School of Chemical Biology & Biotechnology, Peking University

NMR of Organic Compounds

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^{1}H-NMR Spectrums

- The Factors of Chemical Shift in ^{1}H-NMR
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  - *ortho*-Coupling (H-C-C-H , 0~18 Hz)
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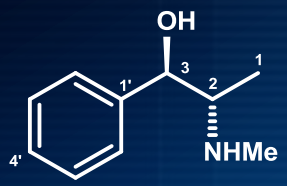
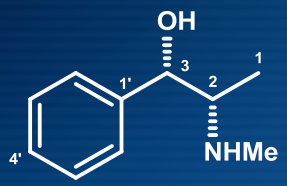
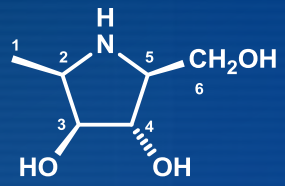
^{1}H-NMR Spectrums



1 ephedrine



2 *d*-pseudoephedrine



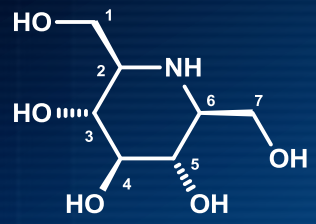
3 2,5-imino-1,2,5-trideoxy-D-glucitol

4 2,5-dideoxy-2,5-imino-D-fucitol

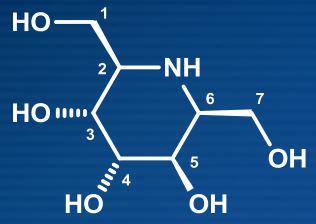
H	1	2
1	0.84 d (6.6)	0.92 d (6.4)
2	2.83 m	2.82 m
3	4.80 d (3.8)	4.19 d (8.0)
Ar-H	7.20~8.05 m (5H)	7.10~7.50 m (5H)
OH, NH	1.90~2.30 br (NH)	2.50~2.70 br (2H)
N-Me	2.51 s	2.42 s

H	3	4
1	1.16 d (6.8)	1.19 d (6.8)
2	3.32 dq (4.4, 6.8)	3.53 dq (3.7, 6.8)
3	3.96 dd (2.2, 4.4)	4.02 dd (2.0, 3.7)
4	3.88 dd (2.2, 4.9)	4.27 dd (2.0, 4.6)
5	3.01 ddd (4.9, 4.9, 6.4)	3.60 ddd (4.6, 6.4, 7.1)
6	3.68 dd (6.4, 11.5) 3.76 dd (4.9, 11.5)	3.69 dd (7.1, 11.2) 3.81 dd (6.4, 11.2)

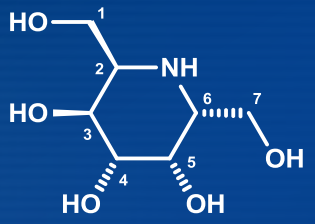
^{1}H-NMR Spectrums



5 β-homonojirimycin



6 β-4,5-di-*epi*-homonojirimycin

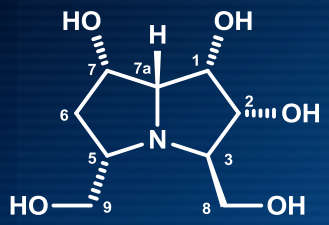


7 α-3,4-di-*epi*-homonojirimycin

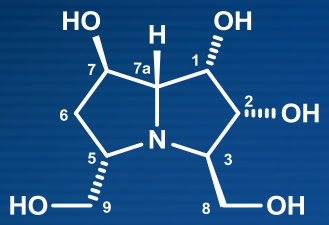
H	5	6	7
1	3.64 dd (11.5, 6.6) 3.89 dd (11.5, 2.9)	3.72 dd (11.7, 5.4) 3.82 dd (11.7, 3.2)	4.21 dd (10.6, 7.7) 4.30 dd (10.6, 4.8)
2	2.66 ddd (9.9, 6.6, 2.9)	2.90 ddd (10.5, 5.4, 3.2)	3.87 ddd (7.7, 6.2, 4.8)
3	3.25 dd (9.9, 9.2)	3.78 dd (10.5, 3.2)	4.26 dd (6.2, 3.3)
4	3.39 t (9.2)	4.01 dd (3.9, 3.2)	4.39 t (3.3)
5	3.25 dd (9.9, 9.2)	3.93 dd (3.9, 1.7)	4.48 dd (4.0, 3.3)
6	2.66 ddd (9.9, 6.6, 2.9)	3.09 dt (6.6, 1.7)	3.65 ddd (8.1, 4.8, 4.0)
7	3.64 dd (11.5, 6.6) 3.89 dd (11.5, 2.9)	3.64 dd (11.2, 6.6) 3.68 dd (11.2, 6.6)	4.42 dd (11.0, 4.8) 4.61 dd (11.0, 8.1)

