Identification of Fatty Acid Polymorphic Modifications by Infrared Spectroscopy

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ABSTRACT

IR spectra in the 7.5-25.0 μ region are shown to be unique for the individual long chain odd carbon numbered saturated fatty acids and for the monounsaturated even carbon numbered fatty acids, their isomers, and polymorphic modifications. IR spectra are presented which illustrate similarities and dissimilarities resulting from chain length differences and polymorphic variations for monounsaturated acids. X-ray crystal long spacings for the saturated odd carbon numbered acids are compared with literature values. X-ray crystal long spacings for monounsaturated *trans* acids are shown to be related to carbon chain length and independent of the location of unsaturation. Diffractograms and IR spectra of the 2 polymorphic modifications of elaidic acids are presented. IR spectra illustrating band differences for *cis* and *trans* isomers are shown.

INTRODUCTION

A recent publication from this laboratory (1) discussed some correlations of X-ray, IR, and NMR analyses of a series of even carbon numbered saturated fatty acids. The IR spectra in the 7.5-25 μ region were proposed as means of identification of the individual acids and their various polymorphic modifications. The investigation has been extended to include both the odd carbon numbered saturated acids and a series of isostructural monounsaturated acids. Although IR has been proposed as the best technique for identifying the various polymorphic modifications, evaluation of purity and singularity of the polymorphic modifications are dependent upon both IR and X-ray diffraction pattern analyses. Monounsaturated acids differ in their crystalline structure relative to their *cis* or *trans* configuration, the location of the site of unsaturation, and whether it is between odd-even or even-odd numbered carbon atoms with respect to the carboxyl group (2).

In the present report X-ray diffraction data and IR spectra of a series of homologous saturated odd carbon numbered acids and a number of isostructural monounsaturated fatty acids are compared.

EXPERIMENTAL

The fatty acids were prepared by the usual fractional distillation of their methyl esters. The *trans* isomers of the unsaturated acids were prepared by the procedure of Mack

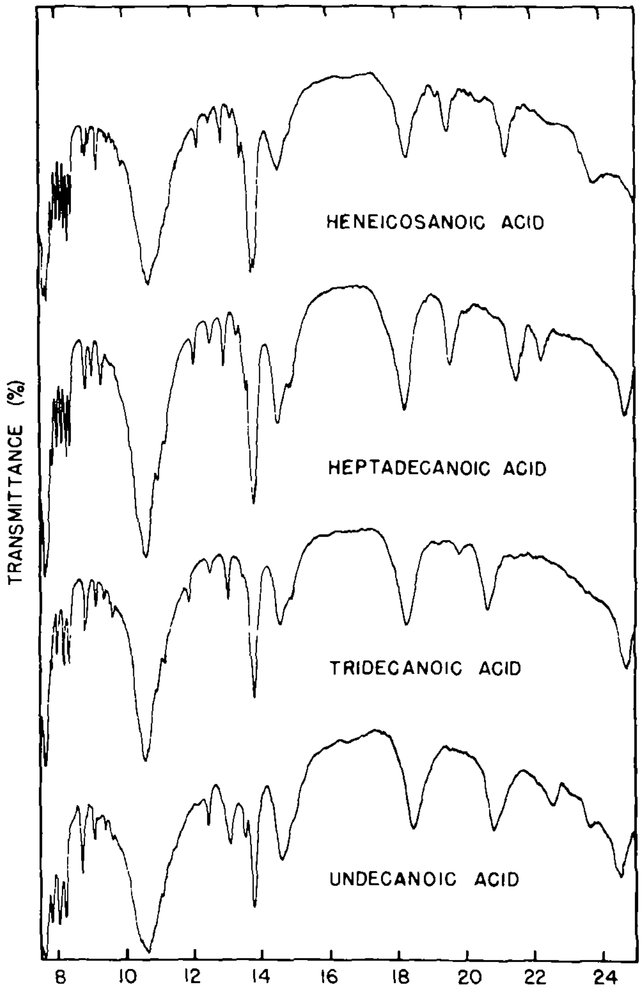

FIG. 1. IR spectra of B′-form of undecanoic, tridecanoic, heptadecanoic, and heneicosanoic acids.

