The most remarkable feature of the spectra of the crystalline acids and esters is the progression of bands between 1180 and 1350 cm.$^{-1}$ spaced at approximately equal intervals of 20 cm.$^{-1}$. These are almost certainly associated with methylene wagging and/or twisting vibrations and form the subject of a separate paper.[4]

C–C Stretching Vibrations.—Evidence suggesting that in the *n*-paraffins the C–C stretching vibrations are confined to a well-defined frequency range have been advanced by several investigators and discussed recently by Brown, Sheppard and Simpson.[17] By analogy the C–C stretching vibrations of the carbon chain of the fatty acids and esters should occur between 850 and 1150 cm.$^{-1}$ and probably account for most of the weak absorption bands observed in this region.

Concluding Remarks

Because of the close similarity of the solution spectra of the acids of different chain length, the identification of individual acids and the qualitative and quantitative analysis of mixtures of saturated acids would appear to be impracticable from measurements made in solution. However some estimate of the mean chain length may be obtained from the determination of the intensity of the 720 cm.$^{-1}$ methylene rocking band.

The solid phase spectra offer better prospects for the identification of individual acids provided the complications of polymorphism can be controlled. For mixtures of saturated acids the effects of polymorphism and compound formation become complex and the application of infrared spectrophotometry in the analysis of mixtures of fatty acids will be limited on this account.

The lack of characteristic structure in the solution spectra of the fatty acids and esters appears to be contrary to the concept of the strict "fingerprint" specificity of the infrared spectrum as an identifying physical constant of an organic compound. However the association of this lack of specificity with the occurrence of extensive rotational isomerism in solution largely resolves the paradox. In most classes of naturally occurring compounds to which infrared spectrometry has hitherto been applied many of the skeletal carbon atoms are present in five- or six-membered ring systems; these are comparatively rigid and the possibilities for rotational isomerism in solution are limited to short side chains. Where the effects of rotational isomerism in solution can be discounted the solution spectra are to be preferred to solid phase spectra in the study of chemical structure, since in the crystal the possibilities of polymorphism and intermolecular interaction are always liable to confuse the interpretation of the spectra.

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Band Progressions in the Infrared Spectra of Fatty Acids and Related Compounds[1]

BY R. NORMAN JONES, A. F. MCKAY AND R. G. SINCLAIR

A progression of absorption bands of uniform spacing and intensity is observed between 1180 and 1350 cm.$^{-1}$ in the spectra of fatty acids in the solid state. The changes induced in these bands by alteration in the chain length, the introduction of substituents and the replacement of the terminal carboxylic acid by other groups has been investigated. It is suggested that the bands arise from interactions among the rocking and/or twisting vibrations of the methylene groups.

In the infrared absorption spectra of crystalline films and nujol mulls of fatty acids, a progression of bands is observed between 1180 and 1350 cm.$^{-1}$ (Fig. 1). These bands are characterized by a uniformity of spacing and intensity which suggests a common origin; they are not observed in the spectra of fatty acids in carbon disulfide solution (compare Figs. 1 and 3 of the preceding paper[2]). The manner and extent to which these bands are influenced by the chain length, the end groups, and chain substituents have been investigated. The experimental methods employed and the sources and characteristics of the compounds are being reported.[2,3]

Results and Conclusions

Typical spectra illustrating the absorption between 1150 and 1350 cm.$^{-1}$ of crystalline fatty acids and derivatives are shown in Figs. 1 and 2.

Effect of Chain Length.—In lauric acid (C-12) (Fig. 2) only three bands are recognizable as belonging to a progression, the low frequency "band head" being at 1195 cm.$^{-1}$. As the carbon chain lengthens, the number of recognizable progression bands increases and in heneicosanoic acid (C-21) (Fig. 1) nine bands can be distinguished, the band of lowest frequency being displaced down to 1184 cm.$^{-1}$. The increase in the number of bands with chain length, the regularity of the spacing and the displacement to lower frequency with increasing chain length are shown diagrammatically in Fig. 3. The widths, positions and relative intensities of the bands are not temperature dependent (see Fig. 5 of the preceding paper[2]) and there is no evidence of

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(1) Published as Contribution No. 2681 from the Laboratories of The National Research Council of Canada. Presented before the High Polymer and Biochemical Divisions of the American Chemical Society, Boston, April 5th, 1951.

