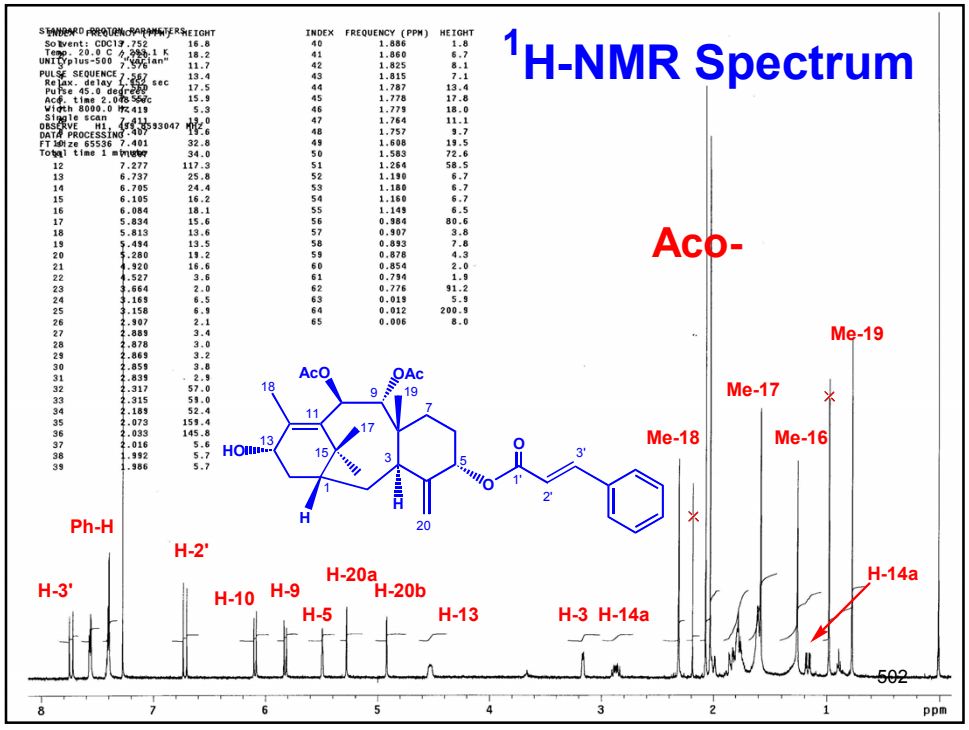
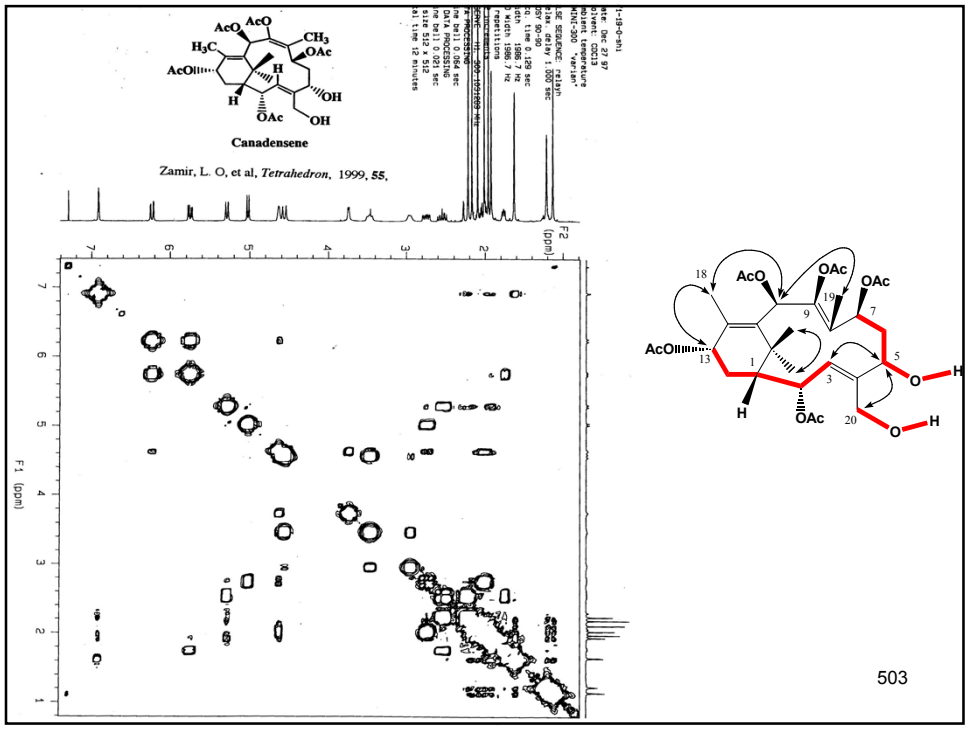
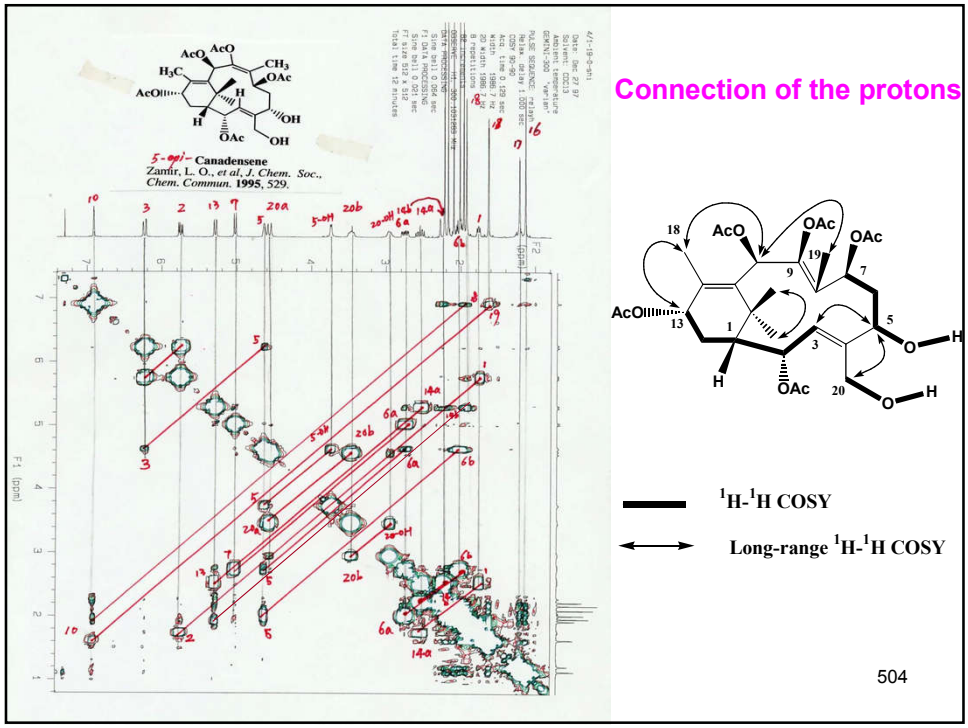
^{1}H-NMR Examples

