

Gas phase infrared spectroscopy in characterization of unsaturated natural products

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Abstract: Characteristic absorptions which occur at 3028-3011 and 970-967 cm^{-1} in gas-phase Fourier-transform infrared spectra (FTIR) allow unambiguous determination of the configuration of the double bonds in long-chain unsaturated compounds bearing a RCH=CHR' type of bond. The intensities of these two bands indicate the number of *cis* or *trans* bonds present in linear polyunsaturated compounds. Terminal vinyl groups can be identified, even when other functional groups are present, by the presence of 3085 and 914 cm^{-1} absorptions. Compounds bearing (*E,Z*) or (*Z,E*) conjugated moieties show a characteristic "fingerprint" consisting of two bands at 978-977 and 948-946 cm^{-1}

Infrared spectroscopy, which was once an invaluable asset to all chemists interested in natural product characterization, has lost its popularity as a result of recent advances in NMR technology. However, NMR spectroscopy is not ideal for samples available in only minute amounts, and in impure form, since for routine NMR analysis microgram to milligram amounts of a relatively pure sample is required. Although mass spectra can be obtained with a few nanograms of material, and provide a great deal of structural information, they are often not very useful in differentiating stereoisomers, or even structural isomers. In this respect, gas-phase IR spectroscopy has much to offer to natural product chemists dealing with nanogram amounts of material. In addition to providing functional group information, IR spectra can often differentiate between isomers.

For the pheromone chemist, exact determination of configuration of double bonds is vital, since the presence of a minute amount of a stereoisomer with the opposite geometric configuration can often inhibit drastically the attractivity of a synthetic pheromone mixture. Sex pheromones of moths are usually mixtures of unsaturated acetates, alcohols and aldehydes. We have shown that the *cis/trans* configuration of double bonds in long-chain monounsaturated compounds bearing RCH=CHR' type bonds can be determined by vapor phase IR absorptions that occur at 3028-3011 and 970-967 cm^{-1} . For example, Fig. 1 shows the infrared spectra of (*Z*)- and (*E*)-11-tetradecenyl acetates. The identification of *trans* compounds, by the presence of the absorption at 970-967 cm^{-1} is well established

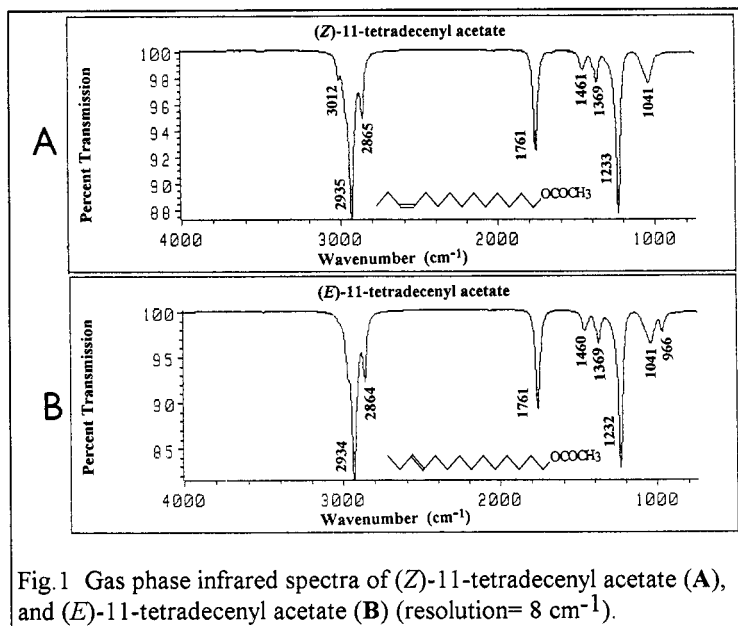


Fig. 1 Gas phase infrared spectra of (Z)-11-tetradecenyl acetate (A), and (E)-11-tetradecenyl acetate (B) (resolution= 8 cm⁻¹).