(2) R. G. Sinclair, A. F. McKay and R. N. Jones, THIS JOURNAL, **74**, 2570 (1952).

(3) R. G. Sinclair, A. F. McKay, G. S. Myers and R. N. Jones, *ibid.*, **74**, 2578 (1952).

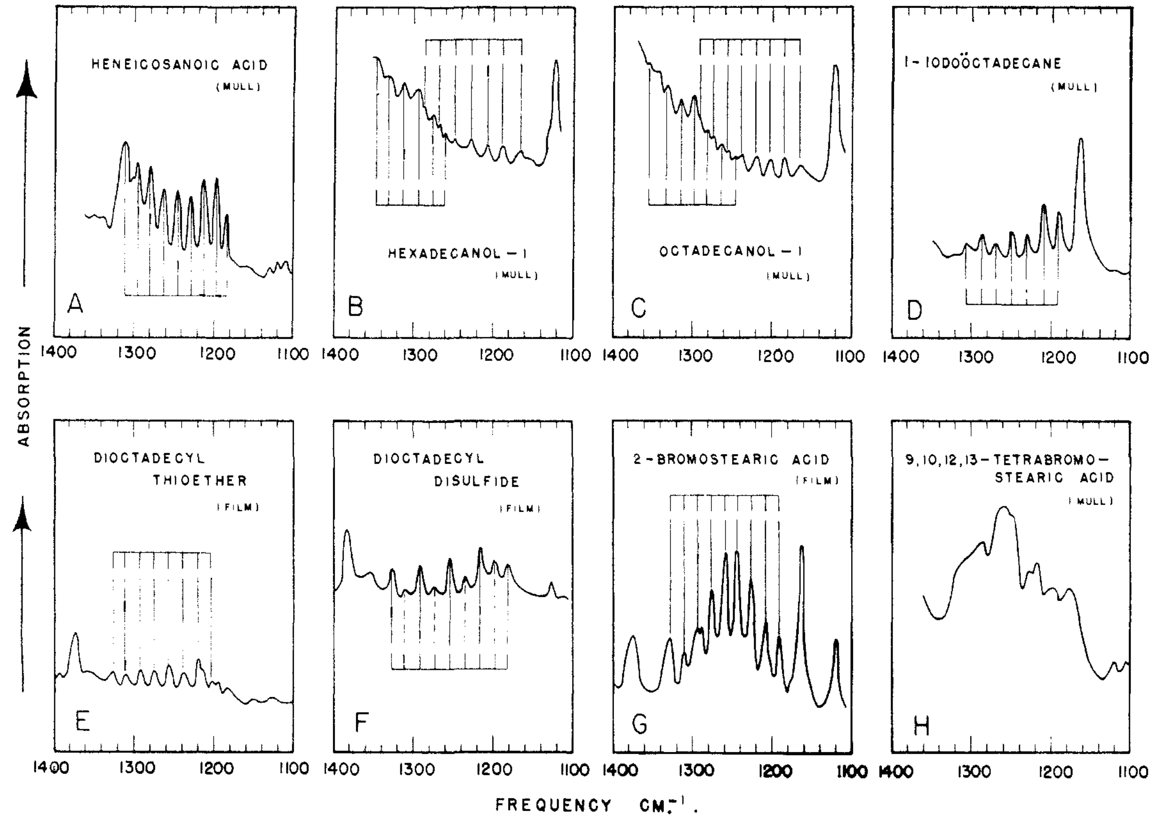

Fig. 1.—Infrared spectra of solid long chain polymethylene compounds between 1150 and 1400 cm.$^{-1}$.

any alternation between successive acids of odd and even chain length.