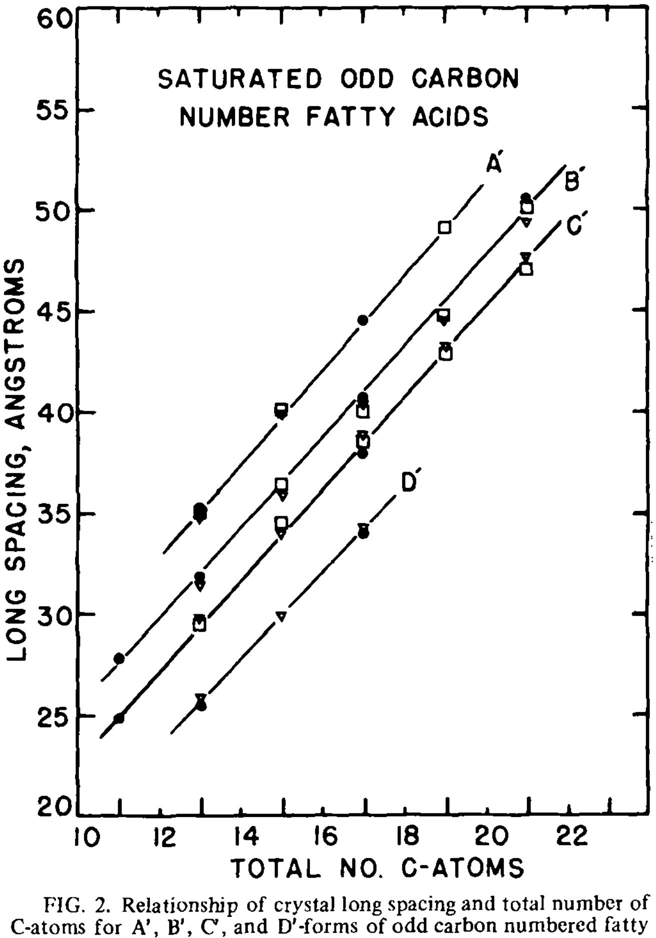

FIG. 2. Relationship of crystal long spacing and total number of C-atoms for A′, B′, C′, and D′-forms of odd carbon numbered fatty acids. Closed circles, our data; open triangles, Francis et al. (6); open squares, Stenhagen and von Sydow (5).

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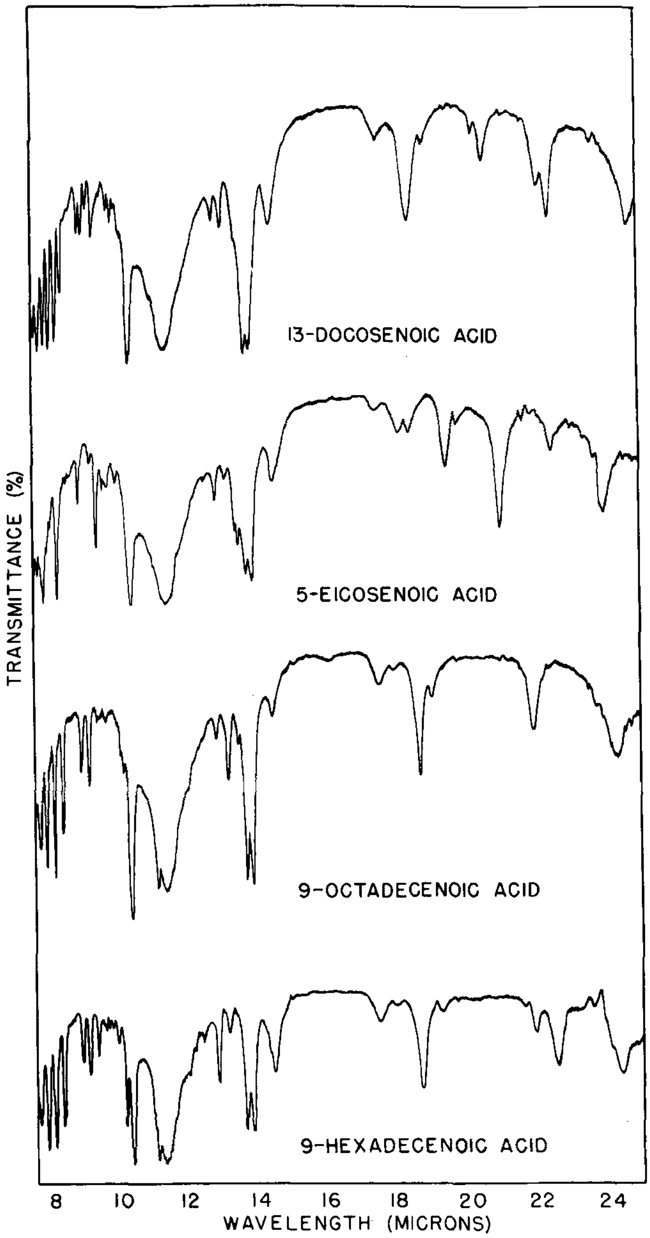

