 1 \text{ cm}^{-1}$ for the *cis*-compounds, and to a strong band at $1670 \pm 1 \text{ cm}^{-1}$ for the *trans*-compounds. Conjugation with the carbonyl group lowers the value by 8 cm^{-1} , and for the terminal double bond the value is 1642 cm^{-1} . The triple-bond vibration gives rise to two Raman bands at $2232 \pm 1 \text{ cm}^{-1}$ (s) and $2291 \pm 2 \text{ cm}^{-1}$ (m). When the triple bond is conjugated with the carbonyl group only one band at 2245 cm^{-1} is observed. The terminal triple bond gives a single band at 2120 cm^{-1} . From a comparison of the i.r. and Raman spectra of the methyl *cis*- and *trans*-octadec-8-enoates an assignment is suggested for the vibrational modes of the *cis*- and *trans*-CH=CH- units.

UNSATURATED fatty acid derivatives such as the methyl octadec-8-enoates (I) can exist in both *cis*- and *trans*-forms. Standard i.r. textbooks, for example that by



Bellamy,¹ indicate that the double-bond vibration should give rise to an i.r. absorption band at 1657 cm^{-1} for the *cis*-compound and at 1673 cm^{-1} for the *trans*-compound. The spectra illustrated in Figure 1 show that an i.r. band of reasonable intensity is observed only when the double bond is in the terminal position (Figure 1,C), or when conjugated with the carbonyl group (Figures 1,D and 1,I). With all the other compounds the local symmetry around the double bond is sufficiently high to cause the double-bond vibration to become effectively i.r.-inactive.

Such a selection rule should not apply to the Raman spectra of these compounds, and it was considered worthwhile to study the Raman spectra to see whether the *cis*- and *trans*-compounds could readily be distinguished. The Raman spectra of the octadecynoic acids have also been studied since, as shown in Figure 2, the i.r. absorption band due to the triple-bond vibration is, like that of the double bond, of negligible intensity unless it is terminal (Figure 2,C) or conjugated with the carbonyl group (Figure 2,F). Apart from a few Raman studies,²⁻⁶ mainly of specific *cis-trans*-pairs of acids, the

present seems to be the first systematic study of the Raman spectra of unsaturated fatty acids and their derivatives.

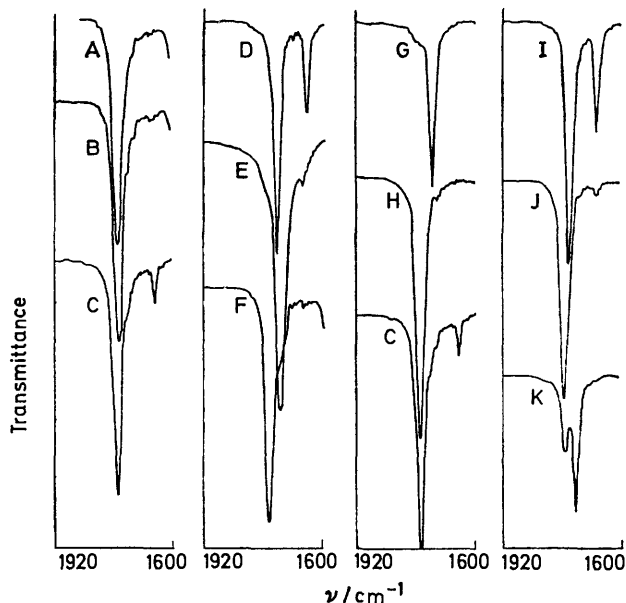


FIGURE 1 I.r. spectra of carbon tetrachloride solutions of A, methyl *cis*-octadec-15-enoate; B, methyl *cis*-octadec-16-enoate; C, methyl octadec-17-enoate; D, methyl *cis*-octadec-2-enoate; E, *cis*-octadec-3-enoic acid; F, methyl *cis*-octadec-4-enoate; G, *trans*-octadec-15-enoic acid; H, methyl *trans*-octadec-16-enoate; I, methyl *trans*-octadec-2-enoate; J, methyl *trans*-octadec-3-enoate; and K, *trans*-octadec-4-enoic acid

¹ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958.

