[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA AND THE DEPARTMENTS OF CHEMISTRY AND BIOCHEMISTRY, QUEEN'S UNIVERSITY]

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

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

The infrared absorption spectra of saturated fatty acids and methyl esters of varying chain length have been measured. In solution, most of the absorption bands are broad; the spectra are qualitatively independent of the chain length but the relative intensity of the methylene rocking vibration at 720 cm.$^{-1}$ increases progressively as the chain is lengthened. In the crystalline state the spectra show much more structure than in solution and significant qualitative differences occur on alteration of chain length. The spectra also differ for polymorphic varieties of the same acid, a factor which complicates the use of such spectra in analysis. The principal absorption bands are assigned to the vibrations of specific molecular groups.

The interpretation of the infrared absorption spectra of complex organic compounds has progressed sufficiently to permit generalizations to be made concerning the absorption bands associated with specific bond structures,[2,3] and the effects on these linkages of such secondary factors as hydrogen bonding, ring strain, conjugation, and inductive and electrostatic charge displacements can sometimes be predicted in a qualitative manner. Nevertheless, in the investigation of any particular class of organic compounds the use of such generalizations is limited, and for the elucidation of the structure of new compounds and the development of analytical techniques, it is desirable to have detailed knowledge of the spectra of related compounds of established structure.

The infrared spectra of the fatty acids are of special interest in view of the biological importance of these compounds, and the comparatively unspecific methods presently available for their chemical characterization, especially on a micro scale. In this and the following paper[4] the effects of alteration in chain length and the physical state on the infrared spectra of saturated straight chain fatty acids and methyl esters are considered; the spectra of the unsaturated acids, esters and bromo-derivatives will be dealt with subsequently.[5]

In the earlier literature little is to be found concerning the infrared spectra of saturated fatty acids, apart from the inclusion of palmitic and stearic acids in some early collections of spectra.[6,7] Shreve Heether, Knight and Swern have discussed the spectra of palmitic and stearic acids, and methyl stearate in recent articles[8] while the spectra of chloroform solutions of the even chain acids from $C_6$ to $C_{18}$ and of their methyl and ethyl esters have been measured under low dispersion by O'Connor, Field and Singleton.[9] Other investigators have published on the spectra of unsaturated acids and esters.[10-12]

## Experimental

The spectra were determined on a Perkin-Elmer 12B spectrometer with 7-cycle G. M.-type amplifier and Brown Electronik recorder. Prisms of lithium fluoride, calcium fluoride, sodium chloride and potassium bromide were used. The estimated accuracy of the band positions reported is ±1 cm.$^{-1}$ between 500 and 2000 cm.$^{-1}$ and ± 2 cm.$^{-1}$ above 2000 cm.$^{-1}$. Measurements at room temperature were made in cells of conventional design while for measurement of samples cooled with liquid nitrogen a cell similar to that described by Wagner and Hornig was employed.[13]

TABLE I

SOURCES AND CHARACTERISTICS OF COMPOUNDS

| Compound | Source[a] | M.p. (cor.), °C. | Mol. wt. as determined from neut. equiv. Found | Calcd. |
|---|---|---|---|---|
| Lauric acid | 2 | ....... | .... | ... |
| Myristic acid | 1 | 54.9 | 228.3 | 228.4 |
| Palmitic acid | 1 | 63.0 | 256.3 | 256.4 |
| Margaric acid | 1 | 60.0-60.3 | .... | ... |
| Stearic acid | 1 | 69.8 | 284.8 | 284.5 |
| Nonadecanoic acid | 5 | 67.8-68.5 | 298.1[b] | 298.5 |
| Eicosanoic acid (arachidic acid) | 5 | 74.2-75.2 | 311.3[b] | 312.5 |
| Heneicosanoic acid | 5 | 72.0-73.5 | 329.1[b] | 326.5 |
| Methyl myristate | 1 | 18.6 | .... | ... |
| Methyl palmitate | 1 | 29.6 | .... | ... |
| Methyl stearate | 1 | 38.55 | .... | ... |
| Methyl eicosanoate | 1 | 46.0-46.5 | .... | ... |
| *n*-Octadecane | 3 | ....... | .... | ... |
| *n*-Hexadecanol | 3 | 46.3-47.8 | .... | ... |
| *n*-Octadecanol | 3 | 55.8-56.8 | .... | ... |
| 1-Iodoöctadecane | 4 | 33.2-34.2 | .... | ... |
| Dioctadecyl thioether | 3 | 68.0-68.6 | .... | ... |
| Dioctadecyl disulfide | 3 | 62.2-62.7 | .... | ... |