^{1}H-NMR Spectrums

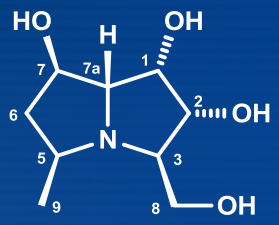
Review Report



8 hyacinthacine C_2



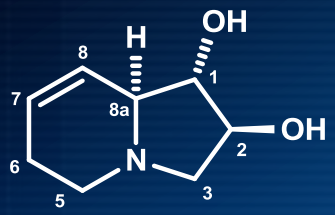
9 hyacinthacine C_3



10 hyacinthacine B_7

H	8	9	10
1	4.16 t (4.4)	4.32 t (4.4)	4.35 t (4.4)
2	3.85 dd (4.4, 7.6)	4.04 dq (4.4, 9.5)	3.97 dd (4.4, 7.6)
3	3.33 ddd (5.0, 5.7, 7.6)	3.50 m	3.29 ddd (7.6, 5.5, 3.5)
5	3.24 m	3.84 (ov)	3.22 m
6	1.78 m, 2.03 m	1.93 m, 2.07 m	1.68 m, 2.16 m
7	4.40 m	4.56 ddd (2.5, 4.4, 2.5)	4.50 m
7a	3.39 dd (4.4, 6.9)	3.85 (ov)	3.45 dd (4.4, 7.6)
8	3.54 dd (5.7, 12.0) 3.61 dd (5.0, 12.0)	3.69 dd (3.2, 12.6) 3.85 dd (3.2, 12.6)	3.57 dd (3.5, 11.5) 3.63 dd (3.5, 11.5)
9	3.66 dd (5.0 12.0) 3.85 dd (6.9, 12.0)	3.79 dd (6.2, 12.0) 3.84 (ov)	1.25 d (7.0)

^{1}H-NMR Spectrums



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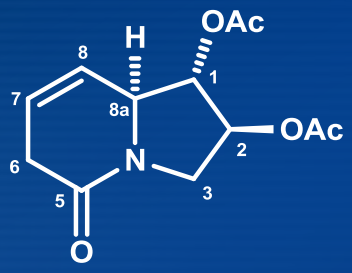
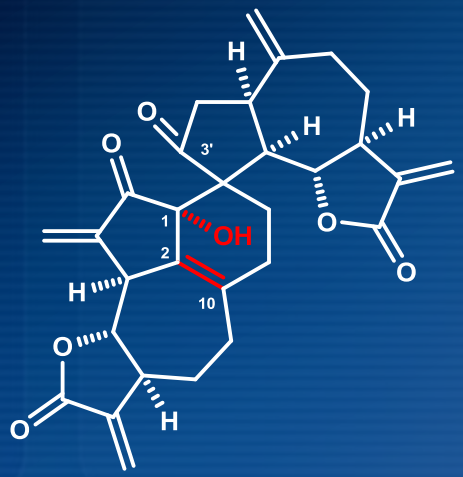


13

H	11	12	13
1	3.72 dd (6.8, 4.5)	3.67 m	5.07 dd (7.8, 4.3)
2	4.06 dt (7.2, 4.9)	4.18 dt (8.0, 6.4)	5.22 ddd (7.8, 3.9, 3.8)
3	2.71 dd (11.1, 4.9) 2.98 dd (11.1, 7.2)	3.39 dd (12.5, 6.4) 3.67 m	3.67 dd (13.7, 7.0) 4.09 dd (13.4, 3.4)
5	2.61 ddd (12.3, 9.0, 5.1) 2.80 ddd (12.3, 5.7, 3.9)	-	-
6	1.95 m, 2.15 m	2.80 m, 2.92 m	2.97 m
7	5.81 ddq (10.2, 1.0, 2.9)	5.82 dddd (12.5, 5.0, 2.5, 2.3)	5.96 dq (10.1, 1.8)
8	5.73 dq (10.2, 2.0)	5.93 m	5.88 m
8a	3.05 dq (7.0, 2.5)	3.97 m	4.13 m
OAc	-	-	2.14 s, 2.06 s

