Assignment of $^{1}H/^{13}C$ NMR Resonances of ethyl trans-crotonate

Morgan K. Stinson and Peter F. Flynn

2-butenoic acid ethyl ester, commonly known as ethyl trans-crotonate (ETC), is a six carbon molecule with a trans-double bond between C2 and C3, and an ester linkage between C4 and C5. The molecular formula for ETC is $\text{C}_6\text{H}_6\text{O}_2$, and the molecular weight is 114.1424 g/mol. There are 2 degrees of unsaturation in the molecule. The IUPAC numbering for ETC is shown in Figure 1.

### $^1H$ NMR Spectrum

The $^1H$ NMR spectra of ETC is shown in Figure 2. The data were recorded at 500MHz (1H), using a spectral width of 5274.2 Hz and 16384 complex points (acquisition time of 3s), and a recycle delay of 1 s.

### $^{13}C$ NMR Spectrum

The $^{13}C$ NMR spectra of ETC is shown in Figure 3. The data were recorded at 500MHz using a spectral width of 31250 Hz and 32768 complex points (acquisition time of 1s). The $^{13}C$ peak assignments were made based on the $^1H$ assignments and the direct $^1H$-$^{13}C$ correlations observed in the gHMQC spectra.

### Gradient-Enhanced Correlation Spectroscopy (gCOSY)

The two-dimensional gCOSY for ETC is shown in Figure 4. This data reveals $^1H$-$^1H$ chemical shift correlations between J-coupled nuclei. The data were recorded using spectral widths in the direct (F2, horizontal axis) and indirect (F1, vertical axis) dimensions of 5274.26 Hz, with 1024 complex points in the F2 dimension and 512 complex points in the F1 dimension. The methyl resonance at 1.282 ppm is coupled to the resonance at 4.1795 ppm, consistent with our previous considerations. This confirms that resonances labeled c and d correspond to the methylene group at position 5. The ethyl resonance at 1.8765 ppm is correlated with the resonances at 6.978 ppm (strong correlation) and at 5.841 ppm (weak correlation). This indicated that resonances labeled a and b correspond to the vinylic protons at positions 2 and 3. Consideration of the intensity of the COSY resonances, together with the fine structure analysis of the resonances reveals that resonance a is the methane moiety at position 2 and that the resonance b corresponds to position 3. The $^1H$ and COSY spectra for ETC reveal the presence of a long-range 4-bond coupling between the methyl $^1H$ resonances at position 1 and the vinyl proton at position 3.

### Gradient-Enhanced Heteronuclear Multiple Quantum Coherence Spectroscopy (gHMQC)

The two-dimensional gHMQC spectra for ETC is shown in Figure 4. This data reveals $^{13}C$-$^1H$ chemical shift correlations between directly bonded hydrogen and carbon nuclei. The data were recorded using a spectral width of 5274.26 Hz in the direct (F2, horizontal axis) and 21378.9 Hz in the indirect (F1, vertical axis), with 1024 complex points in the F2 dimension and 512 complex points in the F1 dimension.

### Gradient-Enhanced Heteronuclear Multiple Bond Correlation (gHMBC)

The two-dimensional gHMBC spectra for ETC is shown in Figure 6. This data reveals $^{13}C$-$^1H$ chemical shift correlations between geminal and vicinal couplings. This data was recorded using a spectral width of 5274.26 Hz in the direct (F2, horizontal axis) and 30177.3 Hz in the indirect (F1, vertical axis), with 1024 complex points. The data provided by the gHMBC spectra further confirms the previous assignments made to both the $^1H$ NMR and $^{13}C$ NMR spectra by analysis of the cross peak resonances.

### Distortionless Enhancement by Polarization Transfer (DEPT)

The one-dimensional DEPT spectra for ETC is shown in Figure 7. The data were collected using a spectral width of 31250 and 32768 complex points (acquisition time of 1s). DEPT is an application of $^{13}C$ NMR used to identify the presence of primary, secondary, tertiary, and quaternary carbons. There are 3 peaks indicative of primary carbons, 2 for positions 2 and 3 in the molecule and the other from TMS. Likewise, 1 secondary carbon in position 5, 2 tertiary carbons in positions 6 and 1, and 2 quaternary carbons from position 4 and the solvent.

### Conclusions

Because of the size and simple structure of ethyl trans-crotonate, proton assignments can be made by examining the fine structure and chemical shift values of the $^1H$ NMR spectra. This assignment can be further confirmed by the Gradient-Enhanced Correlation Spectroscopy (gCOSY) resonances. The $^{13}C$ assignments are given by transcribing the confirmed proton assignments to the $^1H$ projections of the Gradient-Enhanced Heteronuclear Multiple Quantum Coherence Spectroscopy (gHMQC) and identifying the carbon positions in the molecule. These carbon assignments can be examined more closely in the $^{13}C$ NMR spectra and confirmed even further by the Heteronuclear Multiple Bond Correlation (gHMBC) and the Distortionless Enhancement by Polarization Transfer (DEPT).

### References