FIG. 3. IR spectra of stable polymorphic modification of *trans*-9-hexadecenoic, *trans*-9-octadecenoic, *trans*-5-eicosenoic, and *trans*-13-docosenoic acids.

and Bickford (3). The 2 forms of elaidic acid were obtained by using the procedure of Harris et al. (4). The melting points, determined by the thermostatic sealed tube method, are in good agreement with the best literature values.

A conventional IR spectrophotometer (Perkin Elmer Model 337) was used. The instrument was operated at ambient temperature under the following conditions: slit program, normal; scan, slow (24 min.). The spectrophotometer was balanced with air against air. The spectra were obtained either as thin films crystallized between KBr plates or as Nujol mulls between KBr plates. The spectra of acids that melted at ca. 40 C or below were obtained at ca. 0 C by use of a Research Industrial Instrument Company VLT-2 variable temperature IR cell.

A General Electric diffractometer (Model XRD-5) was used to obtain the X-ray diffractograms, employing nickel-filtered Cu radiation and 1° slits. Smooth-faced pressed samples, ca. 1 mm. thick, were used.

RESULTS AND DISCUSSION

IR spectral analyses of long chain saturated even carbon numbered acids have shown that the individual acids and their various polymorphic modifications are readily distinguishable in the 7.5-25.0 μ region of the spectrum. In the present report, spectra are presented illustrating characteristic absorption bands for odd carbon numbered fatty acids. Spectra for the stable B′-form of the odd carbon numbered (Fig. 1) are markedly similar to the stable C-form of the