^{1}H-NMR Spectrums



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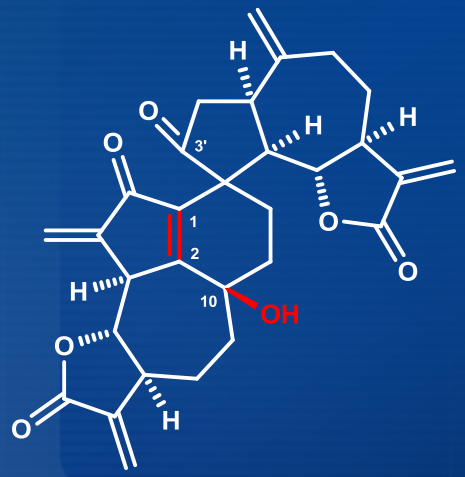
Proposed Structure of Gochnatiolide B
(H. Robinson, *et al.*
phytochemistry, **1983**, *22*, 191.)



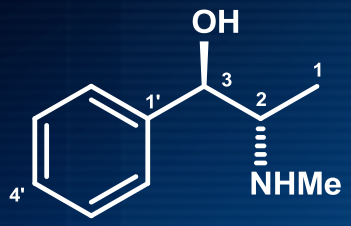
15

Revised Structure of Gochnatiolide B
(X. G. Lei, *et al.*
J. Am. Chem. Soc., **2012**, *134*, 12414.)

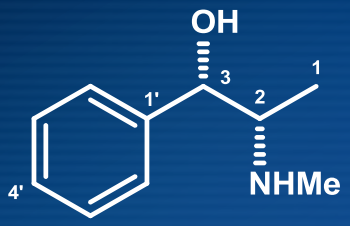
^{13}C-NMR Spectrums

- The Factors of Chemical Shift in ^{13}C-NMR
  - Hybridization (δ: $sp^2 > sp > sp^3$)
  - Inductive Effect (δ: α-C $\uparrow$, γ-C $\downarrow$)
  - Steric Effect (δ: *a*-Me $\rightarrow$ C_γ $\uparrow$)
  - Electrical Effect
  - Conjugative Effect
  - Magnetic Unequivalent Effect
  - Solvent Effect
- Types of ^{13}C-NMR
  - ^{1}H Complete Decoupling
  - DEPT
  - APT (positive signal: C & CH_2, negative signal: CH & CH_3)

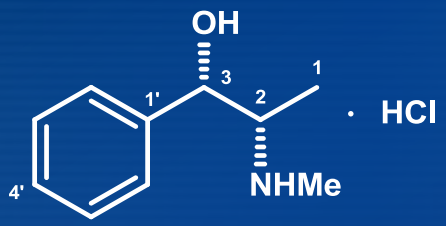
^{13}C-NMR Spectrums



1 ephedrine



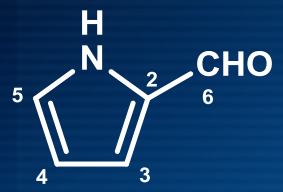
2 *d*-pseudoephedrine



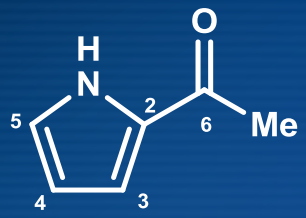
16 pseudoephedrine hydrochloride

C	1	2	16
1	10.6	12.8	12.5
2	60.8	60.5	62.7
3	72.1	75.5	74.2
N-Me	31.7	30.9	33.5
1’	139.4	140.5	141.2
2’, 6’	126.9	127.8	131.6
3’, 5’	129.6	129.8	128.9
4’	129.2	129.8	131.2

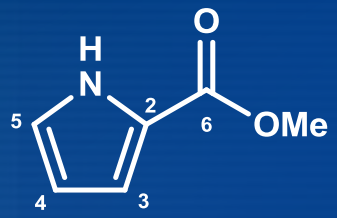
^{13}C-NMR Spectrums



17
2-pyrrolaldehyde



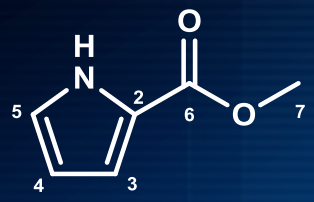
18
2-acetylpyrrol



19
α-carbomethoxypyrrol

C	17	18	19
2	132.1	131.6	122.0
3	121.6	117.1	115.1
4	110.8	110.0	109.8
5	126.8	125.1	122.9
6	178.8	187.7	161.4
Me	-	25.3	-
OMe	-	-	51.2