² Th. Yvernault, *Oléagineux*, 1946, **1**, 189.

³ A. Van Den Hende, *Bull. Soc. chim. belges*, 1947, **56**, 328.

⁴ G. V. Pigulevskii and P. A. Artamanov, *Doklady Akad. Nauk S.S.S.R.*, 1952, **82**, 413.

⁵ A. Hidalgo and M. T. Sardina, *Anales de Quim.*, 1956, **52**, B, 627.

⁶ L. A. O'Neill and N. A. R. Falla, *Chem. and Ind.*, 1971, 1349.

In general the *cis*-series were available as the methyl esters (liquids) and the *trans*- and acetylenic series as

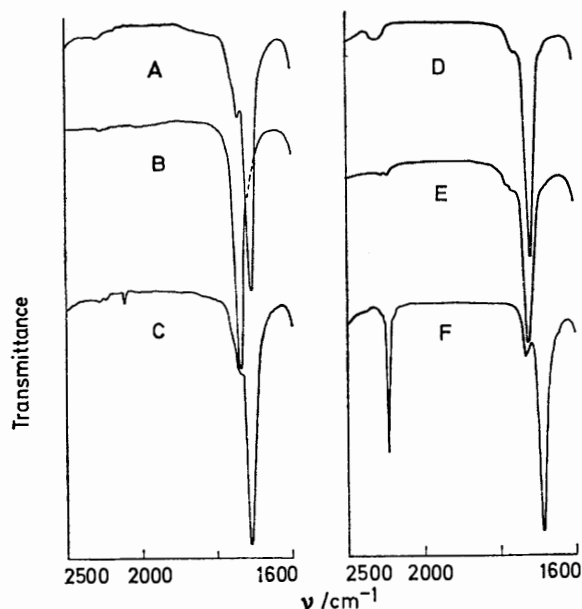


FIGURE 2 I.R. spectra of carbon tetrachloride solutions of A, octadec-14-ynoic acid; B, methyl octadec-16-ynoate; C, octadec-17-ynoic acid; D, octadec-4-ynoic acid; E, octadec-3-ynoic acid; F, octadec-2-ynoic acid

the acids (solids). Figure 3 shows that there are substantial differences between the solid-state and carbon tetrachloride solution Raman spectra. Since the splitting of bands in solid-state spectra might be due to site

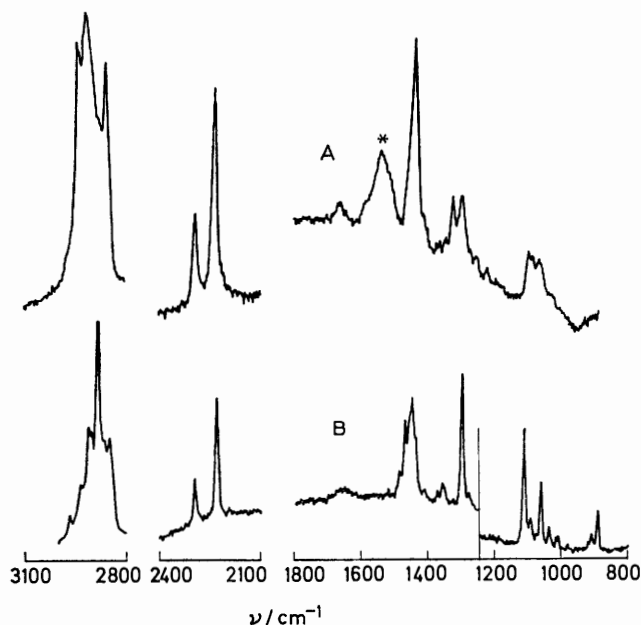


FIGURE 3 Raman spectra of octadec-14-ynoic acid: A, carbon tetrachloride solution, solvent band marked *; B, solid

and factor group effects, it was decided to study the solution spectra whenever possible.