In the range between C-16 and C-21 the number of bands in the progression appears to increase by unity for each added carbon atom, but the total number of bands constituting the progression is difficult to determine as, at the higher frequency end, the bands are superimposed on a strong C–O stretching vibration.[2]

Effect of End Groups.—A similar type of progression is observed in the spectra of crystalline films of fatty acid methyl esters (see Fig. 4 of preceding paper[2]). In these compounds the C–O stretching bands are shifted to lower frequencies so that although the higher end of the progression is clearly recognizable, the lower end is obscured by absorption associated with the carbomethoxy group.[2]

The spectra of nujol mulls of hexadecanol and octadecanol are also shown in Fig. 1. In these spectra there is evidence of two overlapping series of weaker bands. Well defined progressions have also been observed in crystalline films of 1-iodooctadecane, octadecyl thioether and dioctadecyl disulfide.

It is inferred that these bands are primarily associated with the polymethylene chain, but the intensities and character of the bands observed are modified significantly by the nature of the terminal groups.

Effects of Chain Substituents.—The introduction of substituents along the chain also alters the appearance of these bands. If the degree of substitution is excessive, as in tetrabromostearic acid (Fig. 1) the characteristic appearance of the progression is lost, but in 2-bromostearic acid, where the bromine substituent is near the end of the chain the bands are clear and sharp (Fig. 1).

The regular appearance of the bands is also diminished or destroyed by the introduction of unsaturated linkages. Solid films of oleic, linoleic and linolenic acids cooled with liquid nitrogen show several sharp and prominent bands between 1150 and 1350 cm.$^{-1}$ (Fig. 2) but the spacings and intensities are irregular. These acids all possess *cis*-configurations at the double bonds, so that the carbon chains are bent. In elaidic acid, where the configuration at the Δ^9-bond is *trans*, the hydrocarbon chains may be expected to line up in the crystal in a linear extended form in a manner similar to that in the saturated acids and it is significant that the spectrum of solid elaidic acid closely resembles that of one of the saturated acids of short chain length (*e.g.*, lauric). This suggests that in elaidic acid the two sections of the chain on each side of the central double bond are behaving as more or less independent units.

These observations substantiate the view that the presence of a linear[4] chain of adjacent methylene groups in the crystal is a requirement for the development of a well defined progression.

Comparison with the Spectra of *n*-Paraffins.—Further insight into the nature of these bands may be derived from a comparison with the spectrum of *n*-octadecane.

For *n*-tetradecane and other *n*-paraffins of shorter

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[4] By "linear," it is implied that the long axis of the hydrocarbon chain is linear with the successive methylene groups lying alternatively above and below this axis in a zig-zag manner.