^{13}C-NMR Spectrums



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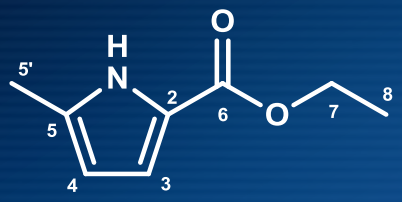

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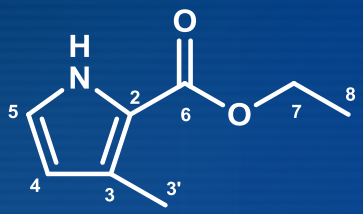

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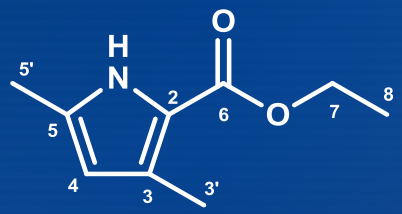
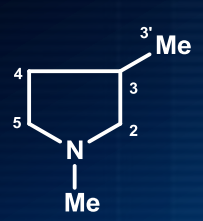


22

C	19	20	21	22
2	122.0	120.8	119.0	117.4
3	115.1	115.8	127.4	128.5
4	109.8	108.4	112.1	110.9
5	122.9	135.4	121.2	132.4
6	161.4	161.2	161.2	161.5
7	51.2	59.8	59.6	59.5
8	-	14.4	14.4	14.5
3’	-	-	12.7	12.9
5’	-	12.9	-	12.9

^{13}C-NMR Spectrums



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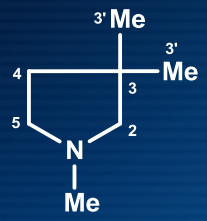
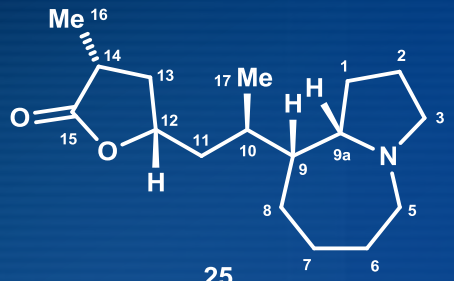


24

C	23	24
2	64.4	71.0
3	32.5	38.3
4	33.3	40.7
5	56.3	56.6
N-Me	42.4	42.7
3'-Me	20.5	29.8



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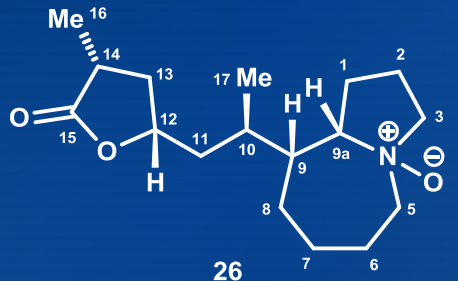
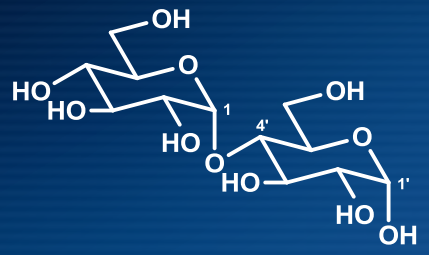


26

C	25	26
1	28.1	25.0
2	23.8	19.3
3	54.3	71.0
5	52.3	67.2
6	25.9	20.7
7	27.7	25.2
8	28.2	25.4
9	45.9	35.8
9a	64.8	81.6
…	…	…

^{13}C-NMR Spectrums



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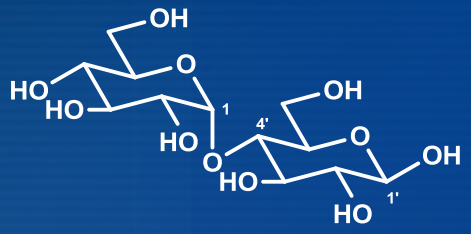

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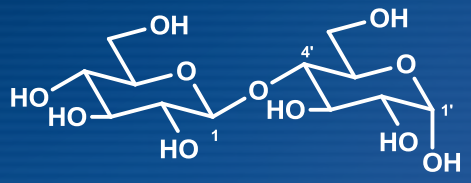

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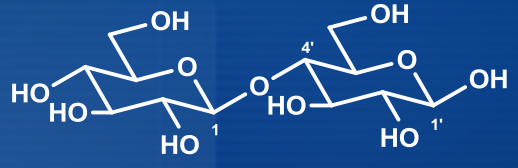
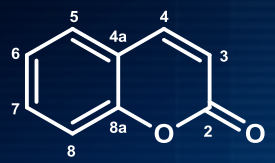