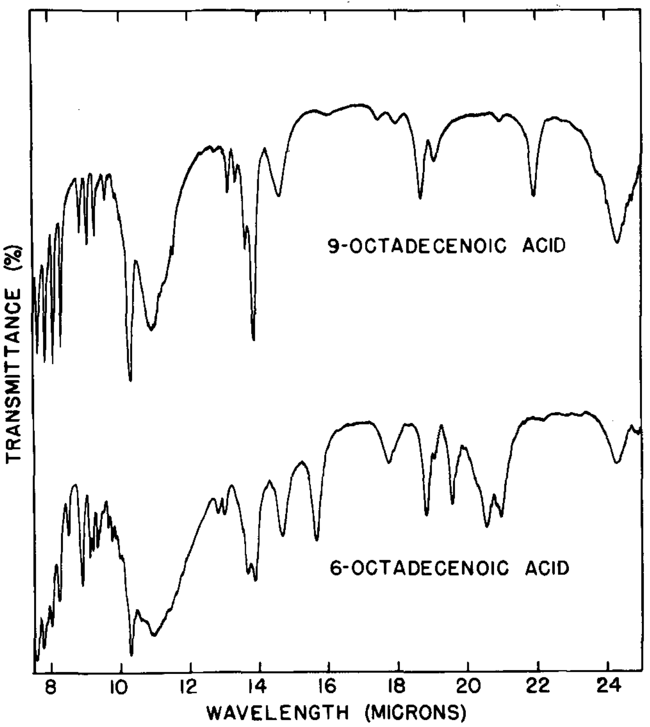

FIG. 4. IR spectra of stable polymorphic modification of *trans*-6-octadecenoic and *trans*-9-octadecenoic acids.

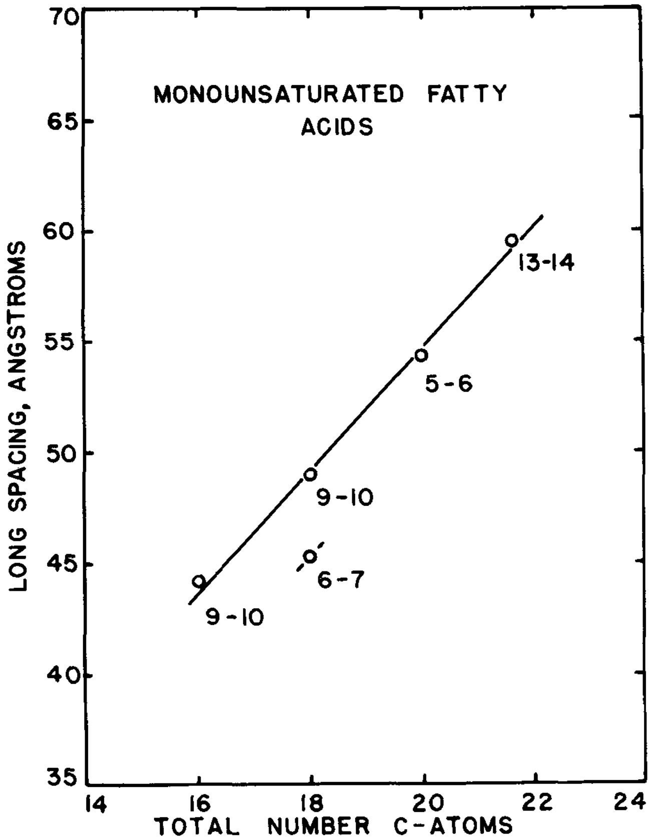

FIG. 5. Relationship of crystal long spacing and total number of carbon atoms for monounsaturated *trans* acids.

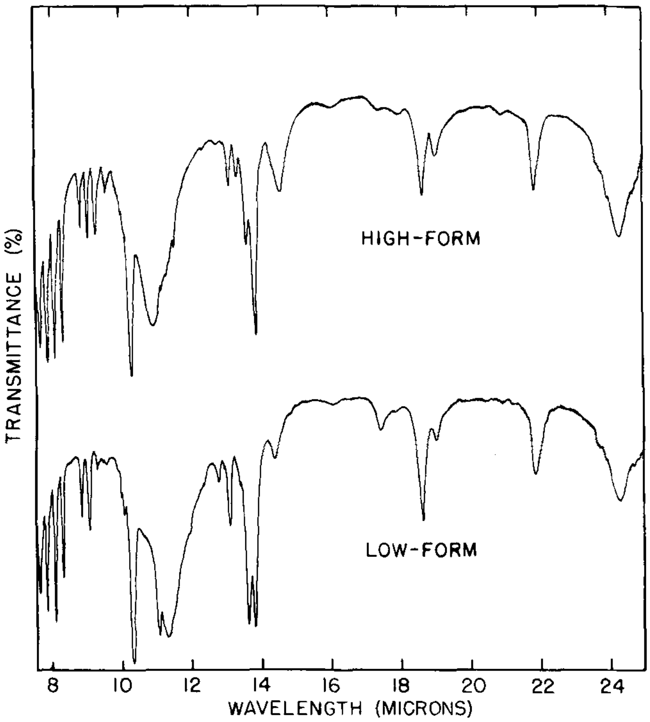

FIG. 6. IR spectra of low- and high-melting polymorphic modifications of *trans*-9-octadecenoic (elaidic) acid.