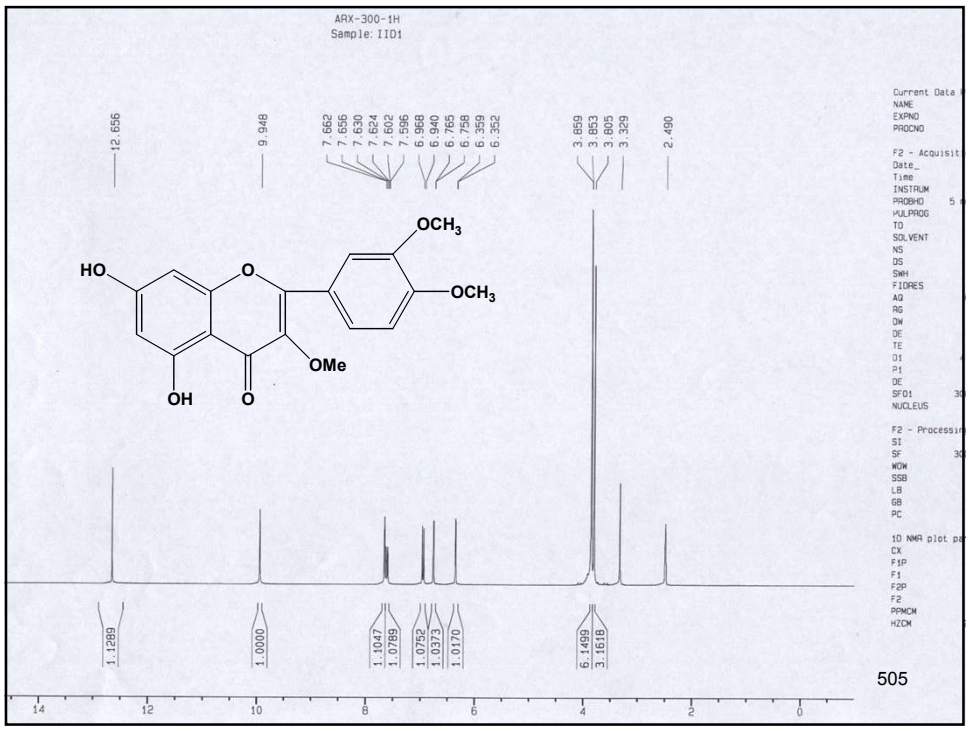
501

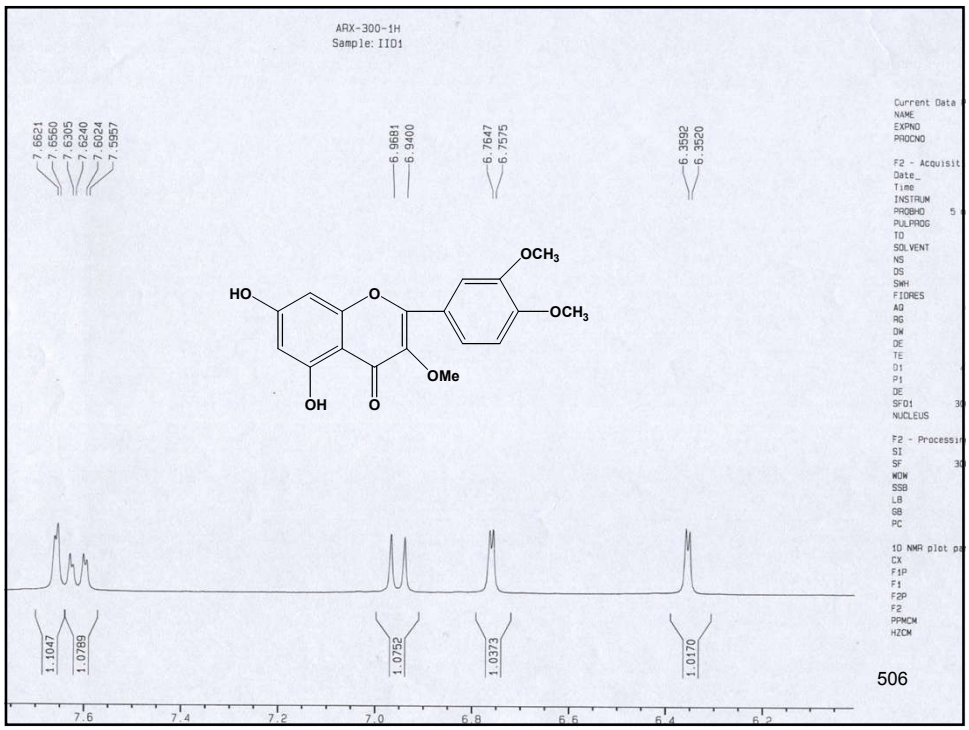


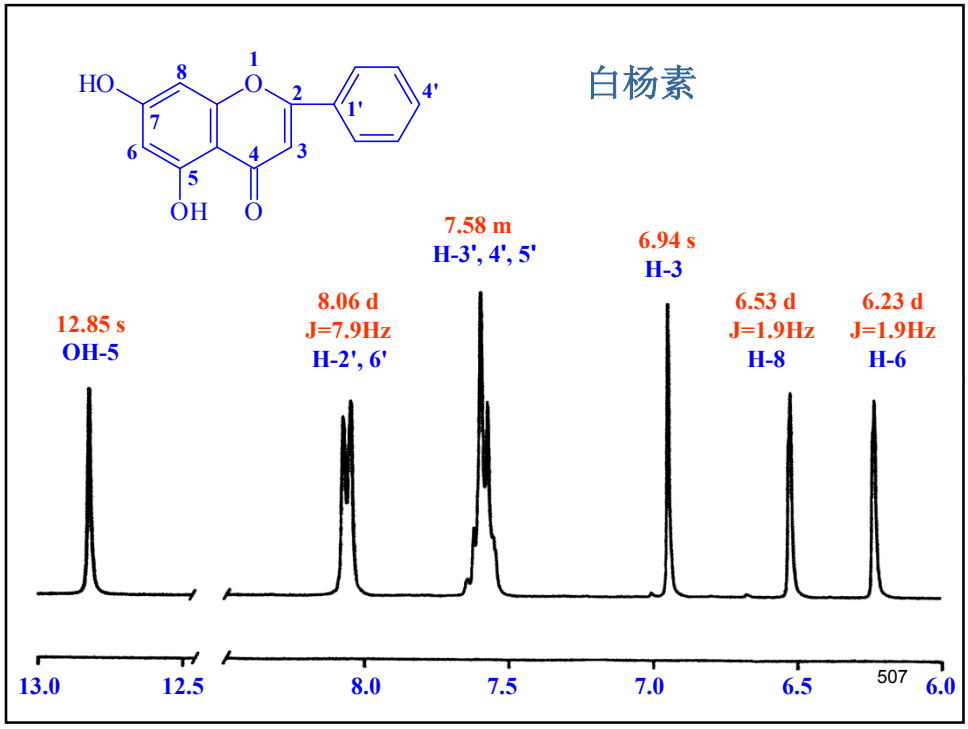
502

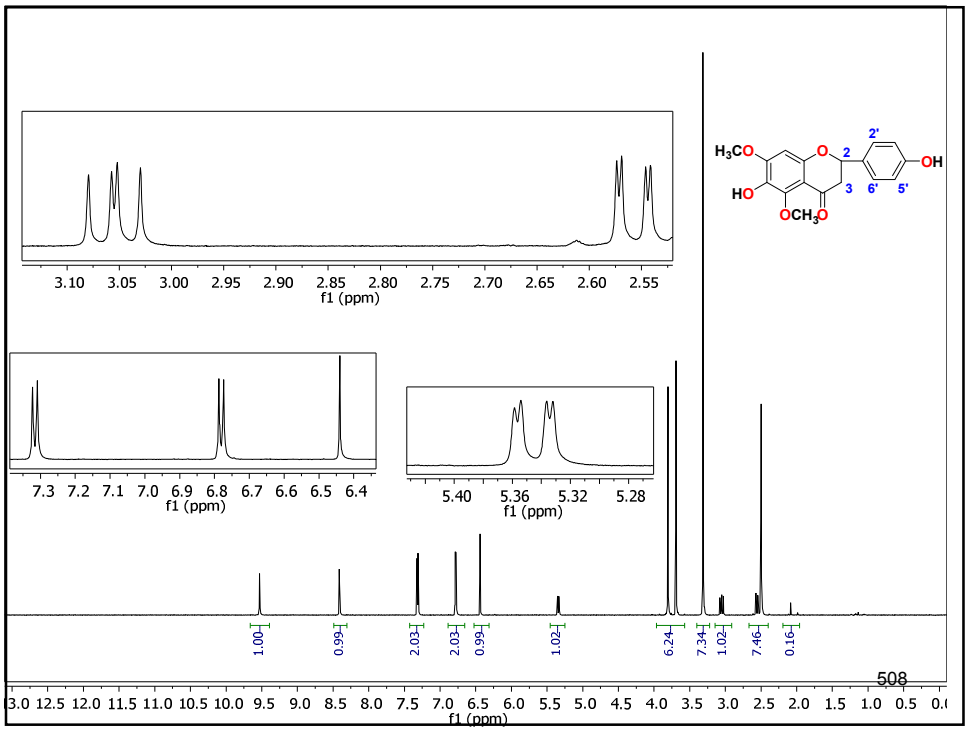

Canadensene
Zamir, L. O, et al, Tetrahedron, 1999, 55,
F2 (ppm)
F1 (ppm)
503

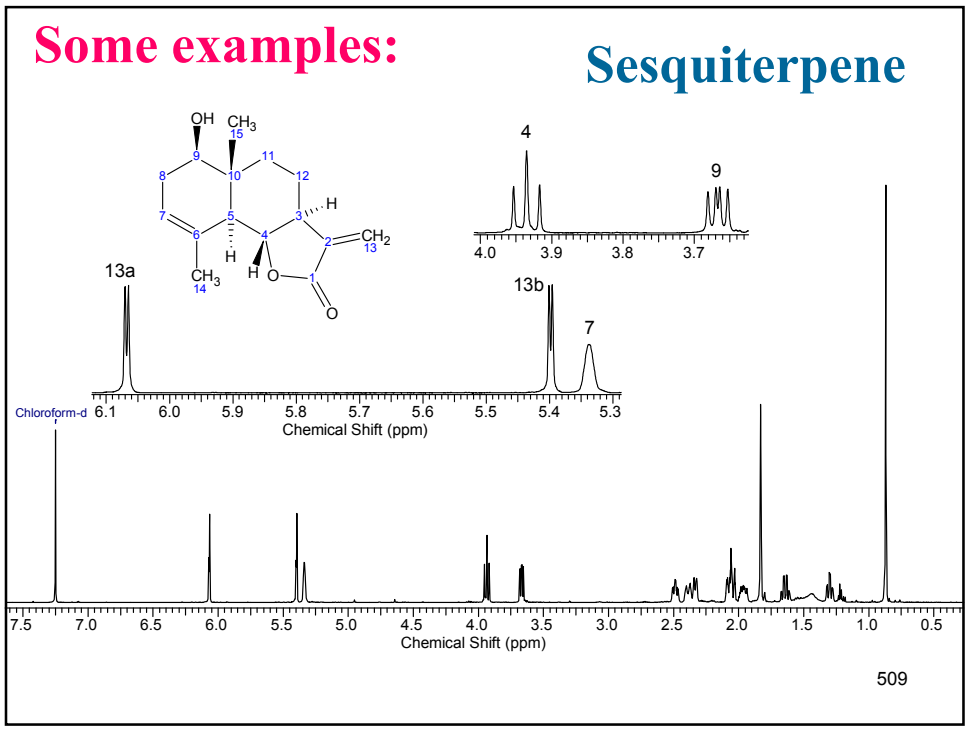

Canadensene
Zamir, L. O., et al., J. Chem. Soc., Chem. Commun. 1995, 529.
Connection of the protons
^{1}H-^{1}H COSY
Long-range ^{1}H-^{1}H COSY
504

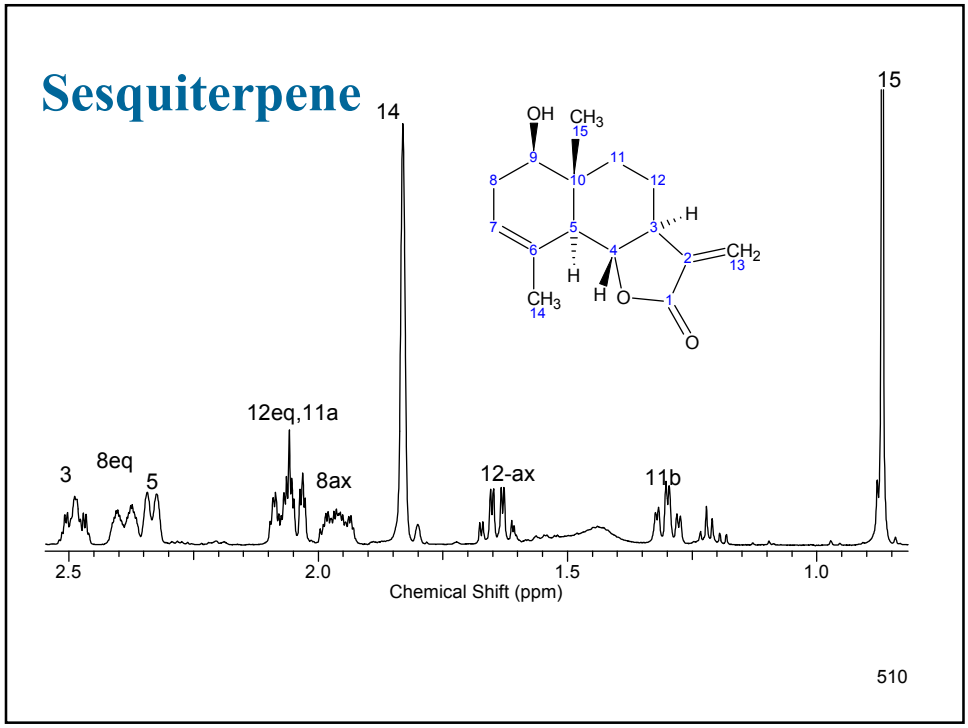

ARX-300-1H
Sample: IID1
12.656
9.948
7.662
7.656
7.630
7.624
7.602
7.596
6.968
6.940
6.765
6.758
6.359
6.352
3.859
3.853
3.805
3.329
2.490
OCH3
HO
O
OCH3
OMe
OH
O
1.1289
1.0000
1.1047
1.0789
1.0752
1.0373
1.0170
6.1499
3.1618
505