30

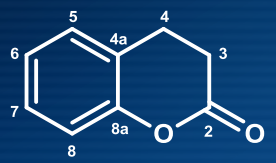
C	27	28	29	30
1	100.7	100.7	103.6	103.6
1’	92.8	96.8	92.9	96.8

^{13}C-NMR Spectrums

Review Report



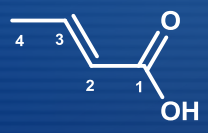
31 coumarin



32 dihydrocoumarin

C	23	24
2	159.6	177.0
3	116.0	34.5
4	143.9	24.8
…	…	…

C	33	34	35
1	169.3	164.3	163.8
2	122.8	122.3	120.6
3	146.0	134.4	132.8
4	17.3	77.0	71.8
5	-	81.1	85.9
6	-	3.2	59.1
7	-	-	72.3
8	-	-	65.2
9	-	-	80.9
10	-	-	3.6
OMe	-	52.2	50.9



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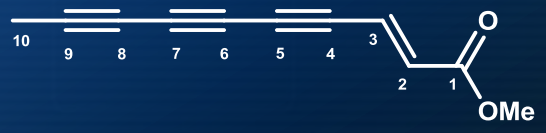
34



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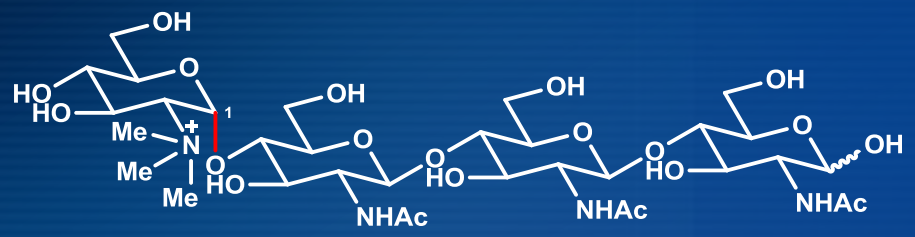
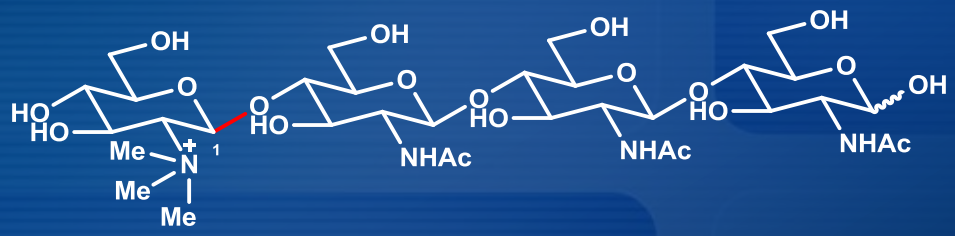
^{13}C-NMR Spectrums



Proposed Structure of TMG-chitotrimycin ($\delta(C_1)$: 94.4)
(H. J. Kanzaki, *et al.* J. Am. Chem. Soc., **2008**, *130*, 4146.)



Revised Structure of TMG-chitotrimycin ($\delta(C_1)$: 95.6)
(B. Yu, *et al.* J. Am. Chem. Soc., **2009**, *131*, 12076.)

1D vs. 2D NOESY

- A single 2D experiment gives all NOE information simultaneously whereas 1D experiments provide NOEs one at a time.
- A standard 2D NOESY often requires a minimum of 1.5 hours.
- A single 1D selective NOESY spectrum only requires 2 minutes.

NOE Spectrums

- 1D NOESY
  - MW < 600
  - Sample is concentrated
  - Only interested in one or two NOEs
  - The peaks to be irradiated are well-separated
- 2D NOESY
  - MW < 600
  - When MW > 1200, may resulting interpretation errors
- 2D ROESY
  - 600 < MW < 1200
  - When MW > 1200, ROESY is less sensitive

Sample Preparation (freeze-pump-thaw method)

(Dissolved O_2 or other paramagnetic species such as Cu^{2+} can reduce or completely quench the NOE.)

- Freeze the sample in liquid N_2 or CO_2 / acetone.
- Evacuate the space above the solution.
- Turn off vacuum but keep sample isolated and allow to thaw. As it thaws, bubbling should be noticed.
- Repeat several times (3~4 times).
- Backfill with N_2.

Review Report

Thank You !

Dr. Hao Jiang

Nov. 05th, 2012