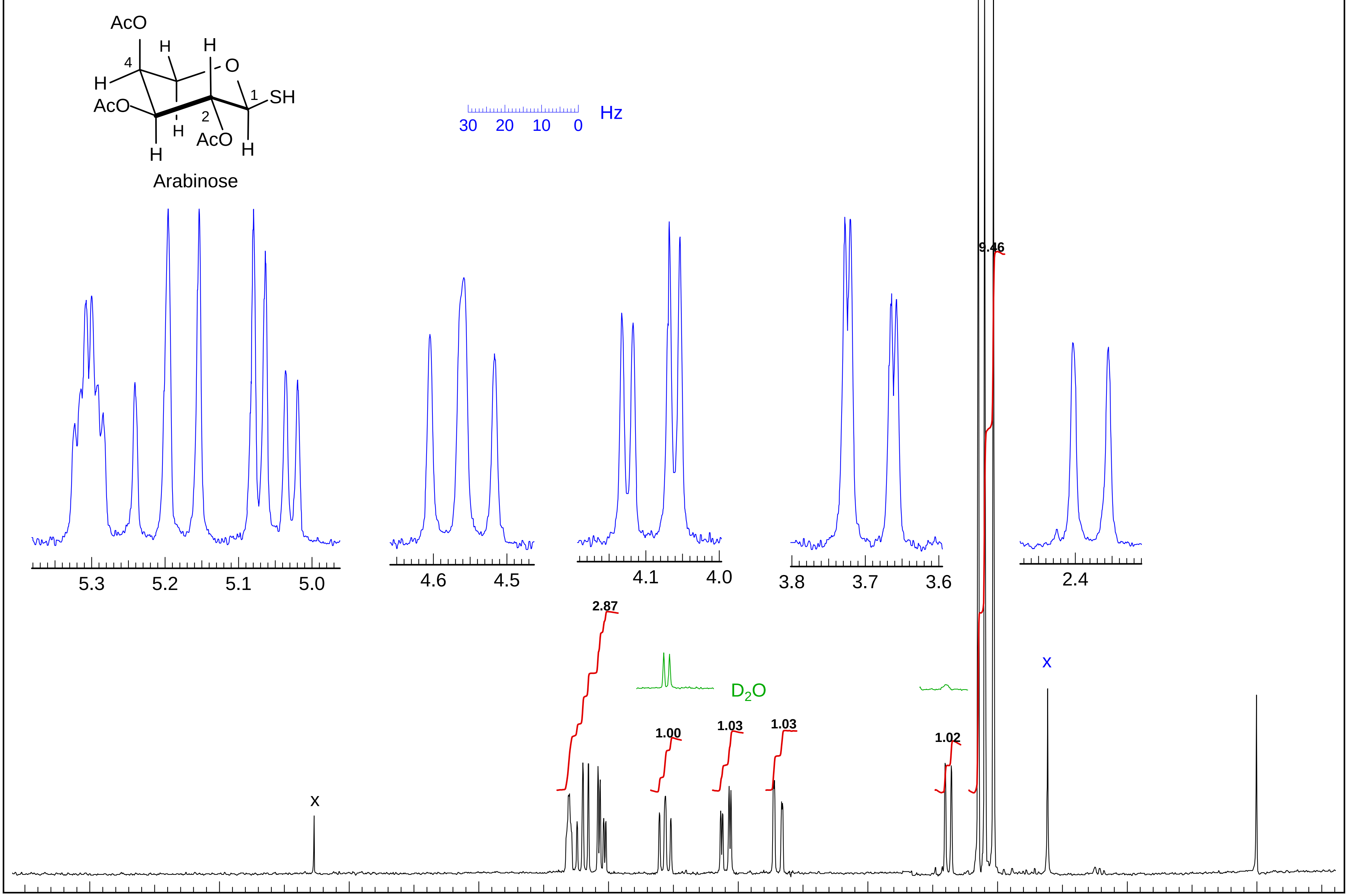
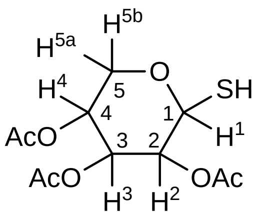
Problem R-00G ($C_{11}H_{16}O_7S$)
200 MHz ^{1}H NMR Spectrum in $CDCl_3$
Source: Paul Savage/Gellman (Reich digitized hard copy 11-20) g