The parent saturated fatty acid of the series studied

in this paper is octadecanoic acid. The Raman spectrum of methyl octadecanoate (methyl stearate) is very similar to that of methyl dodecanoate (methyl laurate) which has been reported by Jones and Ripley.⁷ The Raman spectra of selectively deuteriated derivatives of methyl dodecanoate indicated that the Raman spectrum was dominated by bands due to the vibrations of the $-\text{[CH}_2\text{]}_9-$ group, whereas the i.r. spectrum contained bands due to the vibrations of all the groups in the molecule. The spectra obtained in the present study were similar to that reported for methyl dodecanoate, and in this paper we shall be mainly concerned with the observed differences due to the presence of the unsaturated groups.

Olefinic Fatty Acids and their Derivatives.—Figure 4 shows that both geometrical isomers of methyl octadec-8-enoate give rise to very intense Raman bands due to $\nu(\text{C}=\text{C})$, the values being 1656 and 1670 cm^{-1} for the *cis*- and *trans*-compounds respectively. These Raman

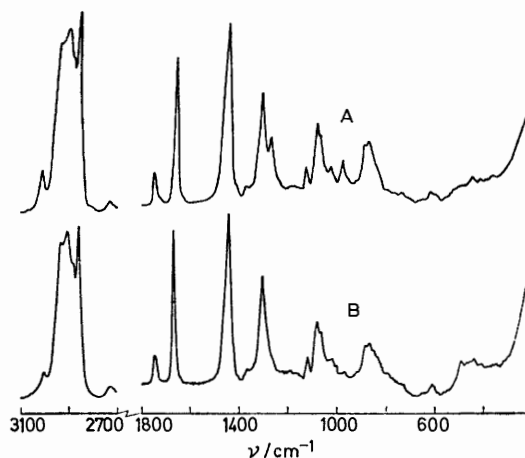


FIGURE 4 Raman spectra of neat liquids of A, methyl *cis*-octadec-8-enoate and B, methyl *trans*-octadec-8-enoate

spectra should be contrasted with the i.r. spectra shown in Figure 5, where it can be seen that the *cis*-compound has a very weak absorption band due to $\nu(\text{C}=\text{C})$, whilst no band is observed for the *trans*-compound since it possesses a centre of symmetry at the double bond.

Table 1 lists the observed Raman spectra of carbon tetrachloride solutions of the methyl *cis*-octadecenoates and of the *trans*-octadecenoic acids. Values of $\nu(\text{C}=\text{O})$ are not listed for the *trans*-acids since this band overlaps with the $\nu(\text{C}=\text{C})$ band owing to the high concentration used (see Experimental section). Table 1 shows that, provided that the double bond is not conjugated with the carbonyl group, Raman spectroscopy provides a convenient method of distinguishing between the *cis*- and *trans*-compounds, with a difference of 14 cm^{-1} between the $\nu(\text{C}=\text{C})$ modes of the two geometrical isomers. Conjugation with the carbonyl group causes a decrease in the frequency of both the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ modes, accompanied by a change in the relative

⁷ R. N. Jones and R. A. Ripley, *Canad. J. Chem.*, 1964, **42**, 305.

intensities of these two bands as indicated in Table 1. Figure 1 also shows that the intensity of the i.r. $\nu(\text{C}=\text{C})$ band is greater for the conjugated compounds (Figure 1,D and 1,I) than for the terminal compound (Figure 1,C).