[a] 1, Compound synthesized for this investigation at Queen's University; 2, Eastman Kodak Co.; 3, Dr. N. H. Grace, National Research Council Ottawa, Ont.; 4, Dr. E. G. Taylor, Williams College, Williamstown, Mass.; 5, Dr. F. A. Vandenheuvel, Atlantic Fisheries Experimental Station, Halifax, N. S. [b] Recalculated from the data of F. A. Vandenheuvel and P. Yates, *Can. J. Research*, 28, 556 (1950).

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(1) Published as Contribution No. 2680 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 5, 1951. These investigations were initiated on the instigation of Professor R. G. Sinclair of the Department of Biochemistry of Queen's University. Professor Sinclair died recently as a result of an accident and his co-authors on these papers wish to take this opportunity to express their regret at the untimely loss of a stimulating friend and collaborator.

(2) G. B. B. M. Sutherland, *Discussions of the Faraday Society*, **9**, 274 (1950).

(3) H. W. Thompson, D. L. Nicholson and L. N. Short, *ibid.*, **9**, 222 (1950).

(4) R. N. Jones, A. F. McKay and R. G. Sinclair, THIS JOURNAL, **74**, 2575 (1952).

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

(6) W. W. Coblentz, *Pub. Carnegie Inst.*, Bulletin No. 35, Washington, D. C., 1905.

(7) J. Lecomte, "Traité de chimie organique," Masson et Cie, V. Grignard, Editor, Vol. II, Paris, 1936, p. 143.

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(12) P. C. Rao and B. F. Daubert, THIS JOURNAL, **70**, 1102 (1948).

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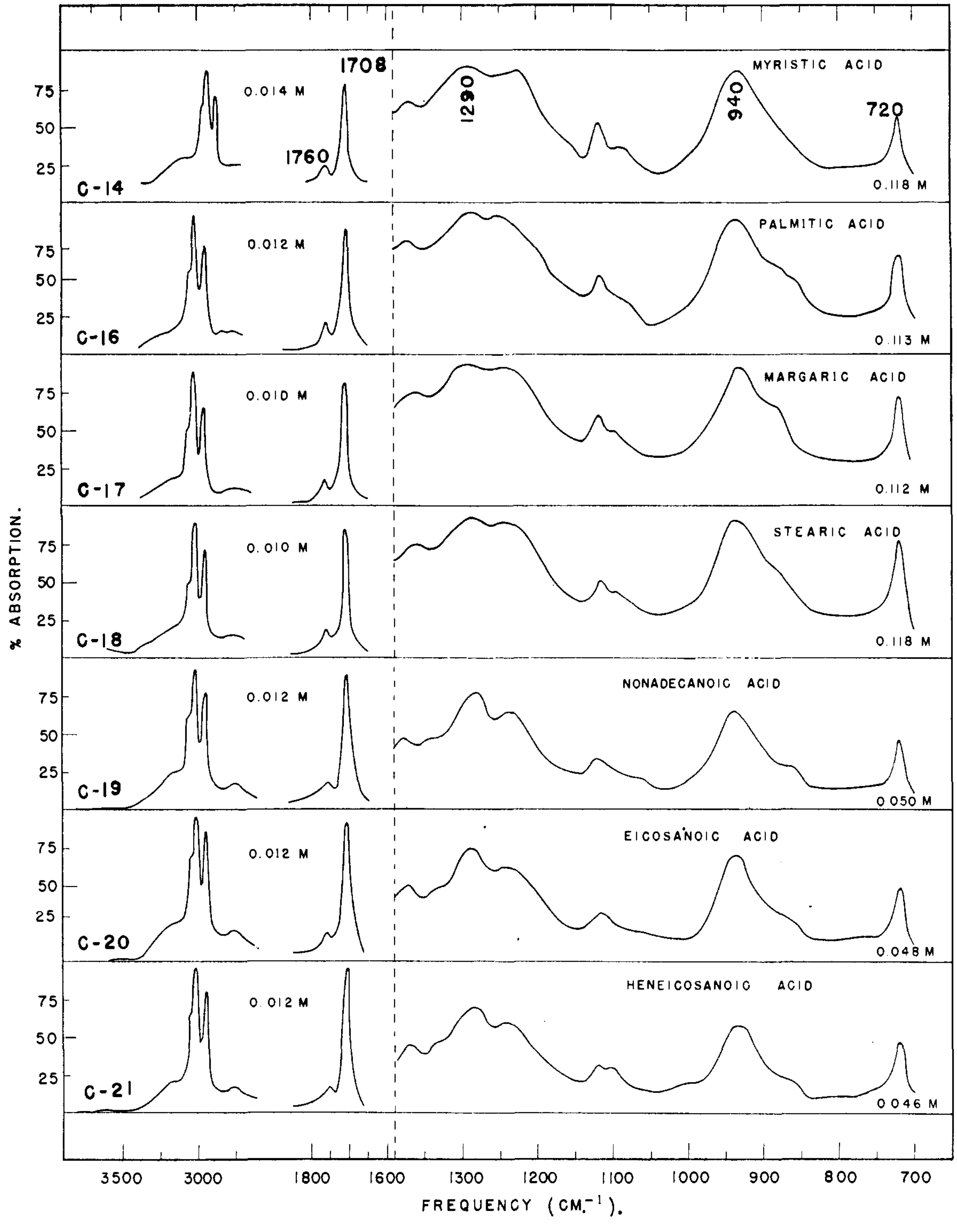