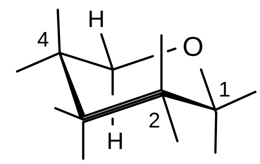


PLT ex-2-2000-gq.plt

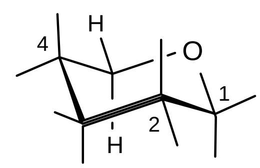
Problem R-00G ($C_{11}H_{16}O_7S$). In this problem you are given the gross structure of a sugar thiol. Your task is to determine the stereochemistry of the four substituents (three OAc, one SH) around the ring.

(a) When the sample is shaken with D_2O the doublet at δ 2.4 disappears and the signal at δ 4.6 changes to a doublet. What information does this provide about the structure of **R-00G**? Add appropriate groups to the drawing to the right below, and enter the data into part (d).

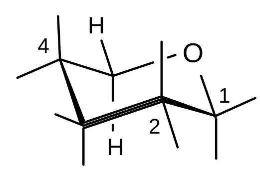




(b) Assign the protons which appear at δ 3.6 to δ 4.2. Use the numbering on the structure. What does the multiplicity of these signals tell you about the structure? Add appropriate groups to the drawing below, and enter the data into part (d).



(c) Interpret the signals at δ 5.0 to δ 5.4. Fill in the complete structure of **R-00G** below.



(d) Summarize your analysis by entering the data for each of the protons in the compound. Use the format: δ 9.3 (dt, J = 14, 6 Hz). You may use first-order analysis.

H-1 ________________________________

H-2 ________________________________

H-3 ________________________________

H-4 ________________________________

H-5a ________________________________

H-5b ________________________________

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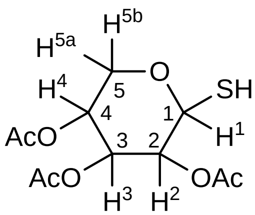
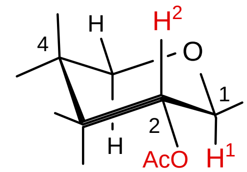


The signal at δ 2.4 is the S-H proton (exchanged with D_2O)

Signal at δ 4.6 has to be the anomeric proton H^1, d, J = 9 Hz

Thus H^1 and H^2 must both be axial



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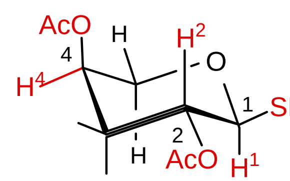
5

From the chemical shift, the protons at δ 3.7 and 4.1 are H^{5a} and H^{5b}. Since both show only small coupling, the proton at H^4 must be equatorial.

We might guess that 5e is the one at 3.7 since it shows the smaller coupling to H^4 (J_{ee} is usually smaller than J_{ae}). Note that a chemical shift argument would give the opposite assignment (eq downfield of axial)



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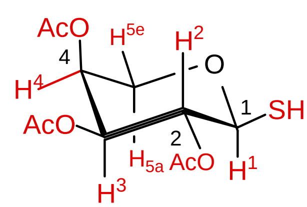
The td (J=3,2) at 5.31 has to be the equatorial proton at H^4 - 3 small couplings to protons at H^5 and H^3

The two remaining protons (H^2 and H^3) at δ 5.06 and 5.2 are coupled to each other by a large (J_{aa}) coupling (leaning), so both must be axial. H^3 has one small coupling, so it is at 5.06.

We already knew H^2 was axial from part (a)



(d) Summarize your analysis by entering the data for each of the protons in the compound. Use the format: δ 9.3 (dt, J = 14, 6 Hz). You may use first-order analysis.