Terminal double bonds are recognized by three characteristic absorptions, namely, the two C-H vibrations at 3085 and 914 cm⁻¹ and the C=C stretch at 1641 cm⁻¹ (1,8). In fact, vinyl groups are recognized easily even when peaks of other strongly absorbing functional groups are present in the

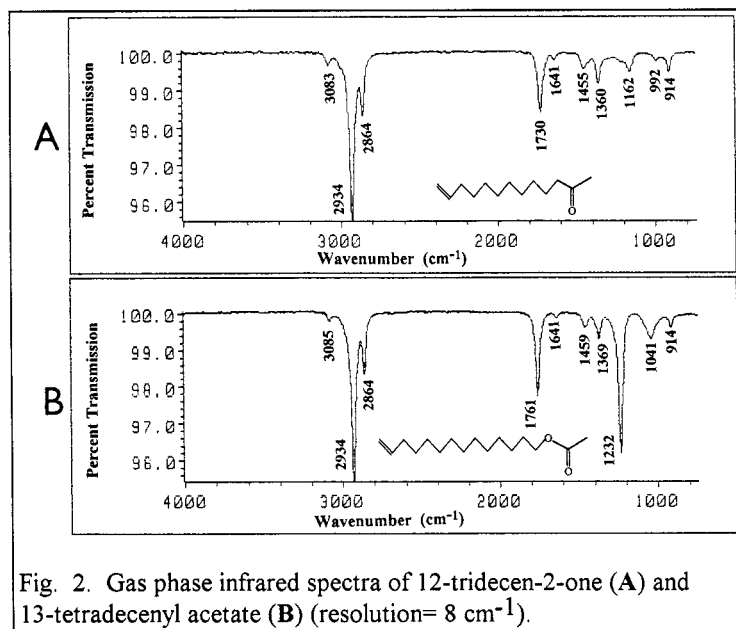


Fig. 2. Gas phase infrared spectra of 12-tridecen-2-one (A) and 13-tetradecenyl acetate (B) (resolution= 8 cm⁻¹).

4,11-hexadecadienol. In the spectrum of the (Z,Z) isomer, the intensity of the *cis* =CH stretch absorption at 3012 cm⁻¹ is nearly as twice that observed for compounds with only one *cis* bond.

(2-4). However, the significance of the *cis* =CH stretch absorption, in the 3028-3011 cm⁻¹ region, is not well appreciated, except in a few occasional examples (5-7). We have shown that for most monoenes this absorption occurs at 3013-3011 cm⁻¹. However, for long-chain acetates, when a double bond is present at the C-2, C-3, or penultimate carbon atoms, the band shows a hypsochromic shift (1).

spectra (9). For example, the three expected absorptions are evident in the spectra of 12-tridecen-2-one and 13-tetradecenyl acetate (Figure 2). The unsaturated ketone spectrum given here was obtained from an extract made from the defensive spray of an individual caterpillar (*Schizura unicornis*) (10).

The generalizations made for monoenes can be extended to polyunsaturated compounds. Figure 3 shows the spectra of all four geometric isomers of

Moreover, there is no band present in the 970-967 cm^{-1} region. The two spectra of (*E,Z*) and (*Z,E*) isomers are virtually identical, and show bands at 3012-3011 and 967 cm^{-1} . The intensity of each of

these bands is equivalent to that of a single double bond. In contrast, the peak area of the 967 cm^{-1} band of the (*E,E*) isomer shows nearly twice the intensity of that observed for a single *trans* bond.

It follows that the number of *cis* and/or *trans* bonds present in a molecule can be deduced unambiguously by evaluating the intensities of these two absorptions. However, this must be done with caution, since these generalizations may not be applicable directly to systems bearing nonisolated double bonds. We have shown previously that the positions of the bands do vary depending on the proximity of the double bond to another functional group or terminal methyl group (1). The =CH stretch band appears typically at 3018-3016 cm^{-1} in the spectra of compounds bearing methylene interrupted *cis* diene moieties. Furthermore, vapor phase spectra allow the determination