ARX-300-1H
Sample: IID1
7.6621
7.6550
7.6305
7.6240
7.6024
7.5957
6.9681
6.9400
6.7647
6.7575
6.3592
6.3520
OCH3
HO
O
OCH3
OMe
OH
O
1.1047
1.0789
1.0752
1.0373
1.0170
506

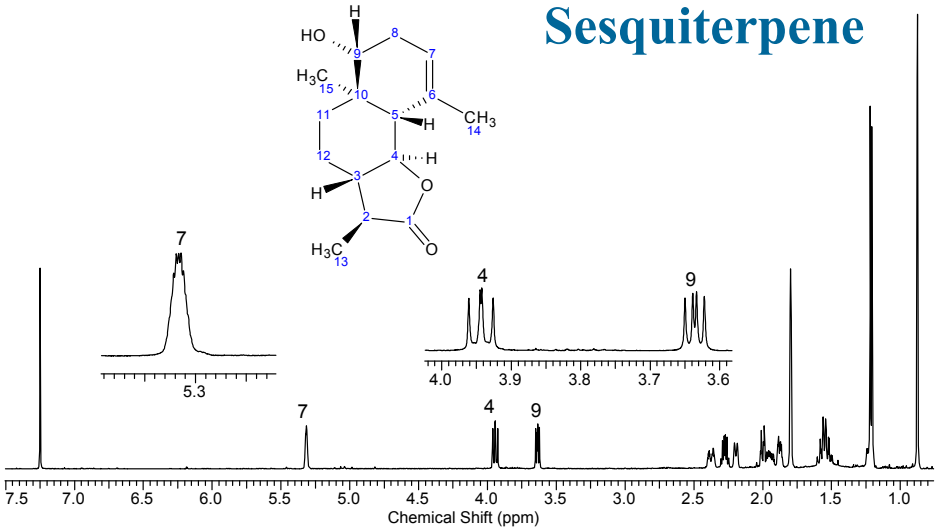

白杨素
HO
OH
O
12.85 s
OH-5
8.06 d
J=7.9Hz
H-2', 6'
7.58 m
H-3', 4', 5'
6.94 s
H-3
6.53 d
J=1.9Hz
H-8
6.23 d
J=1.9Hz
H-6
13.0
12.5
8.0
7.5
7.0
6.5
6.0
507

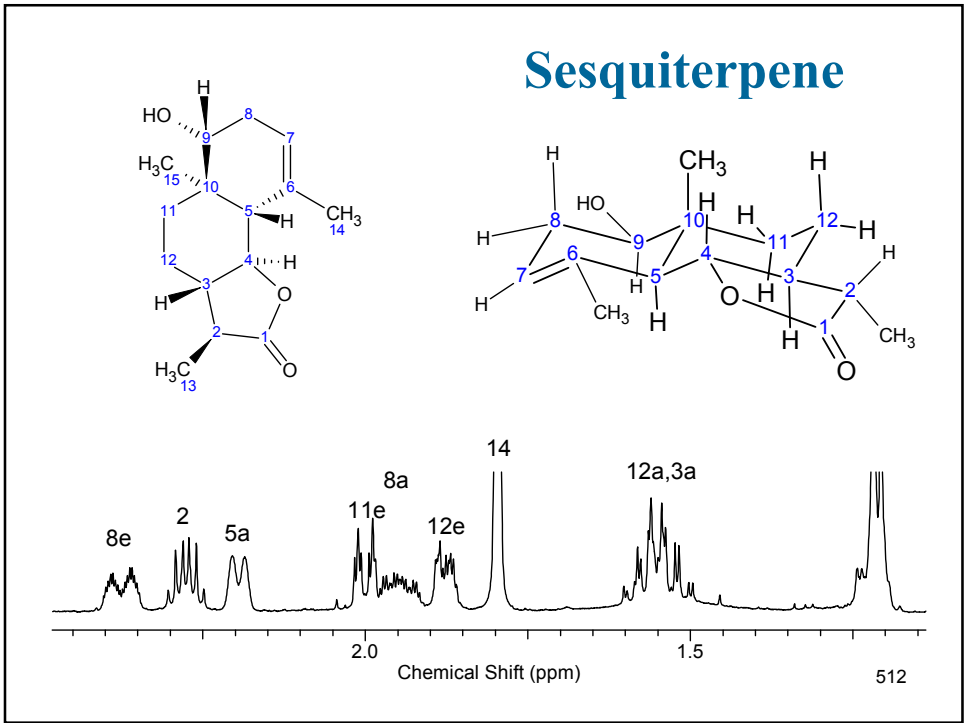

f1 (ppm)
508

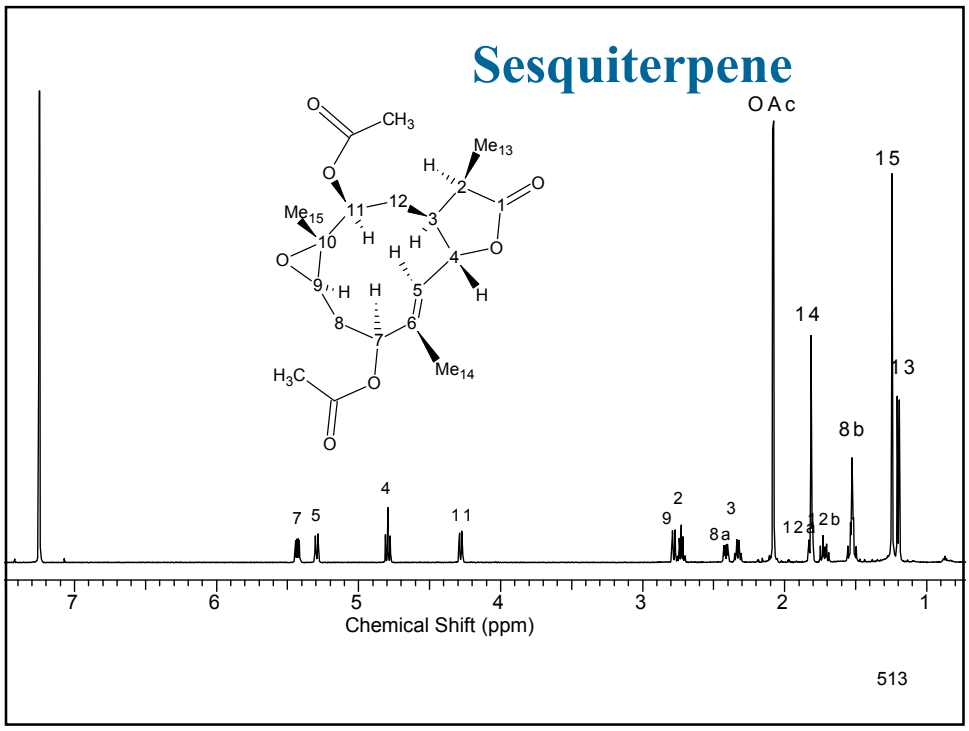

Some examples:
Sesquiterpene
OH
CH3
15
CH2
13
CH3
14
H
O
4
9
13a
13b
7
Chloroform-d
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
Chemical Shift (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)
509

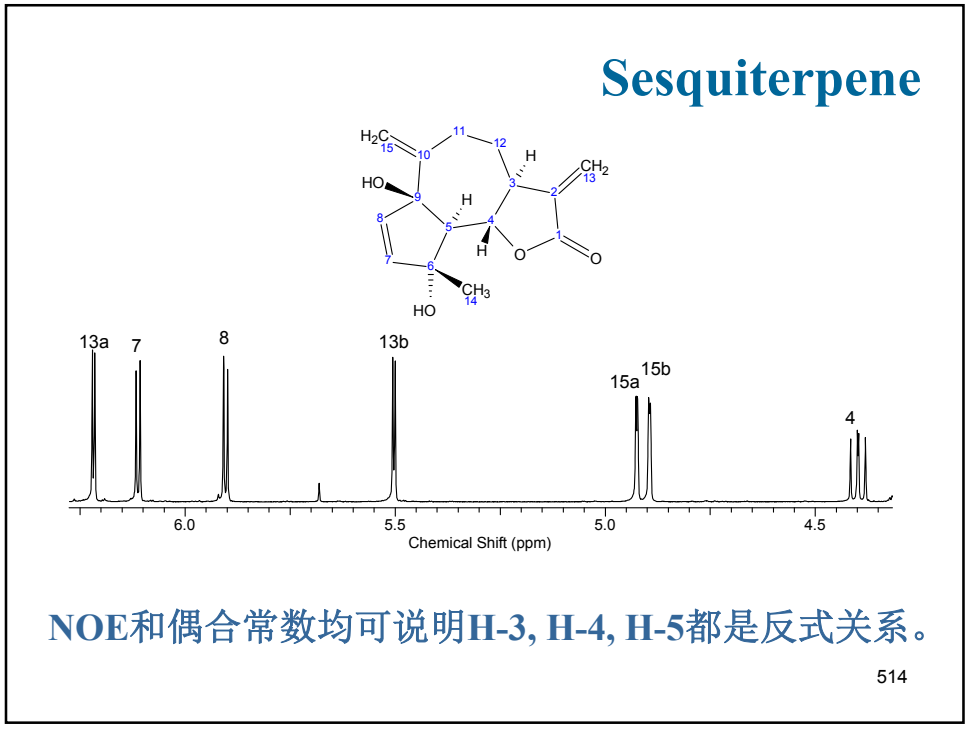

Sesquiterpene
14
15
OH
CH3
15
CH2
13
CH3
14
H
O
12eq,11a
3
8eq
5
8ax
12-ax
11b
2.5
2.0
1.5
1.0
Chemical Shift (ppm)
510