Fig. 1.—Infrared spectra of fatty acids in carbon disulfide solution: 3700–1600 cm.$^{-1}$ $CaF_2$ prism; 1390–700 cm.$^{-1}$ NaCl prism; molar concentrations are indicated; cell thickness 1 mm.

The temperatures of the cooled films were not measured, but sufficient time was allowed for the establishment of thermal equilibrium in the cell, as evidenced by the fact that the spectra showed no further change on prolonging the time of cooling.

The majority of the compounds were prepared at Queen's University and their physical constants are given in Table I.

## Results and Discussion

The spectra of the fatty acids and methyl esters measured in carbon disulfide solution and plotted as per cent. absorption against wave number are shown in Figs. 1 and 2. The spectra of the compounds in the crystalline state, either as films or as mulls in nujol, are shown in Figs. 3 and 4.

In solution both the acids and methyl esters exhibit only broad absorption bands between 650 and 1500 cm.$^{-1}$. Comparison of the $C_{14}$- and $C_{21}$-acids shows that even the introduction of a chain of seven additional methylene groups produces no qualitative change in the solution spectra, and no significant differences are observed between the spectra of the acids of odd and even chain length. A quantitative change with chain length can be demonstrated in the increasing relative intensity of the band at 720 cm.$^{-1}$ as more methylene groups are introduced. This is the methylene rocking vibration (IV) and the apparent molecular extinction coefficient[14] at the maximum increases by about three units for each added methylene group from 37 for myristic acid to 60 for heneicosanoic acid.

