Problem R-98F (C₁₄H₂₀O₁₀)
270 MHz $^1$H NMR Spectrum in CDCl$_3$
Source: Paul Savage/Gellman (Reich digitized hard copy 11/19) g

Disappears with D$_2$O

D$_2$O added
**Problem R-98F** \((C_{14}H_{20}O_{10})\). In this problem you are asked to assign the proton signals and use this to determine the stereochemistry at carbons 1 and 4 of a sugar tetraacetate. You may use **first order** analysis throughout. Use the carbon numbering scheme shown on the structure in your answers. **For each part explain what the signals tell you about the structure of R-98F.**

(a) Assign the signal A in the NMR spectrum of **R-98F**.

(b) Analyze the multiplet B. Assign the protons. Draw a coupling tree on the spectrum.

(c) Analyze the multiplet C,D. Assign the protons. Draw a coupling tree on the spectrum.

(d) Analyze the multiplet E. Assign the protons. Draw a properly labeled coupling tree on the multiplet reproduced below. Note that the D\textsubscript{2}O spectrum has one part of the multiplet slightly shifted due to a medium effect. The signal F disappeared when D\textsubscript{2}O was added. Comment on the changes caused by the addition of D\textsubscript{2}O.

(e) Fill in the blanks on the structure below, label the structure with key coupling constants. Explain here (if you have not already done so above) how you made the stereochemical assignment at C-1 and C-4.
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PLT ex-2-1998-g.plt
**Problem R-98F** \((C_{14}H_{20}O_{10})\). In this problem you are asked to assign the proton signals and use this to determine the stereochemistry at carbons 1 and 4 of a sugar tetraacetate. You may use *first order* analysis throughout. Use the carbon numbering scheme shown on the structure in your answers. For each part explain what the signals tell you about the structure of R-98F.

(a) Assign the signal A in the NMR spectrum of R-98F.

\[ \delta = 5.68, \text{d, } J = 8 \text{ Hz} \]  

This has to be the anomic proton \( H^1 \) from the chemical shifts and only one \( J \). The size of the coupling means it is an axial proton, with an axial proton at \( C^2 \) as well.

(b) Analyze the multiplet B. Assign the protons. Draw a coupling tree on the spectrum.

\[ \delta = 5.03, \text{dd, } J = 9, 8 \text{ Hz} \]  \( H^2 \)  
\[ \delta = 5.10, \text{dd, } J = 9, 8 \text{ Hz} \]  \( H^3 \)  

The downfield chemical shift means these must be \( \alpha \)-acetoxyl protons \( H^2 \) and \( H^3 \). Each has two large \( J \) so the protons are axial, and have axial protons on both sides.

(c) Analyze the multiplet C,D. Assign the protons. Draw a coupling tree on the spectrum.

\[ \delta = 4.40, \text{dd, } J = 11, 4 \text{ Hz} \]  \( C \)  
\[ \delta = 4.34, \text{dd, } J = 11, 3 \text{ Hz} \]  \( D \)  

These are the diastereotopic protons at \( C^6 \), coupled to each other, and to \( H^5 \).  
\[ J_{66} = 11 \text{ Hz}, J_{56} = 3 \text{ Hz, } J_{56'} = 4 \text{ Hz} \]

(d) Analyze the multiplet E. Assign the protons. Draw a properly labeled coupling tree on the multiplet reproduced below. Note that the \( D_2O \) spectrum has one part of the multiplet slightly shifted due to a medium effect. The signal \( F \) disappeared when \( D_2O \) was added. Comment on the changes caused by the addition of \( D_2O \).

\[ \delta = 3.43, \text{d, } J = 5 \text{ Hz} \]  

When \( D_2O \) is added, the signal \( F \) disappears, and \( H^4 \) loses one coupling.

\( E \) are the protons at \( C^4 \) and \( C^5 \).

\[ \delta = 3.56, \text{ddd, } J = 10, 9, 5 \text{ Hz} \]  \( H^4 \)  
\[ \delta = 3.64, \text{ddd, } J = 10, 5, 2 \text{ Hz} \]  \( H^5 \)  

\( H^4 \) and \( H^5 \) are also both axial protons.

(e) Fill in the blanks on the structure below, label the structure with key coupling constants. Explain here (if you have not already done so above) how you made the stereochemical assignment at C-1 and C-4.

\[ \delta \text{ calc: Base: 1.20, } \alpha-OAc: 2.95, \beta-OR: 0.15, \text{ Obs: 4.30} \]
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\(J_{32} = 9 \text{ Hz} \)
\(J_{34} = 8 \text{ Hz} \)
\(J_{23} = 9 \text{ Hz} \)
\(J_{21} = 8 \text{ Hz} \)
\(J_{65} = 4 \text{ Hz} \)
\(J_{66} = 11 \text{ Hz} \)

\(\text{H}^1\)
\(\text{H}^2\)
\(\text{H}^3\)
\(\text{H}^4\)
\(\text{H}^5\)
\(\text{H}^6\)

\(\text{D}_2\text{O} \text{ added}\)