NOE和偶合常数均可说明H-3, H-4, H-5都是反式关系。

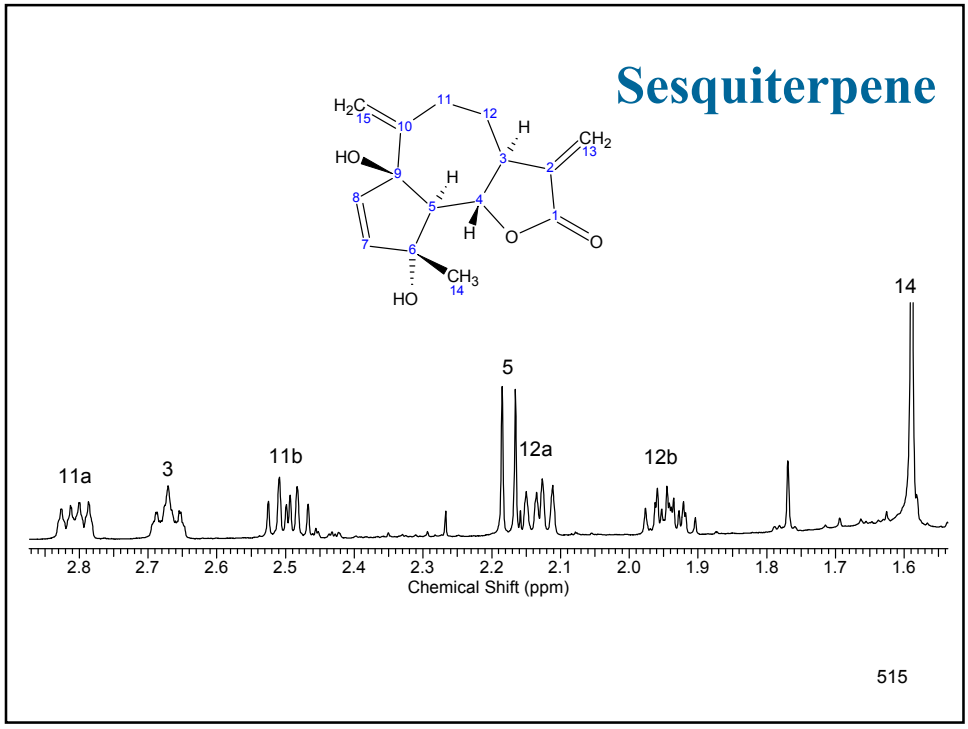


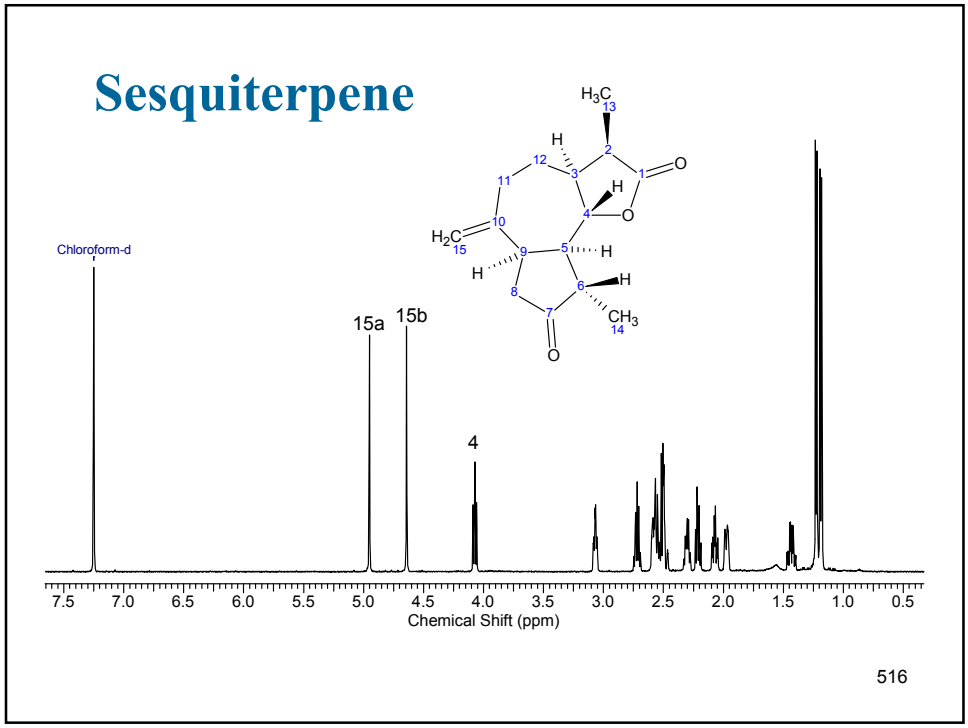


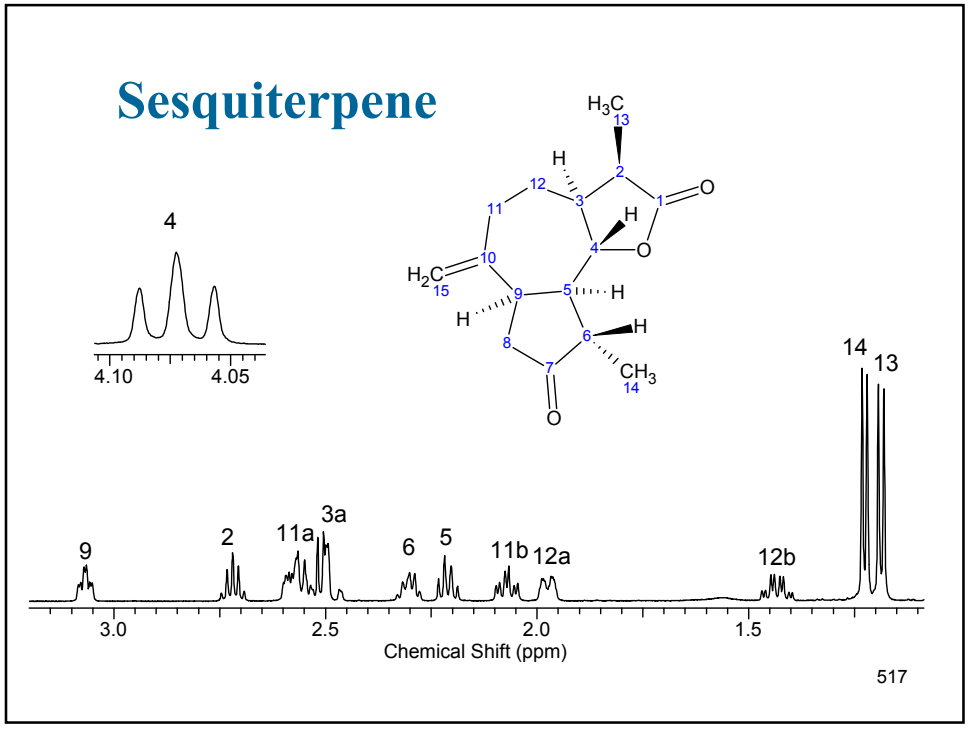


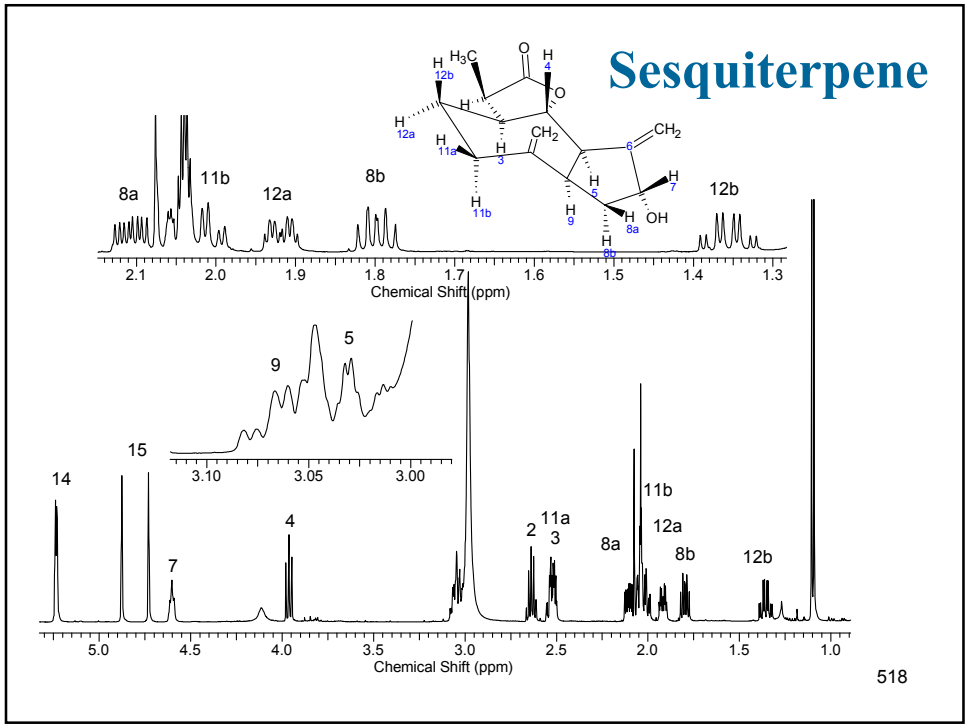


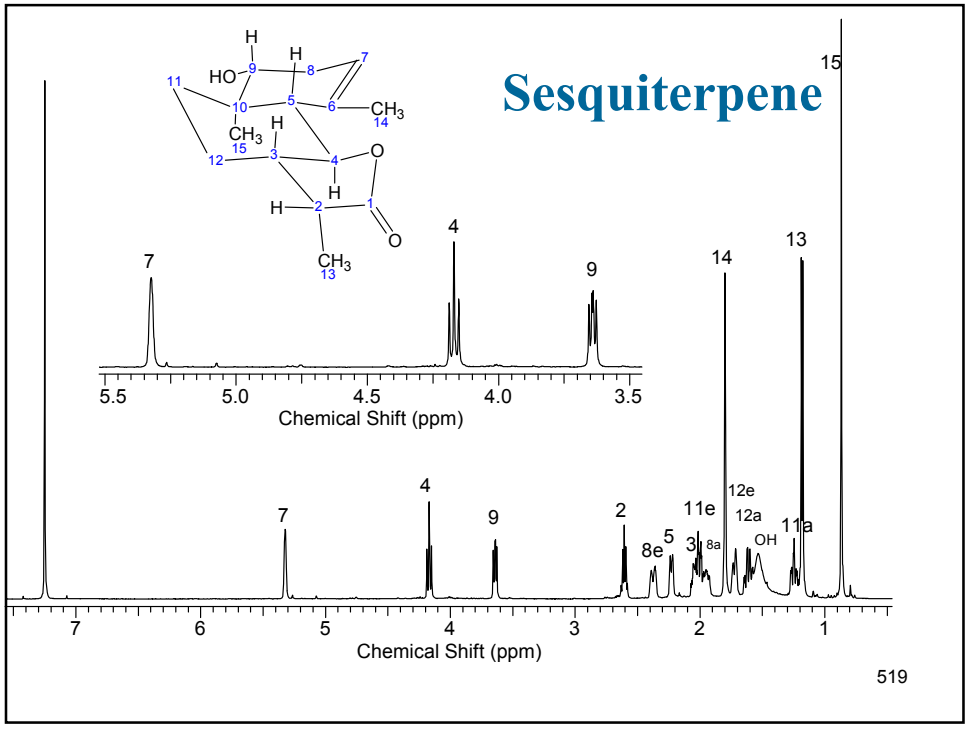
NOE和偶合常数均可说明H-3, H-4, H-5都是反式关系。

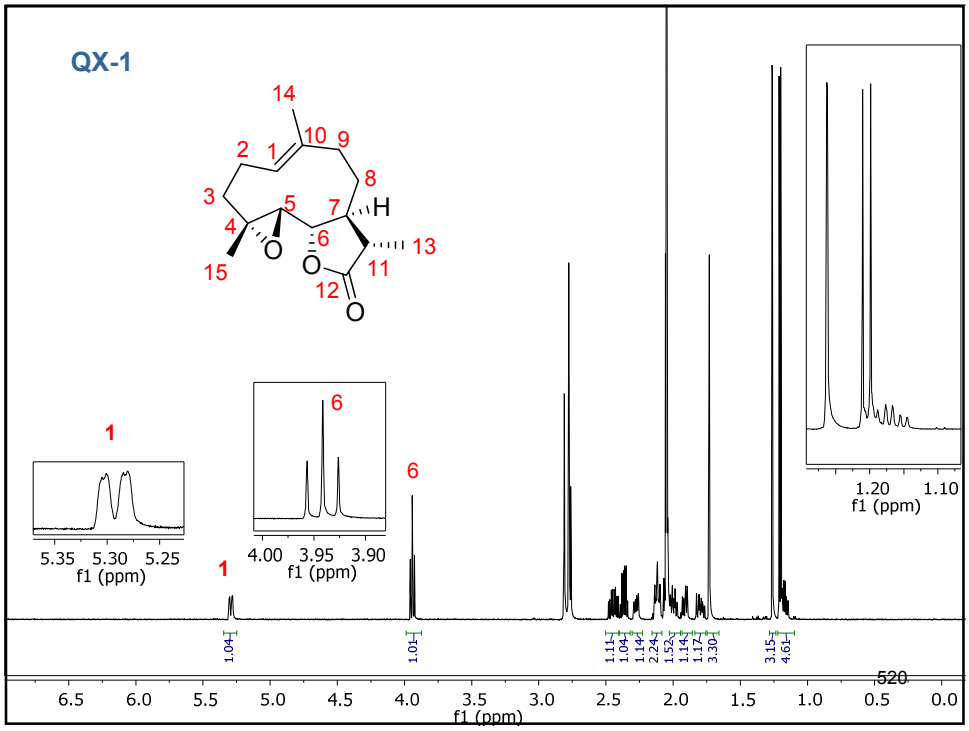

Sesquiterpene
H2C
15
10
11
12
H
CH2
13
HO
9
3
2
8
H
5
4
1
O
7
6
H
O
CH3
14
HO
14
5
11a
3
11b
12a
12b
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
Chemical Shift (ppm)
515

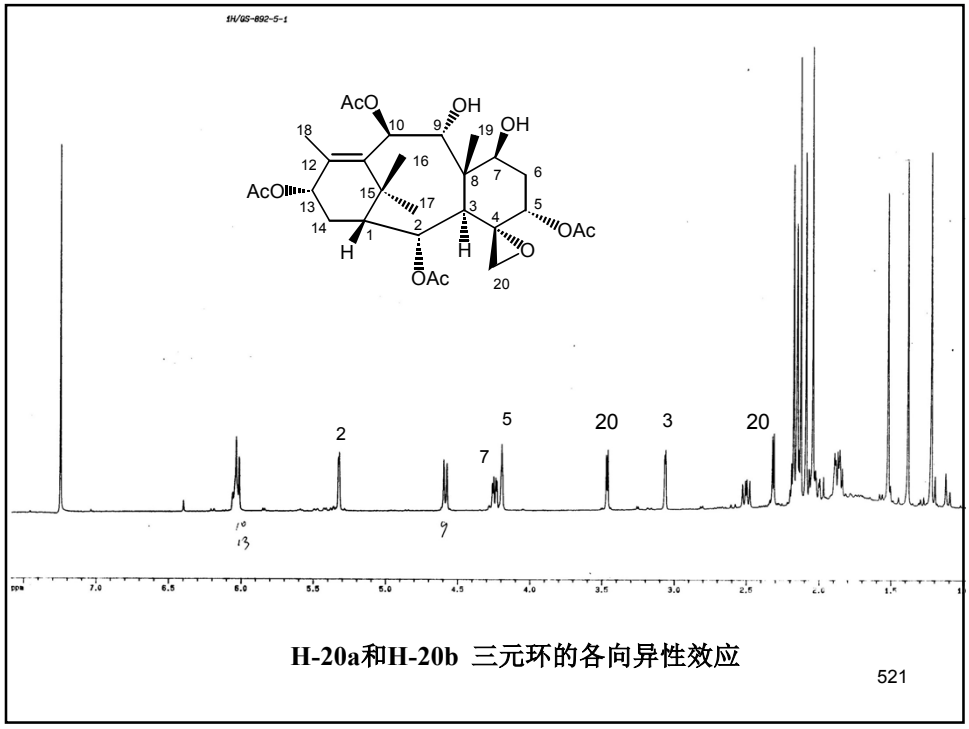

Sesquiterpene
H3C
13
H
12
2
1
O
11
3
H
10
4
O
H2C
15
9
5
H
H
6
H
8
7
CH3
14
O
Chloroform-d
15a
15b
4
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)
516


Sesquiterpene
4
4.10
4.05
9
2
11a
3a
6
5
11b
12a
12b
14
13
3.0
2.5
2.0
1.5
Chemical Shift (ppm)
517


Sesquiterpene
8a
11b
12a
8b
12b
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
Chemical Shift (ppm)
9
5
3.10
3.05
3.00
14
15
7
4
2
11a
3
8a
11b
12a
8b
12b
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)
518


Sesquiterpene
Chemical Shift (ppm)
519


QX-1
f1 (ppm)
520



H-20a和H-20b 三元环的各向异性效应

521

Purity determination (w/w NMR)

While NMR is primarily used for structural determination, it can also be used for purity determination, provided that the structure and molecular weight of the compound is known. This technique requires the use