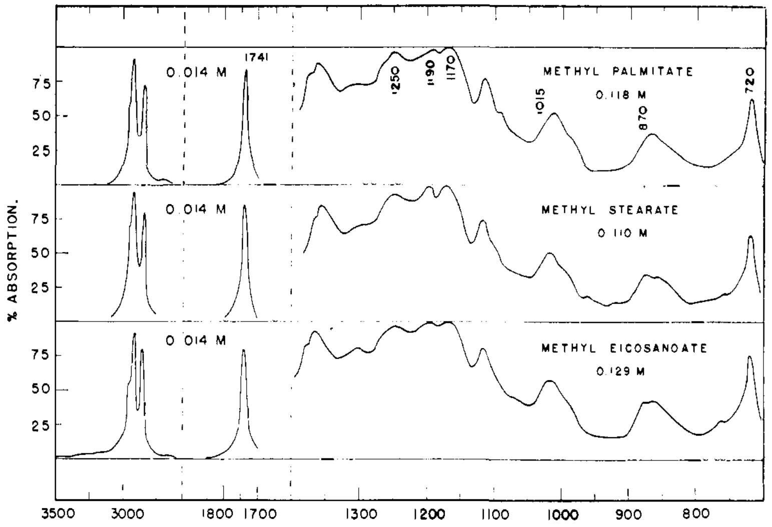

Fig. 2.—Infrared spectra of fatty acid methyl esters in carbon disulfide solution. Experimental conditions as for Fig. 1.

In the crystalline state the spectra of both the acids and the methyl esters show a great deal more structure than in solution (Figs. 3, 4), and the spectra of the acids of different chain length differ quite distinctly from one another, particularly between 1100 and 1400 cm.$^{-1}$.

**Rotational Isomers.**—The lack of specificity in the solution spectra is probably associated with the fact that in the liquid phase free rotation exists about each C–C linkage, and the hydrocarbon chains are folded in a random manner resulting in the presence of many rotational isomers. Each rotational isomer will absorb somewhat differently, particularly in the regions associated with C–C stretching and C–H bending vibrations, and the spectra observed in solution constitute a summation over a large number of different molecular species. This phenomenon has been recognized in connection with the Raman and infrared spectra of *n*-paraffins.[16,17] In the crystalline state the hydrocarbon chains lie parallel in an "all *trans*"-configuration and provided the crystals are homogeneous the spectrum will be that of a single molecular species, the complexity determined by the nature of the unit cell.

**Effects of Polymorphism.**—Studies of the X-ray diffraction patterns of fatty acids have shown that the hydrocarbon chains can be arranged in at least two forms differing in the angle of tilt with respect to the crystal axes, and the mode of hydrogen bonding between the four molecules constituting the unit cell. The effects of this polymorphism on the infrared spectrum are quite large and are illustrated in the case of stearic acid in Fig. 3. The dotted curve was obtained on a nujol mull of a sample crystallized from acetone at 0° and the solid curve from a film obtained by melting this material and allowing it to cool slowly on a rock-salt plate. X-Ray diffraction measurements established that the mull contained a mixture of the $\alpha$ and $\beta$ polymorphs in approximately equimolar proportions while the film gave X-ray spacings of the pure $\beta$-form. The presence of mixtures of polymorphs in the other solid acids examined has not been excluded.

## Characteristic Group Frequencies

**O–H Stretching Vibrations.**—Neither in solution nor in the solid state is there any indication of free hydroxyl absorption between 3650 and 3600 cm.$^{-1}$. The hydroxyl of the carboxylic group is strongly bonded and responsible for the broad absorption band which commences at about 3500 cm.$^{-1}$ and extends into the region of C–H stretching absorption below 3000 cm.$^{-1}$ (Figs. 1, 3).

**C–H Stretching Vibrations.**—The absorption bands in this region require a lithium fluoride prism for optimum resolution (Figs. 3, 4). The two strong bands at 2920 and 2850 cm.$^{-1}$ are attributable to the antisymmetrical (I) and symmetrical (II) methylene stretching vibrations, respectively,[18,19] and the two smaller bands at 2954 and 2870 cm.$^{-1}$ to vibrations of the terminal methyl group. In the methyl esters the band at 2870 cm.$^{-1}$ is not fully resolved. No absorption specific to the C–H stretch of the ester methyl group can be recognized.

**C=O Stretching Vibrations.**—A strong carbonyl band occurs in the solution spectra of the free acids at 1708 cm.$^{-1}$ (Fig. 1), associated with the dimeric carboxylic acid group, and a weaker band at 1760 cm.$^{-1}$ is probably due to the carbonyl group of the monomer. The presence of two carbonyl bands in the spectra of carboxylic acids in solution is well established.[20-22]

In the solid state the acids show a single dimer

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(14) The slit width employed varied between 2.0 and 3.0 cm.$^{-1}$. Although the half-band widths could not be evaluated precisely because of overlapping absorption, the ratio of the slit width to the half-band width was estimated to be less than 0.2. Under these circumstances the true molecular extinction coefficients would not exceed the apparent ones by more than 5% (see reference 15).