The terminal $-\text{CH}=\text{CH}_2$ group gives rise to a band at 1642 cm^{-1} in both the i.r. and Raman spectra. There

mode and the first overtone of the skeletal C-C stretching mode. This fundamental has a value of 1122 cm^{-1} for methyl dodecanoate.⁷ In the terminal and conjugated compounds the value of $\nu(\text{C}\equiv\text{C})$ is sufficiently different from the first overtone value to exclude the possibility of Fermi resonance. In these two compounds $\nu(\text{C}\equiv\text{C})$ appears as a single band in both the i.r. and Raman

TABLE 1

Raman spectra of CCl_4 solutions of the methyl *cis*-octadecenoates and the *trans*-octadecenoic acids (frequencies in cm^{-1})

	<i>cis</i> -Methyl esters			<i>trans</i> -Acids	
	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{H})$
$\Delta 2$	1648(1.0)	1729(0.43)	3040	1660 †	3023 †
$\Delta 3$	1660(1.0)	1745(0.33)	3028	1671 †	3000 †
$\Delta 4$	1658(1.0)	1745(0.24)	3011	1671	3000
$\Delta 5-\Delta 14$	1656 ± 1 (1.0)	1744 ± 1 (0.25 \pm 0.04)	3009 ± 1	1670 ± 1	2999 ± 1
$\Delta 15$	1656(1.0)	1743(0.24)	3009	1670	3000
$\Delta 16$	1657(1.0)	1744(0.25)	3015	1671 †	3000 †
$\Delta 17$	1642(1.0)	1745(0.26)	‡		

Figures in parentheses indicate the relative heights of the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ bands.

† Spectrum of methyl ester. ‡ See text.

is no significant difference between the relative intensities of the $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ Raman bands for a terminal and non-terminal double bond.

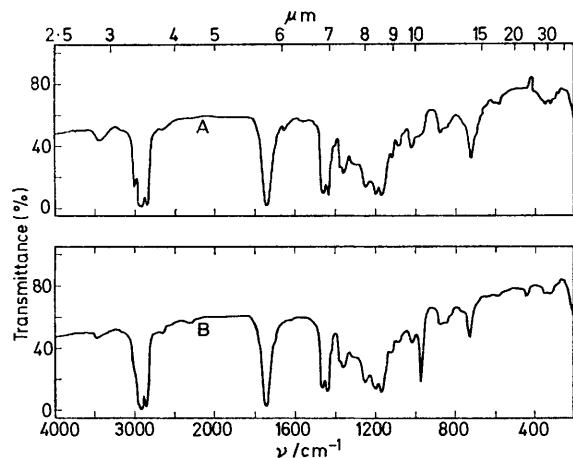


FIGURE 5 I.r. spectra of thin liquid films of A, methyl *cis*-octadec-8-enoate and B, methyl *trans*-octadec-8-enoate

Acetylenic Fatty Acids.—The vibration of the triple bond in the octadecynoic acids gives rise to two Raman bands (Figure 3), while the intensity of the corresponding i.r. band is significant only when the triple bond is in the terminal position (Figure 2,C) or when conjugated with the carbonyl group (Figure 2,F).

Table 2 lists the observed Raman spectra of carbon tetrachloride solutions of the octadecynoic acids. Some of the compounds gave a very high background (see Experimental section) which obscured some of the Raman bands and accounts for the gaps in Table 2. In the $\Delta 4-\Delta 16$ compounds $\nu(\text{C}\equiv\text{C})$ appears as a doublet with components at 2232 cm^{-1} (s) and 2291 cm^{-1} (m). It has been suggested⁸ that the doublet arises from Fermi resonance between the triple-bond stretching

spectra, the values being 2245 cm^{-1} for the conjugated compound and 2120 cm^{-1} for the terminal compound.

The terminal compound also displays a $\nu(\equiv\text{C}-\text{H})$ stretching mode. This gives rise to a strong sharp i.r. absorption band at 3315 cm^{-1} , together with a much

TABLE 2

Raman spectra of CCl_4 solutions of the octadecynoic acids (frequencies in cm^{-1})

	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}=\text{O})$
$\Delta 2$	2245	1648
$\Delta 3$		
$\Delta 4-\Delta 14$	$2232 \pm 1s$ $2291 \pm 2m$	1663 ± 1
$\Delta 15$	$2233s$ $2294m$	
$\Delta 16$	$2234s$ $2296m$	
$\Delta 17$	2120	

weaker component at 3294 cm^{-1} , probably due to $\nu(\equiv^{13}\text{C}-\text{H})$. This mode also gives rise to a weak Raman band at 3312 cm^{-1} . The angle deformation mode $\delta(\text{C}\equiv\text{C}-\text{H})$ gives rise to a strong i.r. absorption band at 629 cm^{-1} .