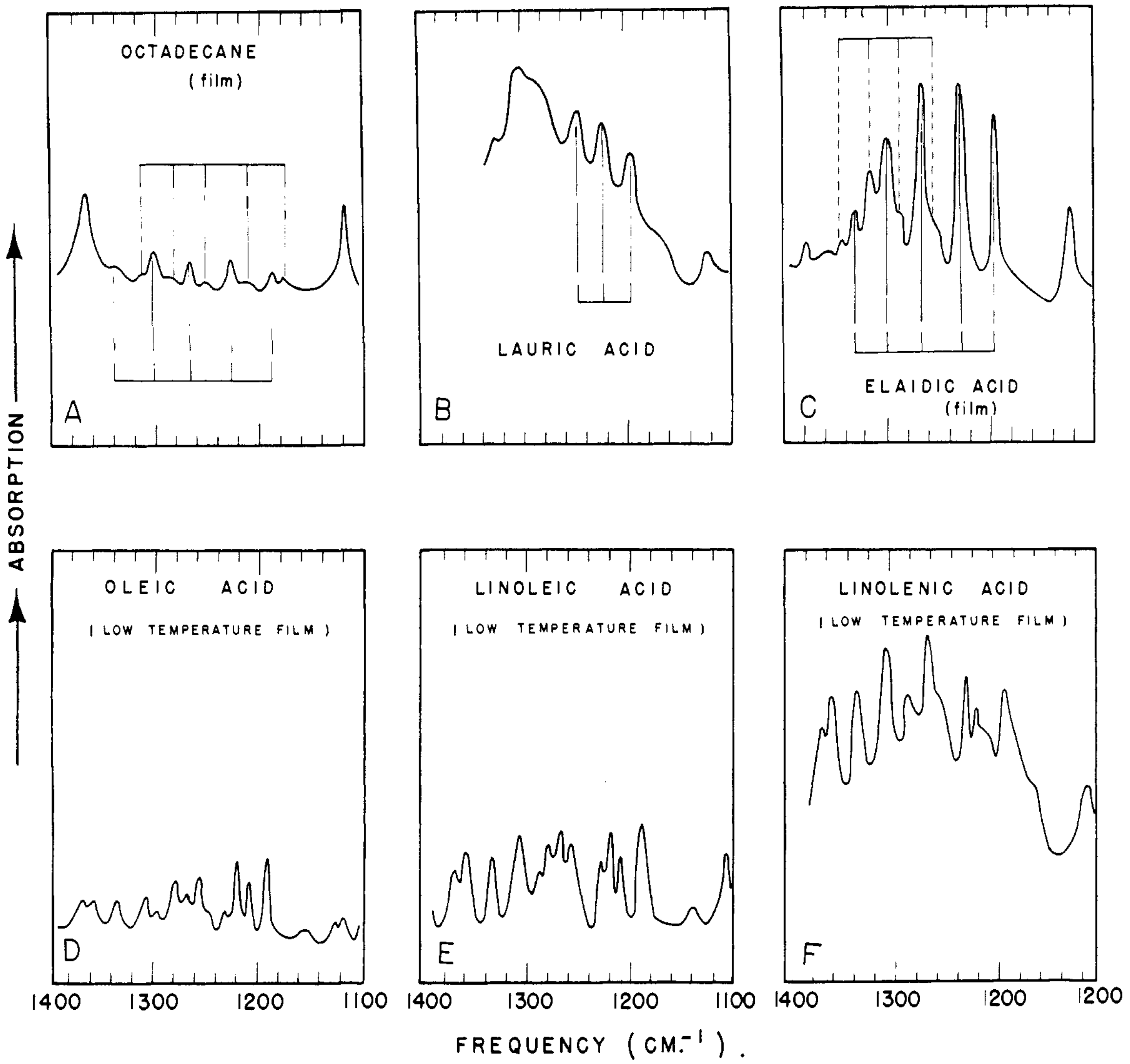

Fig. 2.—Infrared spectra of solid *n*-octadecane and related solid fatty acids between 1150 and 1400 cm.$^{-1}$.

chain length, Brown, Sheppard and Simpson[5] have made tentative assignments of the principal absorption bands by analogy with the spectrum of *trans*-*n*-butane.[6,7] Extension of the arguments used by Brown, Sheppard and Simpson to *n*-octadecane would suggest that the bands between 1160 and 1340 cm.$^{-1}$ are to be attributed to wagging and twisting vibrations of the methylene C–H bonds.

Apart from their much weaker intensity, these bands resemble those in the same region of the fatty acid spectra and suggest that the band progressions in the spectra of the fatty acids are also associated with wagging and twisting vibrations of the C–H bonds of the methylene groups, the number of bands increasing with the chain length as

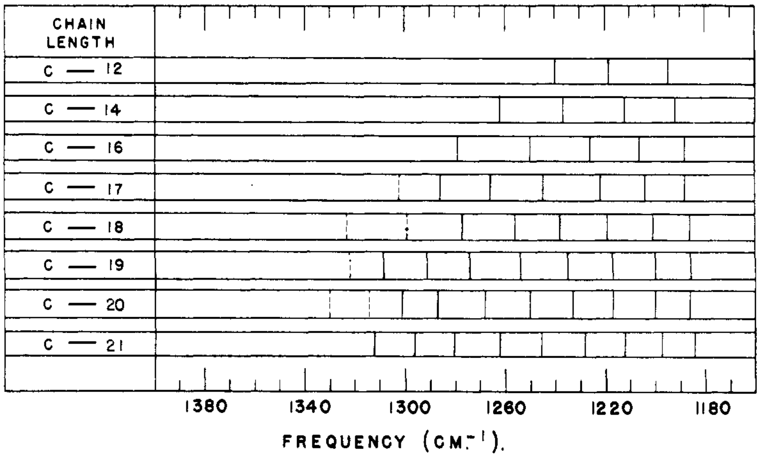

Fig. 3.—Diagram illustrating effect of chain length on band progressions in the infrared spectra of solid saturated fatty acids. The dotted lines indicate the positions of bands whose assignment as members of the progressions is considered questionable.

