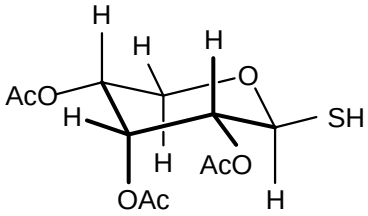
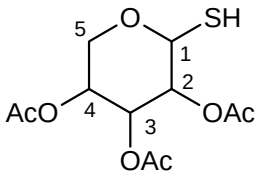
Problem R-13C ($C_{11}H_{16}O_7S$)

270 MHz ^1H NMR spectrum in $CDCl_3$

Source: Paul Savage/Gellman (Reich digitized hard copy) 11/32 g





Ribose

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20

Problem R-13C ($C_{11}H_{16}O_7S$). You are given the structure of a pentose thiol triacetate and asked to determine the relative stereochemistry and conformation from the 270 MHz ^1H NMR spectrum presented on the next page.

(a) Analyze the individual sets of signals and show coupling constants in the standard format. When you have completed the analysis, <u>assign the individual protons</u> (e.g., H_{5ax}). Use the numbering system given on the structure in part (b).

δ 3.75

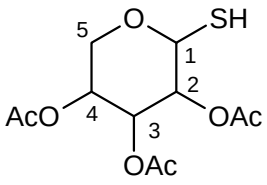
δ 4.05

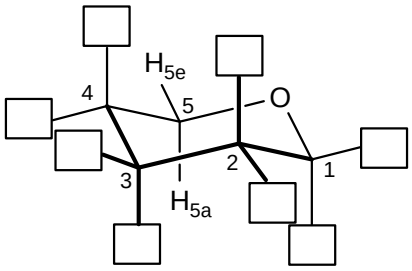
δ 4.95

δ 5.07

δ 5.55

(b) Determine the stereochemistry of **R-05K**. Place the appropriate substituents in each of the boxes on the structure below.





(c) Briefly describe how you made the assignment at C-4.

Problem R-13C. You are given the structure of a pentose thiol triacetate and asked to determine the relative stereochemistry and conformation from the 270 MHz ^{1}H NMR spectrum presented on the next page.

(a) Analyze the sets of signals and show coupling constants in the standard format. When you have completed the analysis, assign the individual protons (e.g., H_{5ax}). Use the numbering system given on the structure in part (b).

2 δ 3.75 dd, J = 12, 9 Hz — This must be H^{5a} from the chemical shift - coupled gem and ax-ax. Thus H^4 must be axial.

2 δ 4.05 ddd, J = 11.5, 4.5, 1 Hz — This must be H^{5e} - coupled gem and eq-ax. There is also a W-coupling to the equatorial H^3

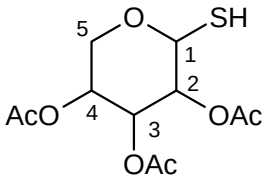
4 δ 4.95 dd, 8, 2.5 - H^2
br d, 8 - H^1 — This is an AB pattern, one half is coupled to an X proton by ca 2.5 Hz, the other half is broadened.
These must be the H^1 and H^2 protons, the H^1 is broadened by exchange of the SH (which is a broad singlet at δ 2.17). The 8 Hz coupling between H^1 and H^2 means both protons are axial. The small coupling (2.5 Hz) of H^2 to H^3 means H^3 is equatorial

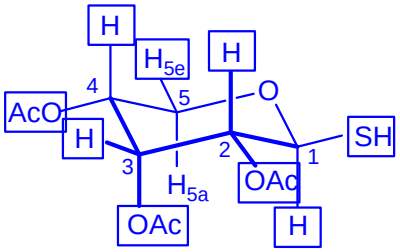
2 δ 5.07 ddd, J = 8.5, 4.5, 3 — This is the proton at H^4, coupled to the axial proton at C^5 (9 Hz) and to the eq protons at C^5 and C^3. Thus H^3 must be equatorial.

2 δ 5.55 td, 2.5, 1 — This is the equatorial H^3 proton, coupled twice eq-ax (2.5 Hz) to H^4 and H^2. There is a small W coupling to H^{5e}.

(b) Determine the stereochemistry of **R-05K**. Place the appropriate substituents in each of the boxes on the structure below.

5





(c) Briefly describe how you made the assignment at C-4.

3 H^{5a} and H^{5e} can be assigned from their chemical shifts (most upfield of the ring protons) and coupling patterns. H^{5a} shows, in addition to the 12 Hz gem coupling, a 9 Hz vicinal coupling, which means H^4 must be axial. H^4 can be assigned from the three couplings, two of which are to the H^5 protons.

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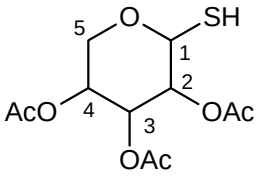
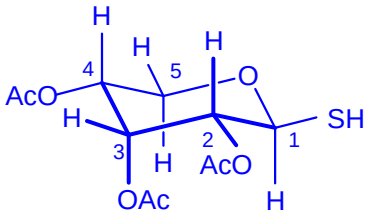
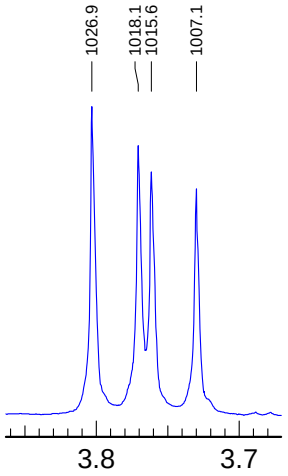




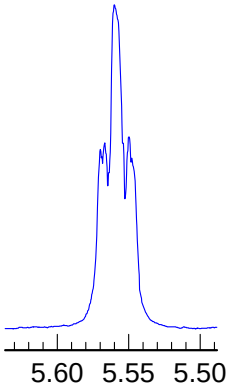
H^{5a}

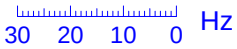
dd, J = 11.3, 8.7 Hz



H^3

dt, 2.5, 1





H^1

br d, 8

H^4

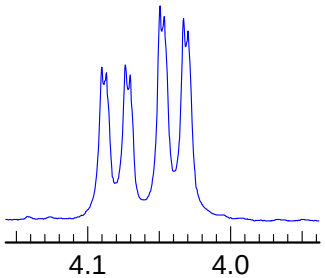
ddd, J = 8.5, 4.5, 3

H^2

dd, 8, 2.5

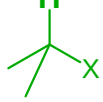
H^{5e}

dd, J = 11.5, 4.5, 1 Hz



Curphy-Morrison:

X	δ_{calc}
SH	1.3
O-Alkyl	2.10
O-Ac	3.45



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