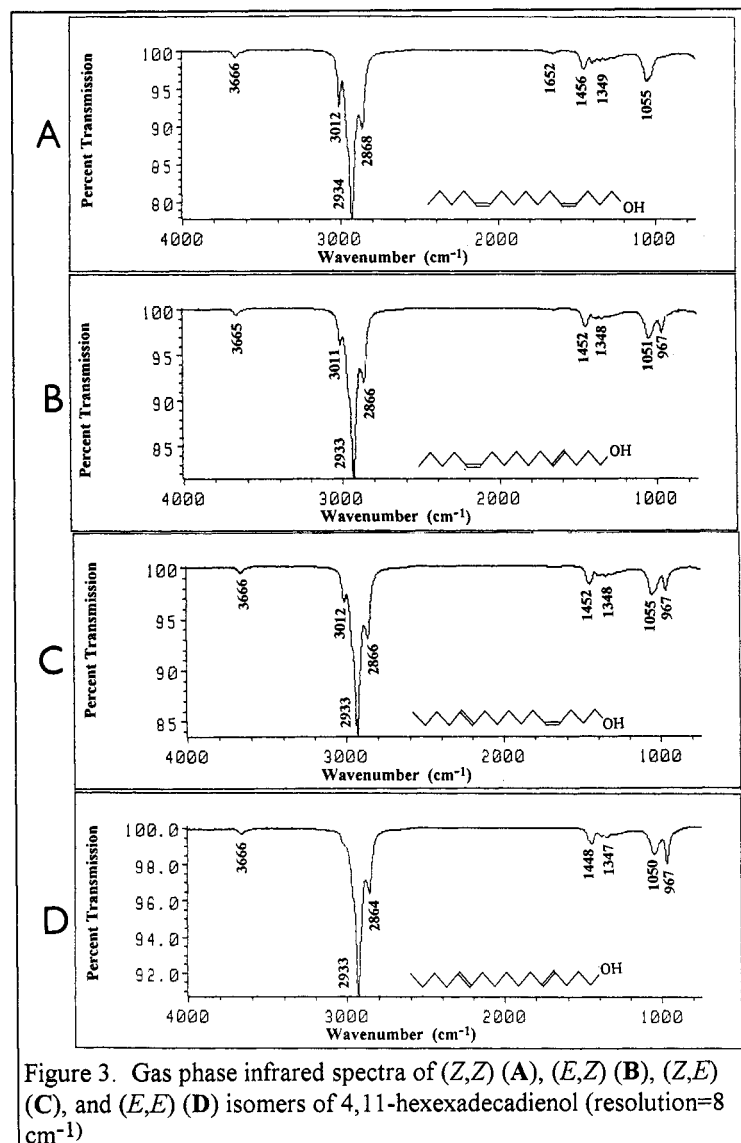


Figure 3. Gas phase infrared spectra of (*Z,Z*) (A), (*E,Z*) (B), (*Z,E*) (C), and (*E,E*) (D) isomers of 4,11-hexadecadienol (resolution=8 cm^{-1})

of the configuration of conjugated double bonds. For example, an (*E,Z*) or a (*Z,E*) conjugated system can be recognized by a characteristic "finger print" pattern consisting of two bands at 978-977 and 948-946 cm^{-1} (Figure 4).

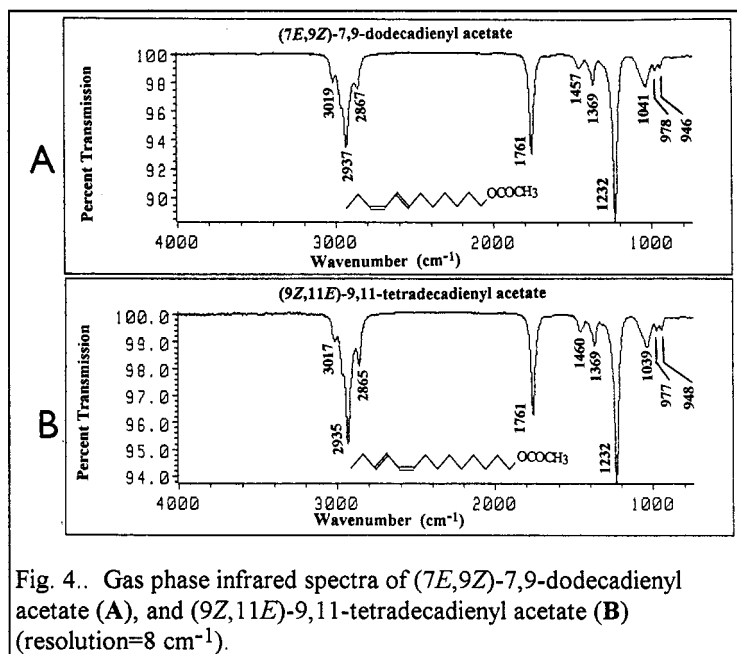


Fig. 4. Gas phase infrared spectra of (7E,9Z)-7,9-dodecadienyl acetate (A), and (9Z,11E)-9,11-tetradecadienyl acetate (B) (resolution=8 cm⁻¹).

From the few examples given, it is evident that valuable information can be obtained from vapor phase infrared spectra and that the potential of this technique is currently very much underutilized. Since state-of-the-art instruments can record useful spectra from 5-50 nanograms of possibly inhomogeneous material, GC/FTIR should be regarded as an indispensable tool in natural products laboratories.

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