of an internal standard of known purity. Typically this standard will have a high molecular weight to facilitate accurate weighing, but relatively few protons so as to give a clear peak for later integration e.g. 1,2,4,5-tetrachloro-3-nitrobenzene. Accurately weighed portions of the standard and sample are combined and analysed by NMR. Suitable peaks from both compounds are selected and the purity of the sample is determined via the following equation.

核磁共振碳谱

^{13}C-NMR Spectrum

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核磁共振碳谱

在决定有机化合物结构时，与^{1}H-NMR相比^{13}C-NMR在某种程度上起着更为重要的作用，两者相辅相成。

自然界存在的碳同位素中，^{12}C虽然丰度比最大(98.9%)但因没有磁性而无法测定，^{13}C虽有磁性 (I = 1/2)，但因观测灵敏度只有^{1}H核的1/64，且丰度比甚小，仅为1.1%，故总的信号灵敏度仅为^{1}H核的1/6000，致使^{13}C-NMR长期不能投入实际应用。近30年来电脉冲-傅丽叶变换(PFT) 核磁共振装置的出现，及计算机的引入，^{13}C-NMR才得到真正应用。

524

核磁共振碳谱

^{13}C-NMR的化学位移是最重要的参数，它直接反映了所观察核周围的基团电子分布的情况，即核所受的屏蔽作用的大小。

δ_C 对核所处的化学环境很敏感，δ_C的范围远比δ_H宽。分子中有不同的构型和构象时，δ_C比 δ_H更敏感。

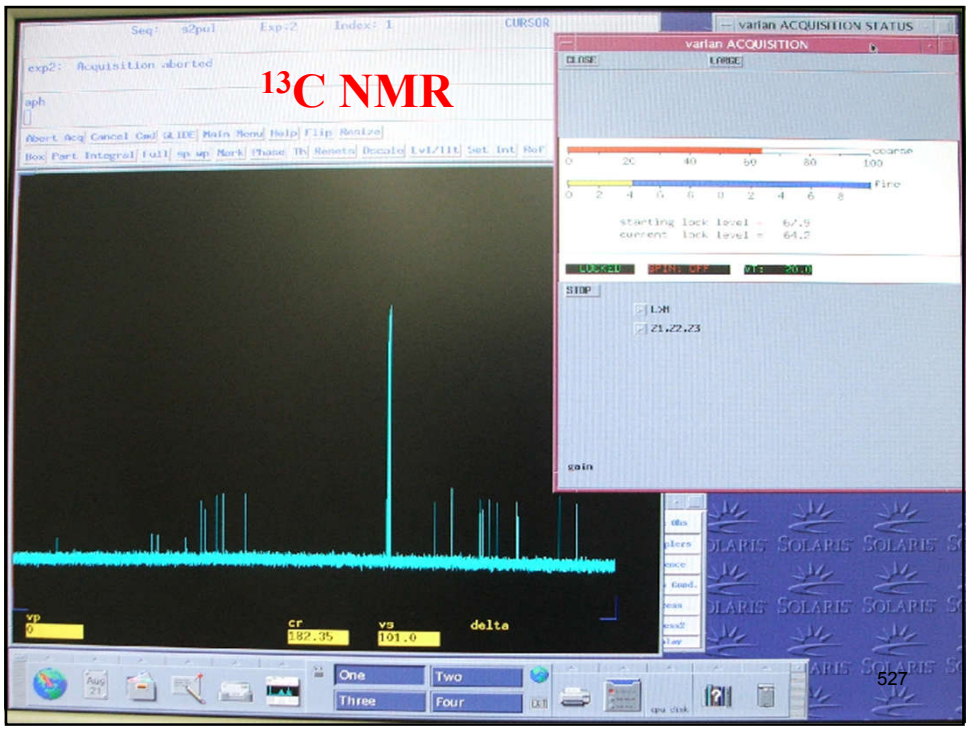
对于季碳，碳谱比氢谱更具优势。

525

^{13}C-NMR Spectrum

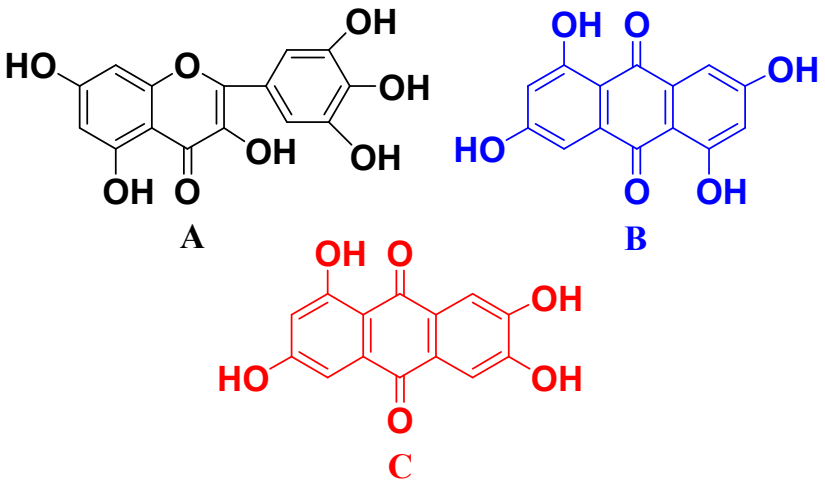
In a ^{13}C-NMR spectrum the area under the signal is not simply proportional to the number of carbons giving rise to the signal because the NOE from proton decoupling is not equal for all the carbons. In particular, unprotonated carbons receive very little NOE, and their signals are always weak.