even carbon numbered fatty acids. Both have broad deep absorption bands at 10.6 μ and bands of medium intensity with shoulders at 14.5-14.8 and 17.8-18.2 μ, respectively. There are characteristic differences between 20.0 and 25.0 μ. Not all of the various polymorphs of odd carbon numbered acids analyzed were sufficiently singular in form to present their spectra. However, the differences observed indicate that there are characteristic bands associated with each acid and its polymorphs.

The crystal long spacings obtained from the X-ray diffraction patterns for undecanoic, tridecanoic, heptadecanoic, and heneicosanoic acids are compared with literature values (Fig. 2) of Stenhagen and von Sydow (5) and Francis et al. (6). The B′-form of the acids, obtained by slow crystallization from the melt, was the only form obtained free of other polymorphs. The A′, C′, and D′-forms obtained by solvent crystallization generally contained small fractions of one or more of the other forms, the predominance of any single form being dependent upon the temperature and concentration at which the crystals were allowed to form (1). The D′-form was observed only in mixtures with other forms. Diffractograms obtained on a strip chart allow easy calculation of the crystal long spacing of one polymorph in the presence of small amounts of a second polymorph.

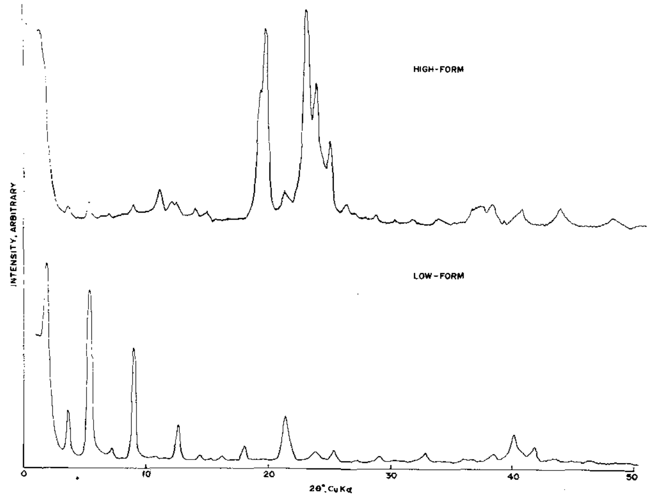

FIG. 7. X-ray diffractogram of low- and high-melting polymorphic modifications of *trans*-9-octadecenoic (elaidic) acid.

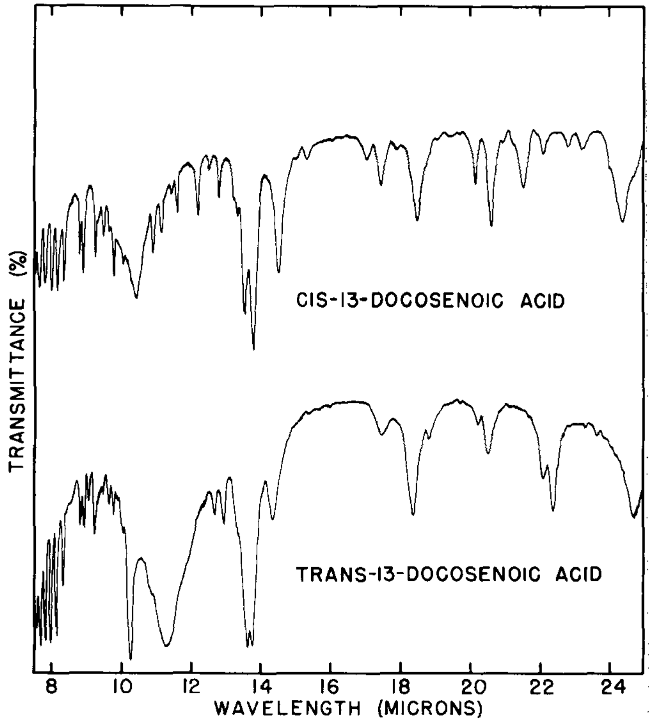

FIG. 8. IR spectra of *cis* and *trans* isomers of 13-docosenoic acids.