H-1 δ 4.55, dd, J = 11, 10 Hz

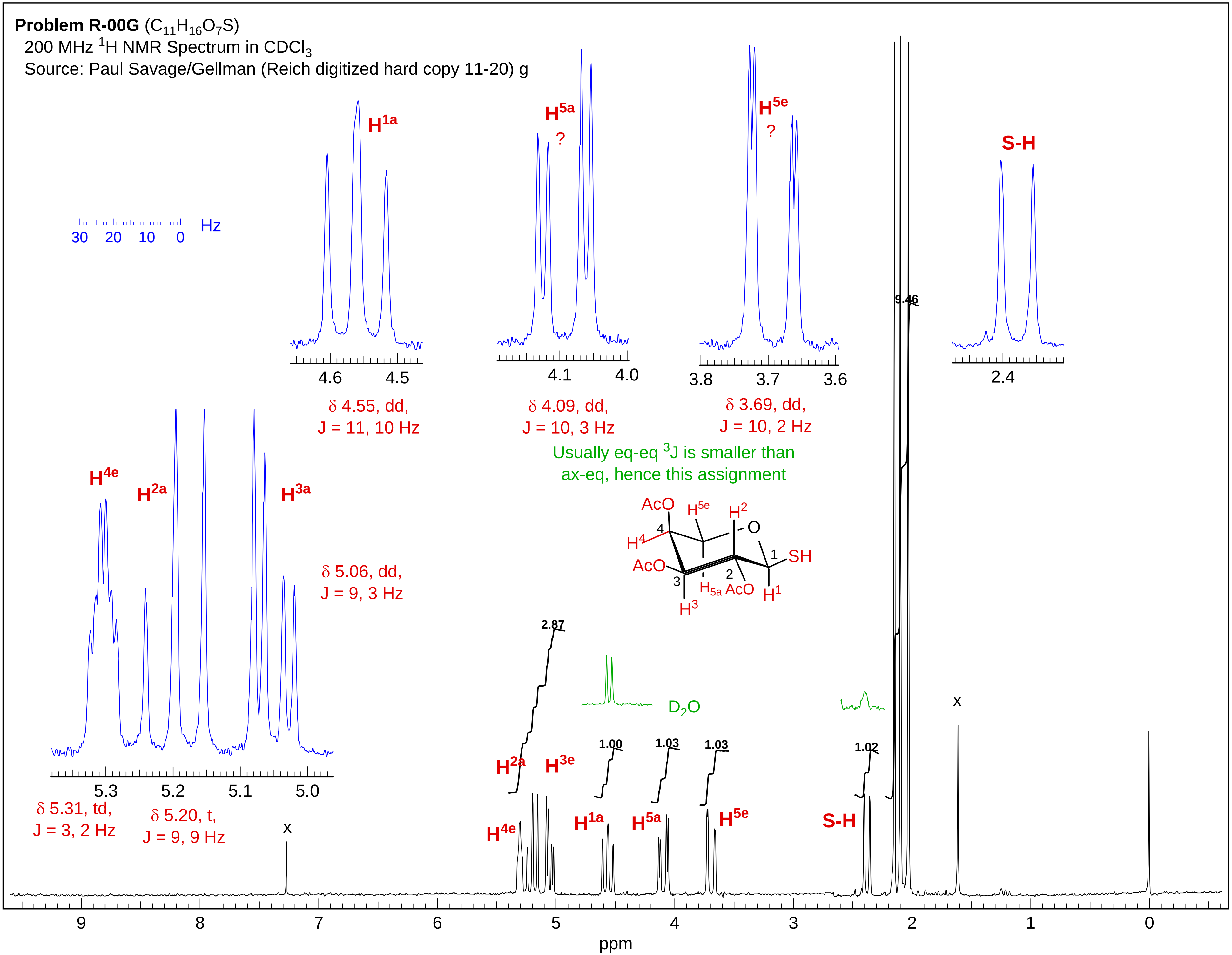
H-2 δ 5.20, t , J = 9, 9 Hz

10 H-3 δ 5.06, dd, J = 9, 3 Hz

H-4 δ 5.31, td, J = 3, 2 Hz

H-5a δ 4.09, dd, J = 10, 3 Hz

H-5b δ 3.69, dd, J = 10, 2 Hz



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