526

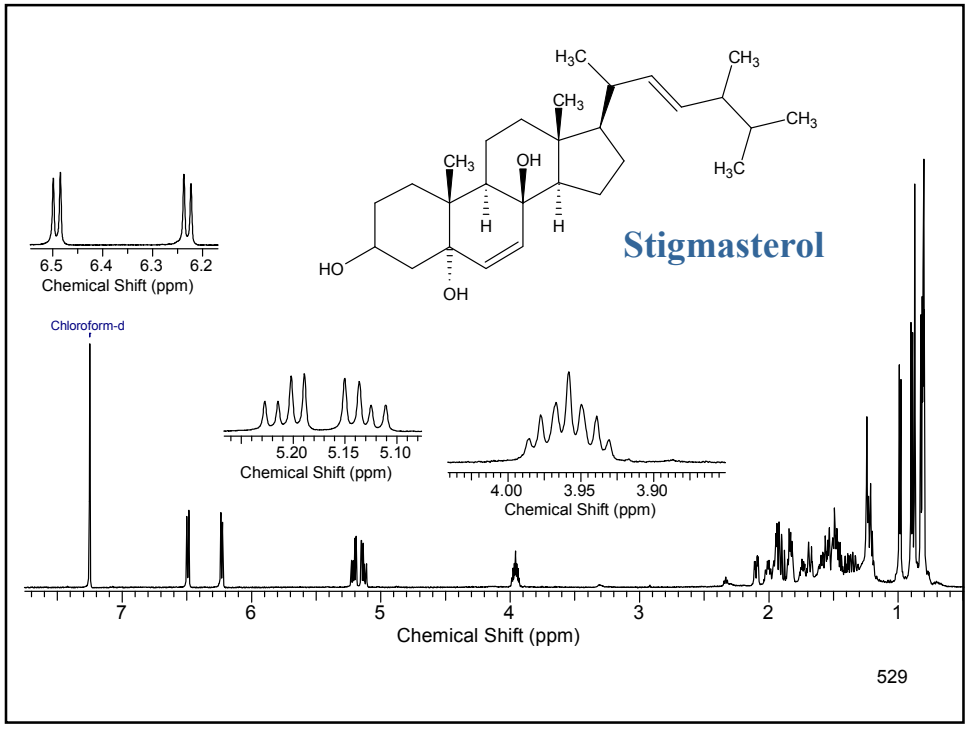


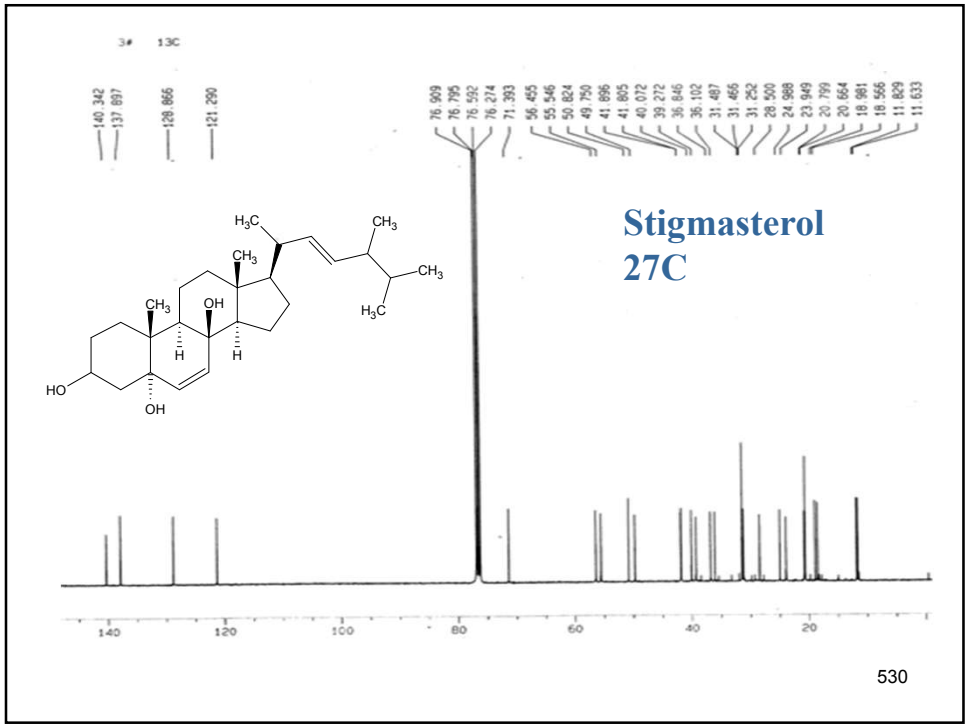
527

^{1}H-NMR and ^{13}C-NMR

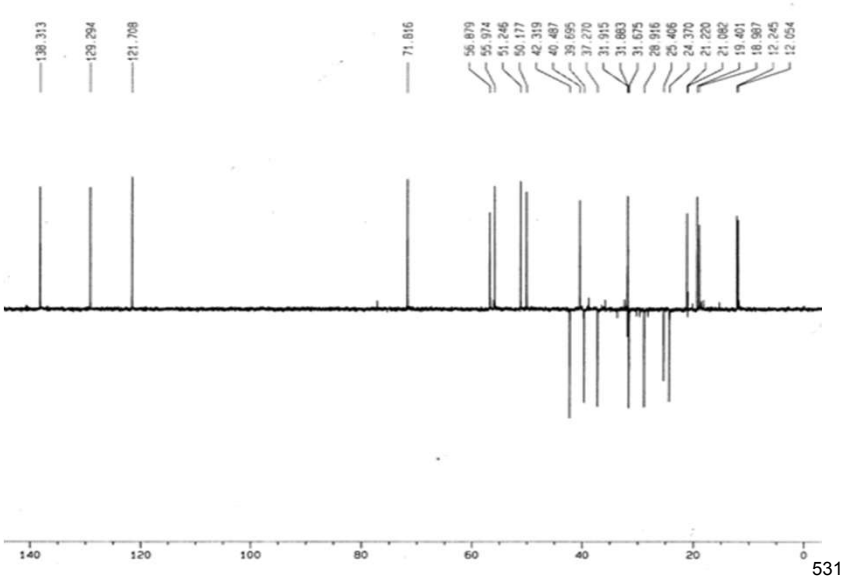


528


Stigmasterol
Chloroform-d
6.5 6.4 6.3 6.2
Chemical Shift (ppm)
5.20 5.15 5.10
Chemical Shift (ppm)
4.00 3.95 3.90
Chemical Shift (ppm)
7 6 5 4 3 2 1
Chemical Shift (ppm)
529

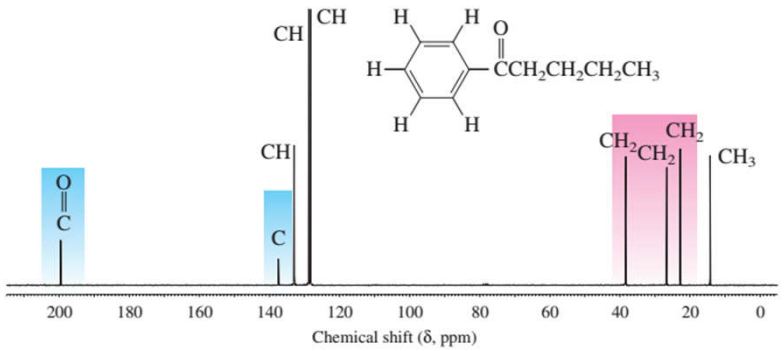

Stigmasterol
27C
140 120 100 80 60 40 20
530

DEPT



531

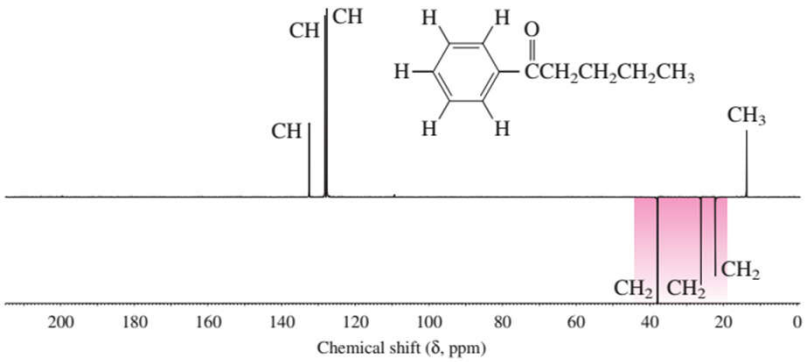
DEPT



Distortionless Enhancement of Polarization Transfer, abbreviated as **DEPT.**

532

DEPT



Distortionless Enhancement of Polarization Transfer, abbreviated as **DEPT.**

533

核磁共振碳谱

影响 ^{13}C-NMR的化学位移的因素

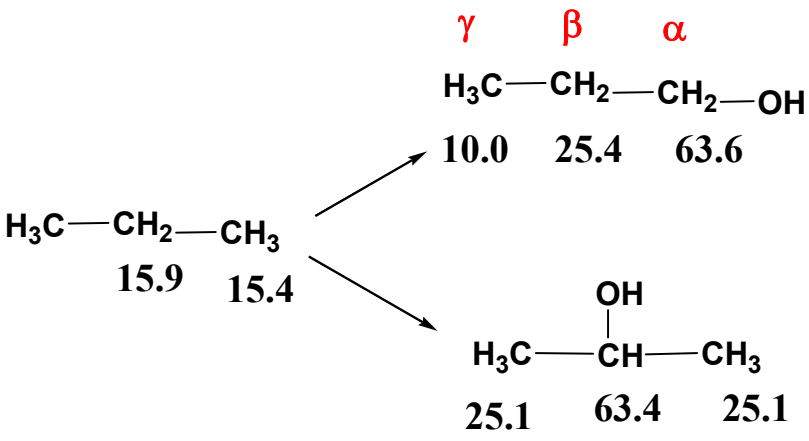
1. 杂化：δ_C值受碳原子杂化的影响， 其次序与δ_H平行。

   一般情况是： $\delta_{sp3} < \delta_{sp} < \delta_{sp2}$

2. 吸电子基团极其密集性：吸电子基团的诱导效应使δ_C核去屏蔽，电负性愈强，去屏蔽效应愈大，吸电子基团愈多，位移也愈大

$$\delta_{C\text{-}F} > \delta_{C\text{-}Cl} > \delta_{C\text{-}Br} > \delta_{C\text{-}I}$$

