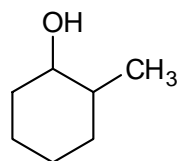**In-Class Exercise Solutions:**
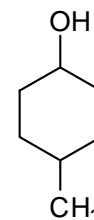**Heteronuclear Correlations in HMQC**

a. Of the structures at right, we can
immediately rule out 4-
methylcyclohexanol because it is
symmetric, and should give only 8
^{1}H resonances and 5 ^{13}C
resonances. Our spectra have (at
least) 11 ^{1}H resonances and 7 ^{13}C
resonances, so our molecule can't
be symmetric.

OH
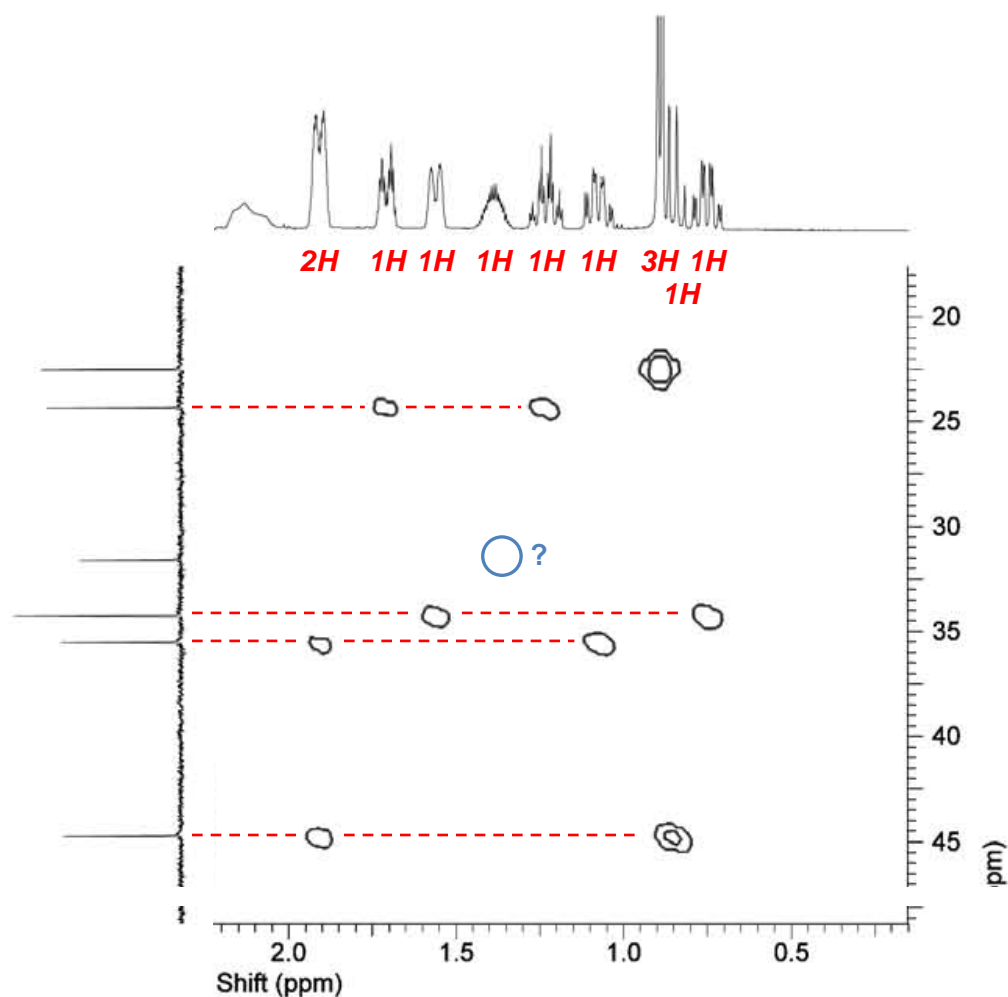CH$_3$

2-methyl-
cyclohexanol

OH

CH$_3$

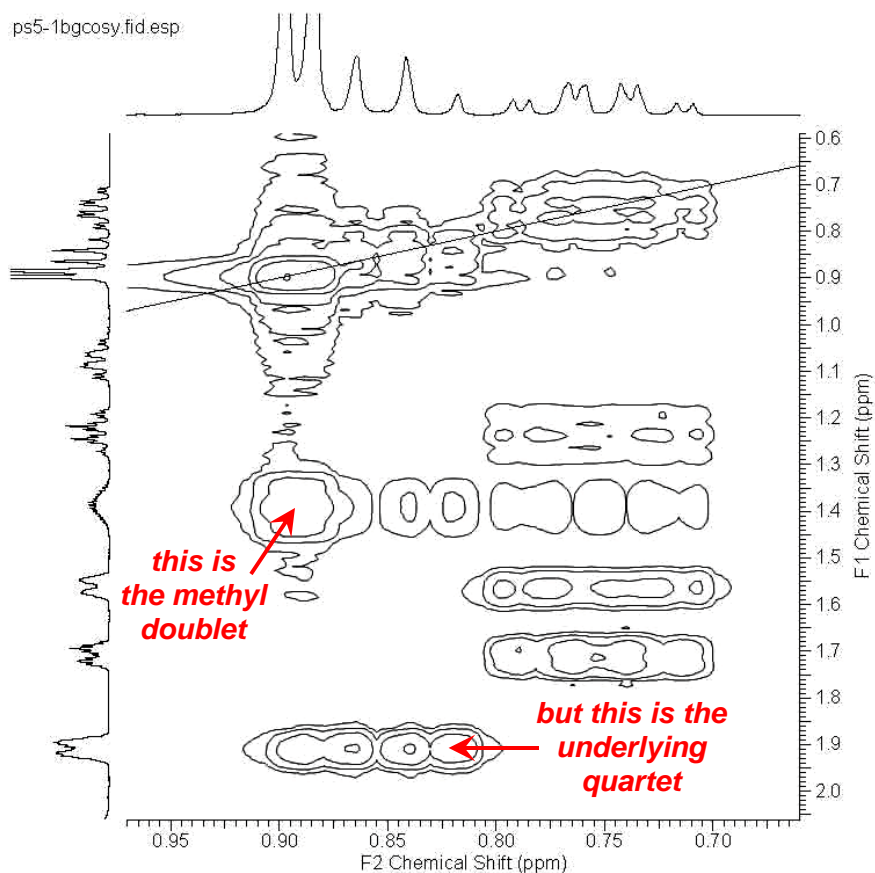3-methyl-
cyclohexanol

OH

CH$_3$
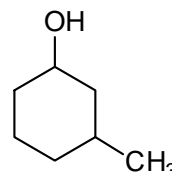
4-methyl-
cyclohexanol

The ^{1}H and COSY spectra look pretty complicated, which is what we might expect
for a molecule with lots of inequivalent, coupled protons. So looking first at the
HMQC, we can already identify proton resonances that come from geminal pairs of
H's (attached to the same carbon).

A couple of things that we learn from this spectrum:

- The 2H signal at δ = 1.9 ppm comes from two protons attached to *different* carbons.

- The methyl group (δ = 0.9 ppm) and the proton α to the alcohol group (δ = 3.5 ppm) stand out very clearly.

- The broad ^{1}H multiplet at δ = 1.4 ppm and the ^{13}C at δ = 32 ppm are unusual in that they show no correlation peaks in the HMQC. We know that this cannot be true; all carbons in our candidate structures have at least one attached proton. My guess is that these two nuclei are attached, and that for some reason the correlation peak wasn't visible.

The methyl group should be coupled to only one vicinal proton, no matter what structure we suggest. In the COSY, that proton looks like the one at δ = 1.4 ppm. I have to admit, it's a little more clear if we expand that part of the spectrum:

I think you could see this in the full expansion of the spectrum too, but this makes it a little easier to see.

That α-methyl proton, which has no geminal partners, has a number of vicinal neighbors. It's not exactly clear how many, but it is not vicinal to the α-alcohol proton; the α-alcohol proton (H_1) is coupled to the underlying quartet, not the methyl doublet. That means the product must be 3-methylcyclohexanol (and we can call the α-methyl proton H_3). H_1 and H_3 share vicinal coupling partners H_{2a} and H_{2b}, however, at δ = 1.9 and 0.85 ppm. H_1 is also coupled to the geminal pair H_{6a} and H_{6b} at δ = 1.9 and 1.1 ppm.

We can't really use the H_{6a} resonance at δ = 1.9 ppm for any crosspeak analysis because it overlaps with H_{2a}, But H_{6b} helps identify H_{5a} and H_{5b} at δ = 1.7 and 1.2 ppm. That leaves us with δ = 1.6 and 0.8 for H_{4a} and H_{4b}. So,

proton	δ (ppm)
H_1	3.52
H_{2a}	1.90
H_{2b}	0.85
H_3	1.39
H_{4a}	1.56
H_{4b}	0.75
H_{5a}	1.71
H_{5b}	1.23
H_{6a}	1.90
H_{6b}	1.07
$-CH_3$	0.89
$-OH$	2.15

carbon	δ (ppm)
C_1	70.8
C_2	44.7
C_3	31.6
C_4	34.3
C_5	24.3
C_6	35.5
$-CH_3$	22.5

b. I think the key to this part of the problem was the δ = 0.85 ppm quartet for H_{2b}. This proton has three coupled partners— H_1, H_3, and H_{2a}—all with the same coupling constant of ~11.4 Hz. That's a little large for a vicinal ^3J, and indicates that the dihedral angles between H_1 and H_{2b} and between H_3, and H_{2b} must be large and equal. (Or small and equal, but that can't really happen in a chair cyclohexane.) The only geometry that supports this would be a *cis*-disubstituted chair.