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(5) J. K. Brown, N. Sheppard and D. M. Simpson, *Discussions of the Faraday Society*, **9**, 261 (1950).

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a consequence of the coupling between the vibrations of adjacent methylene groups.

In the spectrum of tetradecane where six bands are observed between 1187 and 1305 cm.$^{-1}$, Brown, Sheppard and Simpson tentatively assign the two of lowest frequency to the twisting mode and the other four to the wagging mode. In the fatty acids, where the spacing and relative intensities of the bands are very uniform there would seem to be no justification, at present, to assign individual bands specifically to wagging or twisting modes. Possibly, as a consequence of the polar end group one of these modes may have become very weak relative to the other and the whole series of bands observed may be due to one of these modes of vibration only. Both types of vibration may be active in the spectra of the alcohols, each accounting for one of the two progressions observed.

The existence of band progressions such as these, arising from interactions between the vibrations of neighboring methylene groups in linear polymethylene chains is predicted by recent theoretical work of Deeds and Shaffer,[8] although these investigators did not limit their occurrence to the solid phase only.

In the above discussion it has been tacitly assumed that in the crystalline state each n-paraffin hydrocarbon or fatty acid molecule behaves as an independent vibrating unit. However, the possibility that intermolecular forces play a part in generating these bands must also be considered,[9,10] and they might alternatively have their origin in a combination of internal vibrations with lattice vibrations.[11,12] It has recently been observed that the bands in stearic and eicosanoic acid exhibit a very strong polarization[13] effect, and a careful study of such polarization effects on single crystals may aid in their interpretation.

Acknowledgments.—The technical assistance of Mr. R. Lauzon and Mr. D. S. Keir is gratefully acknowledged. The investigation was aided by a grant from the Ontario Cancer Treatment and Research Foundation.

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The Infrared Absorption Spectra of Unsaturated Fatty Acids and Esters[1]

BY R. G. SINCLAIR, A. F. MCKAY, G. S. MYERS AND R. NORMAN JONES

The infrared absorption spectra of several unsaturated fatty acids, methyl esters and brominated derivatives have been determined at room temperature and when cooled with liquid nitrogen. The absorption bands characteristic of the unsaturated linkages are described and discussed. A spectrographic method is proposed for the determination of the degree of unsaturation of mixtures of *cis*-unsaturated acids, based on the measurement of the optical densities of the absorption bands at 3020 and 2920 cm.$^{-1}$. The spectra of liquid films or solutions of stearic, oleic, linoleic and linolenic acids do not differ sufficiently to permit the spectrographic analysis of the individual acids in complex mixtures. However, cooled solid films of binary mixtures of oleic and linoleic acids show large and progressive changes with concentration, especially between 680 and 750 cm.$^{-1}$ and the quantitative analysis of pairs of the above unsaturated acids from solid film measurements would appear to be feasible.

The identification and quantitative analysis of the unsaturated fatty acids present in extracts of biological material is a problem of particular interest in view of the essential part played by linoleic acid in animal metabolism. A comparative study of the infrared spectra of unsaturated fatty acids and esters has been undertaken in order to evaluate the extent to which infrared spectrometry might be applied to this problem. When these investigations were commenced, it was known from the work of McCutcheon, Crawford and Welsh,[2] that the *cis-trans* configuration of the ethylenic linkage modifies the infrared spectra of unsaturated fatty acids in a characteristic manner, and this has subsequently been confirmed by other investigators.[3-6] Recently Shreve, Heether, Knight and Swern[6] have described the infrared spectra of some monounsaturated fatty acids and methyl esters, but little has been published concerning the spectra of the more highly unsaturated fatty acids.

Experimental

The methods employed in measuring the spectra have been described in a preceding paper.[7] Most of the compounds were prepared at Queen's University, and unless already reported[7] their characteristics are summarized in Table I.

Results and Discussion

The absorption bands associated with the methylene groups of the chain, the terminal methyl group, and the carboxy and carbomethoxy groups are similar to those of the saturated acids and methyl esters. These have been discussed in preceding papers,[7,8] and this communication will be concerned only with those features of the infrared

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[1] Published as Contribution No. 2682 from The Laboratories of the National Research Council of Canada.

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