(15) R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, THIS JOURNAL, **74**, 80 (1952).

(16) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

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

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(19) E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).

(20) M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938).

(21) R. C. Herman and R. Hofstadter, *ibid.*, **6**, 534 (1938).

(22) M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).

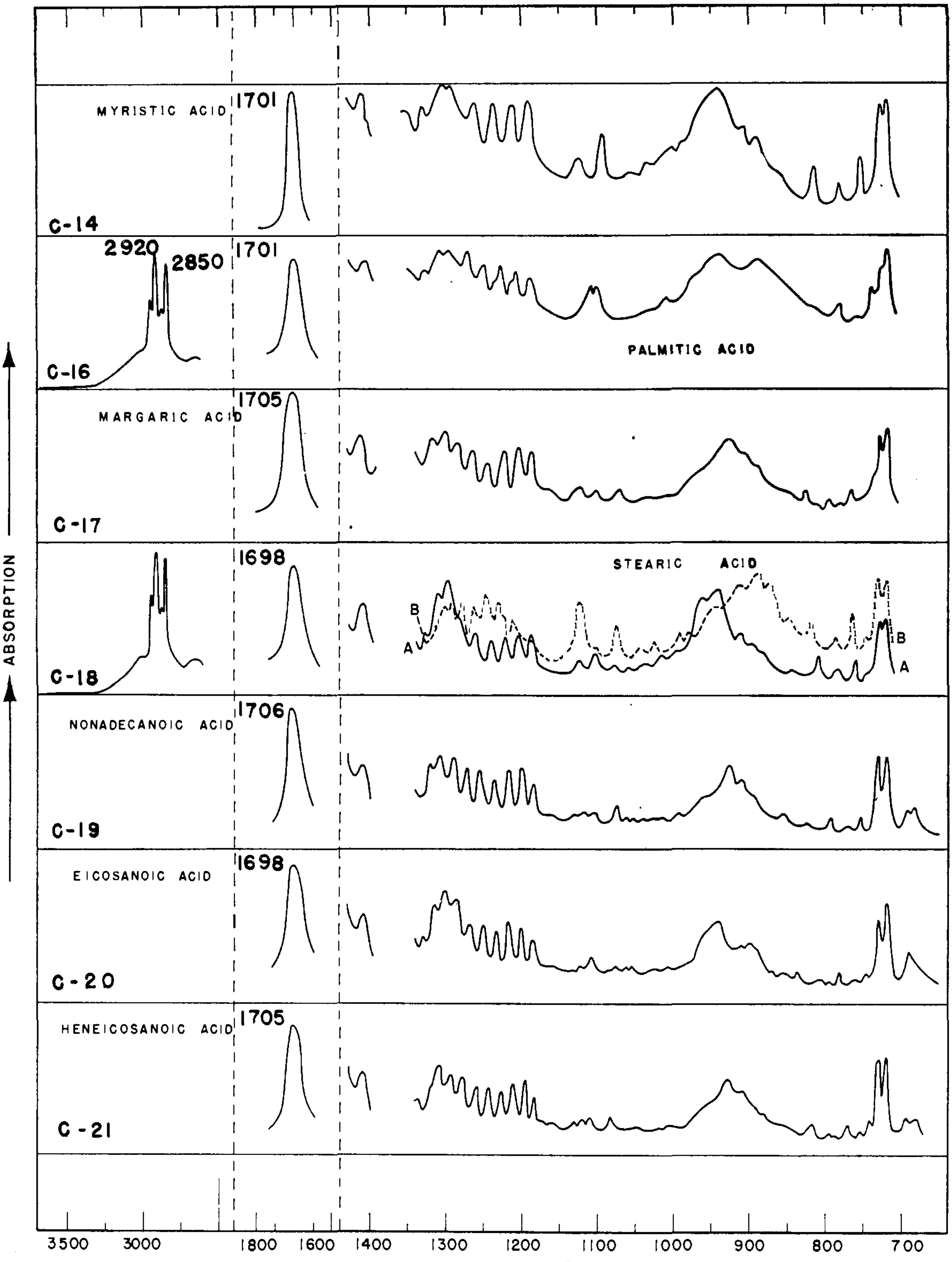


Fig. 3.—Infrared spectra of fatty acids in the crystalline state (as mulls in nujol): 3700–2500 cm.$^{-1}$ LiF prism; 1800–650 cm.$^{-1}$ NaCl prism. The sample thicknesses employed in different regions of the spectrum are not necessarily the same.