The unsaturated fatty acids, like their saturated counterparts, exhibit spectral uniqueness with respect to chain length and polymorphic form. The unsaturated acids exhibit further differences as a result of *cis trans* and positional isomerism. The IR spectra of some monounsaturated *trans* acids, 9,hexadecenoic, 9-octadecenoic, 5-eicosenoic, and 13-docosenoic, are reproduced in Figure 3. Comparison of the spectra reveals that each has a broad, deep band at 11.4 μ and medium or weak bands at 14.5 and 17.6 μ, characteristic of acids in a single polymorphic modification (1). Again carbon chain length differences are reflected in spectral differences in the region beyond 18 μ.

Since acids of the same number of carbon atoms having unsaturation at odd and even positions in the carbon chain, relative to the carboxyl group, are known to exhibit different crystal long spacings (2), spectral differences also would be expected. Spectra of 2 positional isomers petroselaidic and elaidic (6-octadecenoic and 9-octadecenoic acids) are compared in Figure 4. Each has a broad deep band at 10.8 μ and the same band of medium intensity at 14.5 μ, which suggest a single polymorphic modification. Since one spectrum shown is for the stable, high melting form of elaidic acid, the other spectrum probably represents the stable form of petroselaidic acid also.

Crystal long spacings of the above monounsaturated *trans* acids are plotted against carbon chain length in Figure 5. It is known that the crystal long spacings of saturated acids vary linearly with carbon chain length, and thus it is not surprising that the crystal long spacings of the monounsaturated acids are similarly related to carbon chain length. The linear relationship seems to be independent of the location of the unsaturation in the carbon chain. However, the long spacing of the 6-7 unsaturated acid shown suggests that odd-even location of unsaturation may produce a parallel relationship to that of the even-odd location.

Elaidic acid (9-octadecenoic) exhibits 2 closely melting polymorphic forms. Spectra for these 2 forms are presented in Figure 6. Although similar in many respects, the typical shift of the broad deep band from 10.8 to 11.4 μ and the medium bands at 14-15 and 17-18 μ, respectively, readily characterize the 2 polymorphs. The bands between 18 and 25 μ are associated with chain length and are identical, as would be expected.

X-ray diffraction analysis allows for further identification of the 2 polymorphs. The diffractograms presented in Figure 7 are markedly dissimilar. That of the low-melting polymorph is typical of diffractograms obtained for most saturated fatty acids and for the other *trans* acids examined here. All of the orders are recognized easily and clearly defined. In the diffractogram of the high-melting form, only the reflections in the region of the side or short spacings are observed. A similar diffraction pattern was observed by Lovegren et al. (7) for a tempered sample of 2-elaidodipalmitin and was attributed to a change in crystalline structure.

Cis and *trans* acids are readily distinguished on the basis of the strong *trans* band (C-H stretching) at 10.3 μ. However, other differences are also evident in the spectra of erucic and brassidic, (*cis*-13-docosenoic and *trans*-13-docosenoic acids), when they are compared over the 7.5-25.0 μ region (Fig. 8). The most noticeable differences are the shift of the broad, deep band from 10.8 in the *cis* acid to 11.4 μ in the *trans* acid and the absence of the medium doublet at approximately 22.3 μ in the *cis* acid. The differences, of course, could, and probably do, arise from polymorphic form variations. Additionally, the 2 spectra were observed at different temperatures (the *trans* acid at room temperature and the *cis* acid at 0 C); because band shifts are known to be affected by temperature changes, some of thee differences also could result from temperature effects.

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