534



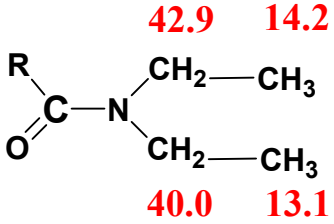
535

核磁共振碳谱

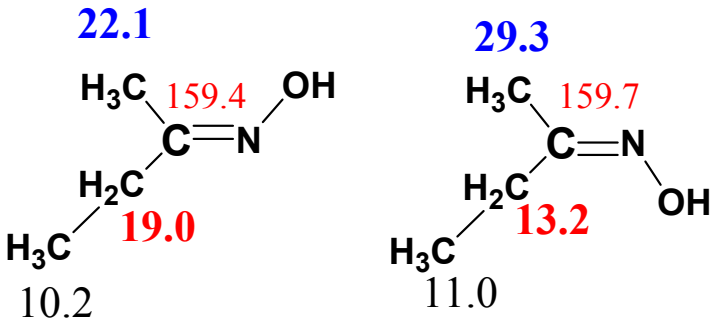
影响 ^{13}C-NMR的化学位移的因素

3. 构型的影响：构型的不同δ_C值也不相同。

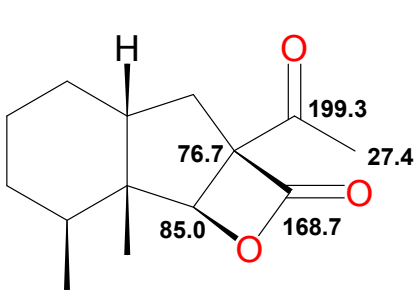
在烯烃的顺反异构中， 烯碳的δ_C相差1-2 ppm，顺式在较高场。与烯碳相连的饱和碳的δ_C相差要多些，约3-5 ppm, 顺式也在高场。



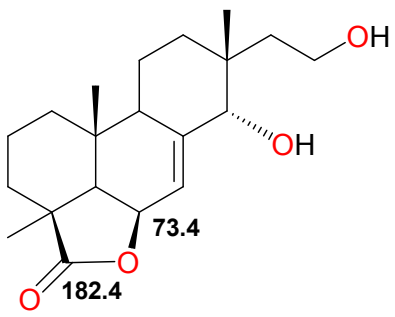
536



537

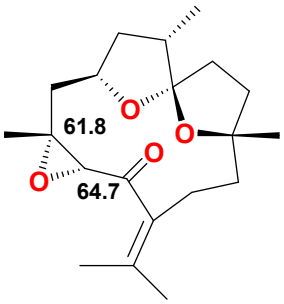


Tetrahedron, 2013, 69: 8505

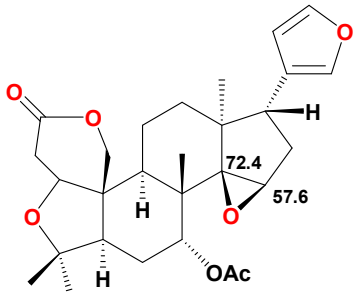


Phytochem. Lett., 2012, 5: 78

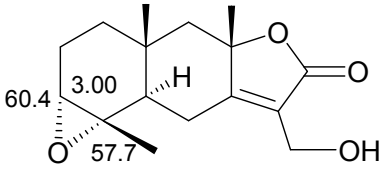
538



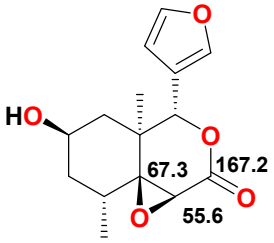
Phytochem,2010, 71: 1387



Phytochem,2012, 83: 136

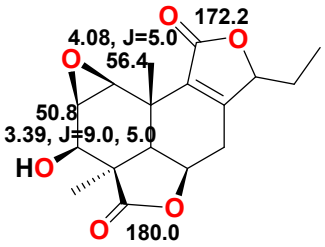


Phytochem. Lett., 2012, 5: 78

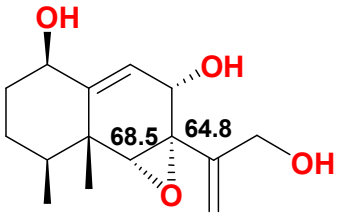


Phytochem,2008, 69: 2993

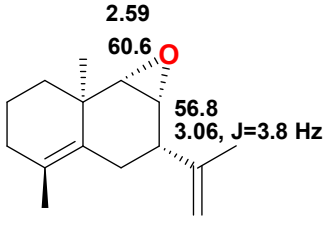
539



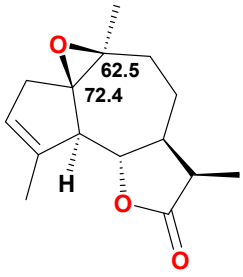
Phytochem Lett,2012, 5: 297



Phytochem Lett,2010, 3: 148

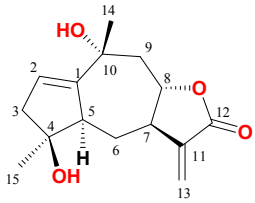


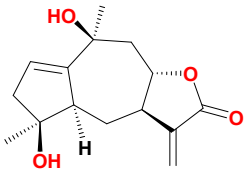
Phytochem,2002, 61: 79



Biochemical Systematics and Ecology，2012，45：115–119

540

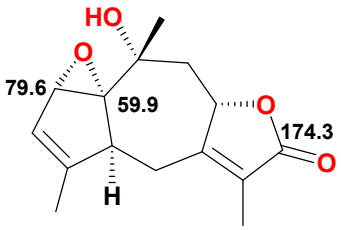




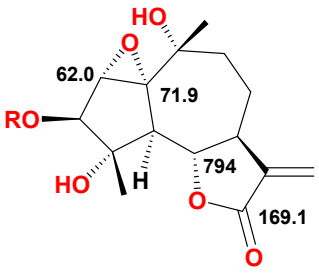
Position	2		3	
	δ_H (mult, J, Hz)	δ_C (DEPT)	δ_H (mult, J, Hz)	δ_C (DEPT)
1		151.8 (C)		151.8 (C)
2	5.68 br s	125.0 (CH)	5.57 br s	122.0 (CH_2)
3	2.51 d (17.4) 2.33 dd (17.4, 3.2)	45.9 (CH_2)	2.40 br s (2H)	46.7 (CH_2)
4		81.5 (C)		81.3 (C)
5	2.82 dd (12.6, 4.8)	54.7 (CH)	2.70 br d (12.0)	55.4 (CH)
6	2.18 ddd (12.6, 4.6, 3.2, H_{eq}) 1.01 br dd (12.2, 12.2, H_{ax})	32.0 (CH_2)	2.06 ddd (13.2, 4.7, 4.4, H_{eq}) 1.34 br dd, overlapped	32.5 (CH_2)
7	3.07 dddd (11.8, 9.2, 3.1, 3.0)	45.6 (CH)	3.39 m	42.2 (CH)
8	3.83 ddd (11.2, 9.2, 4.4)	81.8 (CH)	5.15 ddd (11.7, 4.5, 3.5)	77.5 (CH)
9	2.49 dd (13.8, 4.4, H_{eq}) 2.08 dd (13.8, 11.2, H_{ax})	46.5 (CH_2)	2.29 dd (13.8, 4.0, H_{eq}) 1.76 dd (13.8, 12.1, H_{ax})	42.5 (CH_2)
10		70.2 (C)		69.6 (C)
11		139.8 (C)		140.4 (C)
12		170.0 (C)		170.1 (C)
13	6.21 d (3.0) 5.52 d (3.0)	120.1 (CH_2)	6.26 d (2.8) 5.59 d (2.4)	121.6 (CH_2)
14	1.58 s	30.7 (CH_3)	1.54 s	29.9 (CH_3)
15	1.39 s	23.3 (CH_3)	1.36 s	24.5 (CH_3)

541

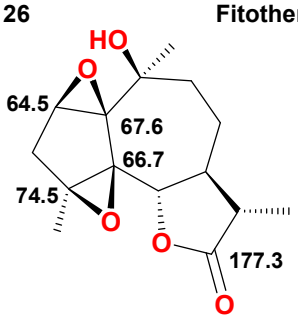
***Bioorganic & Medicinal Chemistry Letters* 2011, 21: 366**