absorption band only (Fig. 3). In the acids of odd chain length the maximum is at 1705 cm.$^{-1}$ but in the acids of even chain length it is shifted significantly to lower frequency (1698–1701 cm.$^{-1}$). The C=O frequency of solid stearic acid is not displaced by cooling the film with liquid nitrogen (Fig. 5). In the methyl esters the carbonyl maximum is at 1741 cm.$^{-1}$ both in the solid state and in solution.

**Other Carboxy Vibrations.**—Two absorption bands associated with the carboxylic acid group have been reported by several investigators[20–22] as occurring near 900 and 1250 cm.$^{-1}$. In the fatty acid solution spectra a strong band occurs near 940 cm.$^{-1}$, its asymmetry indicates that two or more components are present. In the solid acids strong complex absorption occurs between 880 and 960 cm.$^{-1}$. These bands are replaced in the methyl ester solutions by bands at 870 and 1015 cm.$^{-1}$. The absorption in this region is very sensitive to temperature change and on cooling a film of $\beta$-stearic acid with liquid nitrogen the asymmetrical peak at 940 cm.$^{-1}$ shifts and resolves into two peaks with maxima at 958 and 974 cm.$^{-1}$ (Fig. 5). Changes in these bands also constitute the main difference between the spectra of the $\alpha$- and $\beta$-polymorphs of stearic acid (Fig. 3).

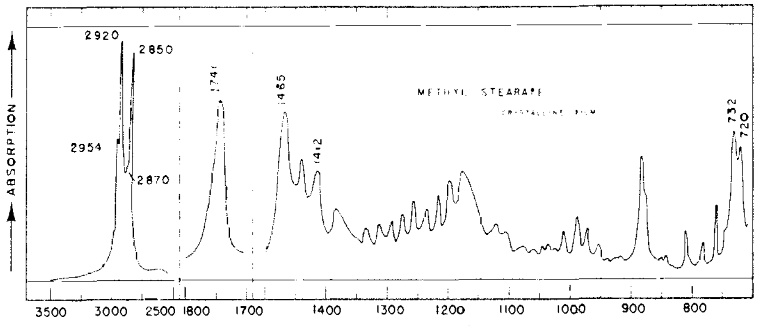


Fig. 4.—Infrared spectrum of crystalline film of methyl stearate: 3500–2500 cm.$^{-1}$ LiF prism; 1800–1700 cm.$^{-1}$ $CaF_2$ prism; 1500–700 cm.$^{-1}$ NaCl prism.

A strong band occurs at 1290 cm.$^{-1}$ in the solution spectra and at 1300 cm.$^{-1}$ in the solid spectra of the free acids. This band may also be associated with the carboxylic acid group as the absorption of the methyl esters differs in this region. Like the 940 cm.$^{-1}$ band, the absorption band or bands near 1290 cm.$^{-1}$ are temperature dependent (Fig. 5) being displaced to higher frequency on cooling.[23]

The methyl esters in solution possess three strong bands at 1170, 1190 and 1250 cm.$^{-1}$ (Fig. 2) some or all of which are probably associated with C–O stretching vibrations of the carbomethoxy group and are analogous to bands observed in the spectra of acetates and other alkyl esters.[24,25] These conclusions concerning the C–O stretching vibrations are in agreement with those of Shreve, Heether, Knight and Swern.[8]