Vibrational Assignment of the *cis*- and *trans*-CH=CH- Modes.—From a comparison of the vibrational spectra of methyl octadecanoate, the *cis*- and *trans*-octadecenoates, and of the octadecynoic acids, it should be possible to arrive at an assignment of the vibrational modes of the *cis*- and *trans*-CH=CH- units. Descriptions of the vibrational modes have been given by Sheppard and Sutherland,⁹ and the suggested assignment is given in Table 3. The *trans*-unit possesses a centre of symmetry and no coincidences are observed between the i.r. and Raman bands. Some coincidences are observed for the *cis*-unit.

Whilst there are several characteristic differences between the Raman spectra of the *cis*- and *trans*-compounds, the most significant difference in the i.r. spectra

⁸ N. Sheppard and D. M. Simpson, *Quart. Rev.*, 1952, **6**, 1.

⁹ N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1949, **A**, **196**, 195.

is the presence of a band at 966 cm^{-1} in the *trans*-compounds which is absent from the spectra of the *cis*-compounds (Figure 5). The presence or absence of this i.r. band (due to the out of plane bending mode of the

TABLE 3

Assignments (in cm^{-1}) of the vibrational modes of the *cis*- and *trans*-CH=CH- units

	<i>cis</i>		<i>trans</i>	
	I.r.	Raman	I.r.	Raman
$\nu(\text{C-H})$ asym.	3005s			
$\nu(\text{C-H})$ sym.		3009s		2999s
$\nu(\text{C}=\text{C})$	1656w	1656vs		1670vs
$\delta(\text{CH})$	1405w			
In plane		1268s		
$\delta(\text{CH})$		977m	966s	
Out of plane				

olefinic hydrogens) has been used to differentiate *trans*-compounds from *cis* and/or saturated compounds.¹⁰

Table 3 shows that all of the possible modes could not be observed owing to overlap with bands arising from the saturated part of the molecule, and also because carbon tetrachloride solutions were studied. The observed bands have wavenumber values and relative intensities in close agreement with the results of Sheppard *et al.*^{8,9}

The Vinyl Group.—Methyl octadec-17-enoate possesses the vinyl group $-\text{CH}=\text{CH}_2$, and there are several differences between its vibrational spectra and those of the other olefinic fatty acids. Table 4 shows the modes of the vinyl group that can be distinguished, together with their activities and intensities.

TABLE 4

$\nu(\text{C-H})$	3080 cm^{-1}	I.r.(m), R(s)
$\nu(\text{C}=\text{C})$ antisymmetric	3066 cm^{-1}	I.r.(w)
$\nu(\text{C}=\text{C})$ symmetric	3000 cm^{-1}	R(s)
$\nu(\text{C}=\text{C})$	1642 cm^{-1}	I.r.(s), R(vs)
$\delta(\text{CH}_2)$ in plane	1419 cm^{-1}	R(s)
$\delta(\text{CH})$ out of plane	996 cm^{-1}	I.r.(s)
$\delta(\text{CH}_2)$ out of plane	911 cm^{-1}	I.r.(vs)

The present study confirms some of the assignments suggested by Jones and Ripley⁷ for methyl dodecanoate. The Raman band at 2876 cm^{-1} was assigned to the symmetric stretching mode of the terminal methyl group. This band is present in the spectra of all the olefinic compounds except for that of methyl octadec-17-enoate, in agreement with the above assignment. The Raman band at 2950 cm^{-1} was assigned to the CH_3 symmetric stretching mode of the CO_2Me group, and in agreement with this assignment this band was found to be present in all the ester spectra, but absent from all the acid spectra.

Conclusions.—The present study shows that Raman

¹⁰ O. D. Shreve, M. R. Heether, H. B. Knight, and D. Swern, *Analyt. Chem.*, 1950, **22**, 1498.

¹¹ F. D. Gunstone and I. A. Ismail, *Chem. Phys. Lipids*, 1967, **1**, 209.

spectroscopy is a more useful method than i.r. spectroscopy for the identification of olefinic and acetylenic bonds in fatty acids and their derivatives. The $\nu(\text{C}=\text{C})$ and $\nu(\text{C}\equiv\text{C})$ modes give i.r. bands of reasonable intensity only when the unsaturated groups are terminal or conjugated with the carbonyl group; in most other cases the bands are not observed. These vibrational modes give strong Raman bands irrespective of the position of the unsaturated groups, and the wavenumber values of the bands indicate whether the unsaturation is *cis*-olefinic, *trans*-olefinic, or acetylenic and whether it is terminal or non-terminal, conjugated or non-conjugated.

Even though the band due to the $\nu(\text{C}=\text{C})$ mode is not observed in the i.r. spectrum of a non-terminal, non-conjugated olefinic bond, i.r. spectroscopy can be used for identification since the *trans*-olefinic bond gives a strong i.r. band at 966 cm^{-1} due to the out of plane bending mode of the olefinic hydrogens.¹⁰ Hence if it is known that a double bond is present in a fatty acid the presence or absence of this band can be used to determine whether it is *trans* or *cis*. There is no characteristic i.r. band to identify a non-terminal, non-conjugated acetylenic bond.

The advantage of Raman spectroscopy lies in the fact that from a single spectrum of an unknown fatty acid it would be possible to determine whether it is saturated, *cis*-olefinic, *trans*-olefinic, or acetylenic. Such a complete identification would not be possible from the i.r. spectrum.

EXPERIMENTAL

The monounsaturated olefinic^{11,12} and acetylenic¹² fatty acids and esters were prepared as described. The samples were examined as solutions in carbon tetrachloride. For Raman spectroscopy concentrations of the order of 20% (w/w) were used, *ca.* 15 mg of sample being used. The solutions had to be diluted considerably for i.r. spectroscopy, the final concentration being of the order of 5%.

Because of the high concentrations required for Raman spectroscopy, solutions of the acids contain associated species rather than the monomeric species. This accounts for the very low values of $\nu(\text{C}=\text{O})$ recorded in Table 2.

Raman Spectra.—The Raman spectra were excited by use of the 5208 \AA line of a CRL Model 52K krypton laser and recorded on a Cary 81 spectrometer. The solutions were examined by the standard capillary cell technique which required about $60\text{ }\mu\text{l}$ of solution. The spectra were recorded by use of 4.5 cm^{-1} slits with an exciting power of 30 mW at the sample. Solids were examined in the standard solid holder which requires *ca.* 3 mg of sample. The instrument was calibrated with krypton emission lines.

The problem of the high background which is encountered in the Raman spectra of some compounds, especially polymer samples, has been reviewed by Gall *et al.*¹³ All the fatty acid samples gave a high background, the order of intensity being *cis* < *trans* < acetylenic fatty acids. The background decays on irradiation with the laser radiation, and reasonable spectra could be obtained from

¹² J. A. Barve and F. D. Gunstone, *Chem. Phys. Lipids*, 1971, **7**, 311.

¹³ M. J. Gall, P. J. Hendra, D. S. Watson, and C. J. Peacock, *Appl. Spectroscopy*, 1971, **25**, 423.

the carbon tetrachloride solutions after irradiation for 1 h with the *cis*-compounds, for 2 h with the *trans*-compounds, and for 3 h with the acetylenic compounds. The background was extremely intense for some of the acetylenic compounds, so much so that even prolonged irradiation (5 h) failed to reduce its intensity sufficiently to obtain a Raman spectrum. The gaps in Table 2 are therefore not

due to a lack of sample but rather to our inability to obtain a spectrum owing to the high background.

Infrared Spectra.—The i.r. spectra of the carbon tetrachloride solutions were recorded on a Perkin-Elmer Model 225 spectrometer. The instrument was calibrated with a polystyrene film.

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