**C–H Bending Vibrations.**—The four C–H deformation modes of vibration of the methylene group, bending (III), rocking (IV), wagging (V) and twisting (VI) have been investigated extensively on the spectra of $n$-paraffins.[17] The bands at 1460–1465 cm.$^{-1}$ and at 720 cm.$^{-1}$ in the spectra of both fatty acids and esters are to be attributed to bending and rocking methylene vibrations, respectively. The splitting of the 720 cm.$^{-1}$ rocking band into two components in the solid phase spectra is in accord with the observation of Stein and Sutherland for $n$-paraffins below the transition point.[26] Some or all of the absorption bands occurring between 1460 and 1400 cm.$^{-1}$ can probably be attributed also to methylene bending vibrations. The methylene group adjacent to the carboxyl group should absorb at a lower frequency and may account for the band at 1405–1410 cm.$^{-1}$. In the solution spectra this region is obscured by carbon disulfide absorption, but is being reinvestigated at higher dispersion in carbon tetrachloride solution. The small band at 1372 cm.$^{-1}$ is most probably due to the terminal methyl group.

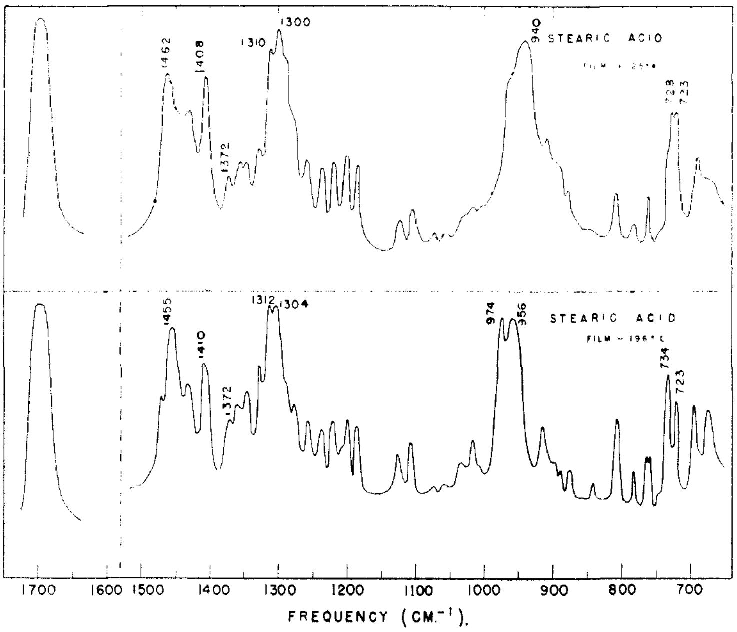
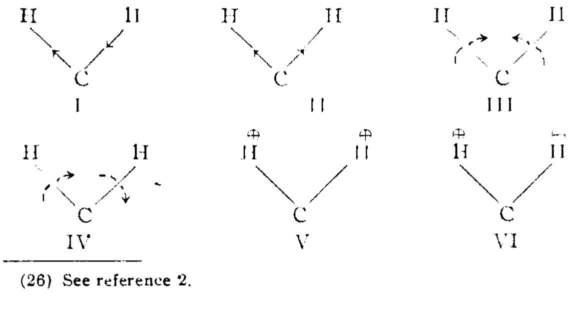


Fig. 5.—Curve A, infrared spectrum of a crystalline film of stearic acid measured at room temperature; curve B, spectrum of the same film when cooled with liquid nitrogen to a temperature of approximately −196°.



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(23) Absorption near 1378 and 1442 cm.$^{-1}$ has also been attributed to the C–O stretching vibrations of monomeric and dimeric carboxylic acid groups, respectively (see references 20, 22), but in the fatty acids and esters the absorption bands in these regions would seem more reasonably assigned to methyl and methylene vibrations (*vide infra*).

(24) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

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(26) See reference 2.

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.

**Acknowledgments.**—The authors wish to thank Dr. G. S. Myers and Dr. F. A. Vandeheuvel for supplying certain of the compounds, Dr. W. H. Barnes for X-ray diffraction measurements and Mr. R. Lauzon and Mr. D. S. Keir for technical assistance in the determination of the spectra. The investigation was supported by a grant from The Ontario Cancer Treatment and Research Foundation which is also gratefully acknowledged.

OTTAWA, CANADA RECEIVED NOVEMBER 1, 1951

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL OF CANADA AND THE DEPARTMENTS OF CHEMISTRY AND BIOCHEMISTRY, QUEEN'S UNIVERSITY]

# 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).