Phytochem, 2013, 87: 126

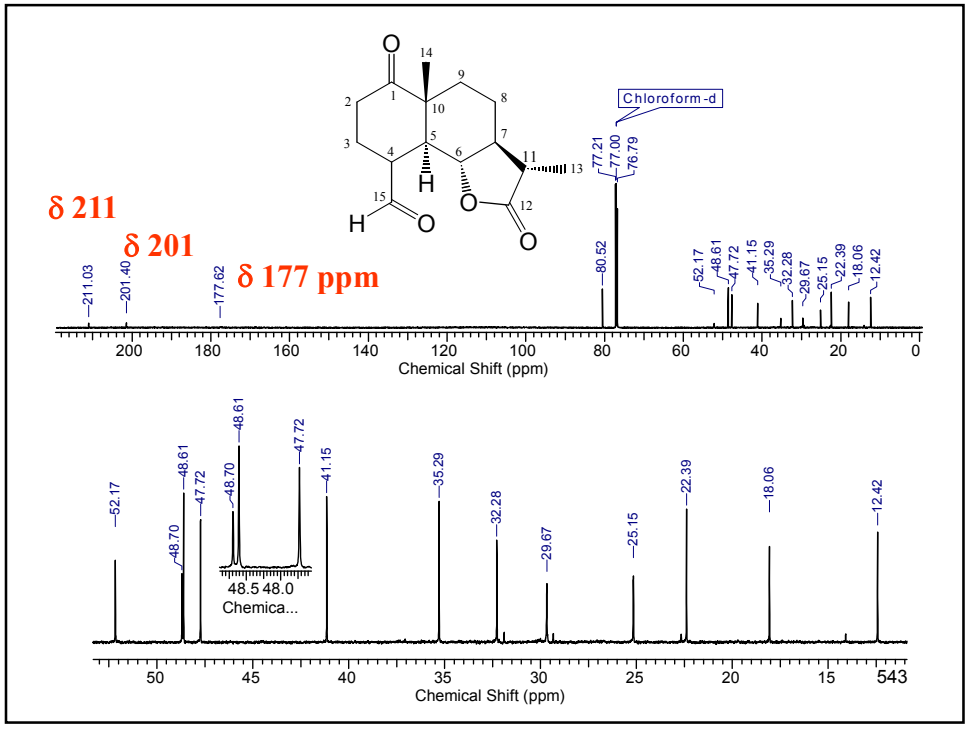


Fitotherapia, 2013, 85: 169



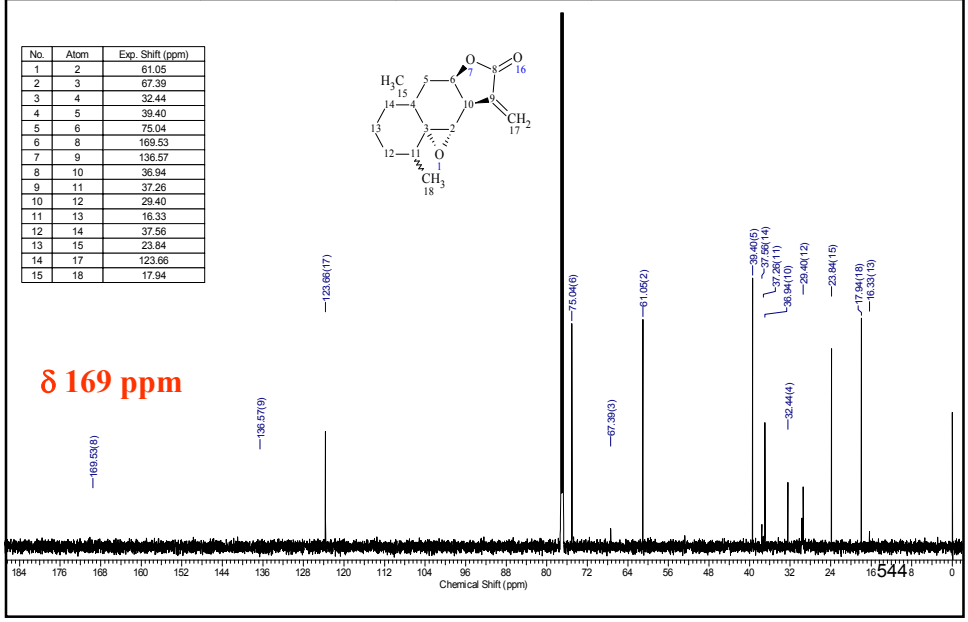
Phytochem, 2001, 58: 1189

542



Formula $C_{15}H_{20}O_3$	FW 248.3175						
Acquisition Time (sec)	0.9789	Comment	09st412 Yucheng Gu ZML-16			Date	Dec 9 2009
Date Stamp	Dec 9 2009	File Name	\\friapfil04\NMRprocessor\MReid Projects\09st412\CARBON_01.fid\fid				
Frequency (MHz)	150.85	Nucleus	13C	Number of Transients	2048	Original Points Count	32768
Points Count	262144	Pulse Sequence	s2pul	Receiver Gain	60.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	16433.1406	Spectrum Type	STANDARD	Sweep Width (Hz)	33472.80	Temperature (degree C)	25.000

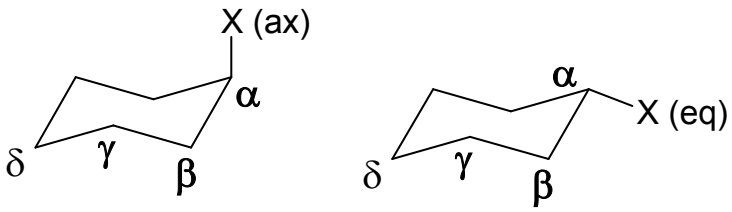
No.	Atom	Exp. Shift (ppm)
1	2	61.05
2	3	67.39
3	4	32.44
4	5	39.40
5	6	75.04
6	8	169.53
7	9	136.57
8	10	36.94
9	11	37.26
10	12	29.40
11	13	16.33
12	14	37.56
13	15	23.84
14	17	123.66
15	18	17.94



核磁共振碳谱

影响 ^{13}C-NMR的化学位移的因素

4. 环己烷上的取代基处于直立(ax)或平伏(eq)对与δ_C值影响也不相同。

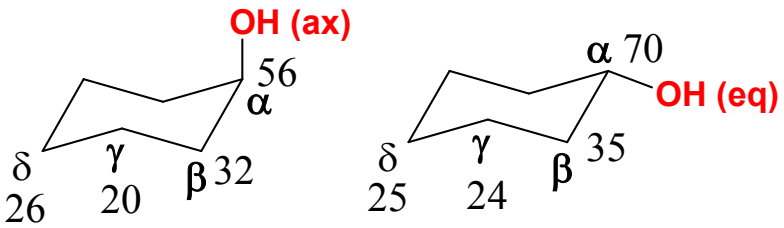


545

核磁共振碳谱

影响 ^{13}C-NMR的化学位移的因素

4. 环己烷上的取代基处于直立(ax)或平伏(eq)对与δ_C值影响也不相同。



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核磁共振碳谱

影响 ^{13}C-NMR的化学位移的因素

5. 介质、溶剂的影响：不同的介质可使δ_C值变化几个ppm，甚至10 ppm以上。

分子中有可解离的基团，在不同的PH值下，可使δ_C值有明显的变化。

如分子中有： NH_2, COOH, OH, SH等

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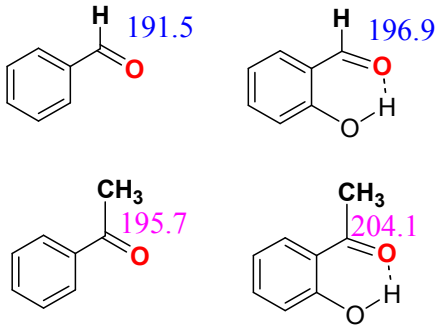
核磁共振碳谱

影响 ^{13}C-NMR的化学位移的因素

5. 氢键的影响：特别是分子内氢键，对有关的碳原子的δ_C值也有影响。



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核磁共振碳谱

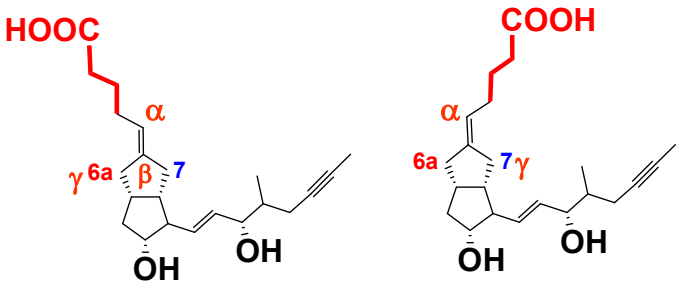
影响 ^{13}C-NMR的化学位移的因素

6. 温度的影响：温度变化，分子状态发生变化，碳原子的δ_C值也会有变化。

7. 顺磁物质的影响：顺磁物质对NMR谱线的位移、线宽有强烈的影响 。

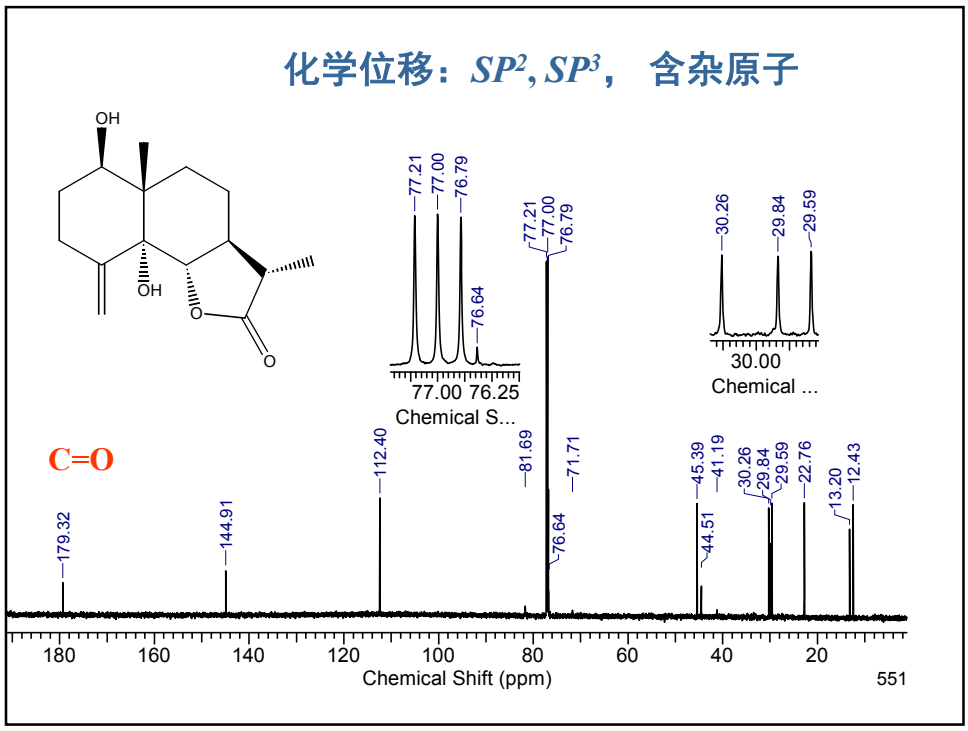
549

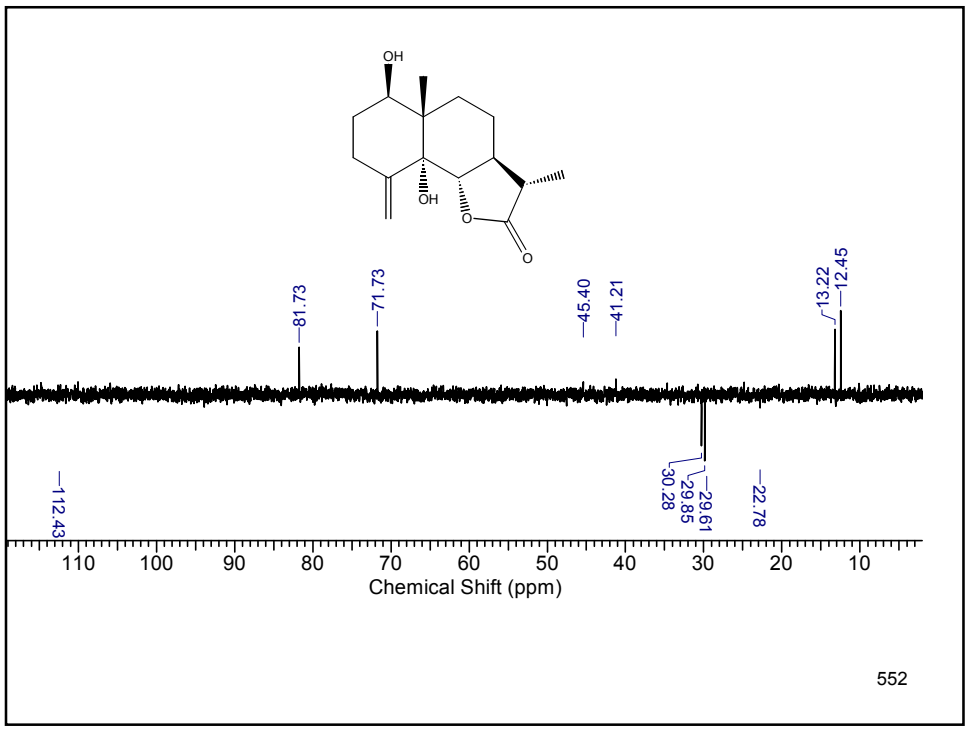
- 化学位移
  - ^{13}C化学位移
    - 取代基的γ-旁式效应将使γ-位置的碳原子产生高场位移

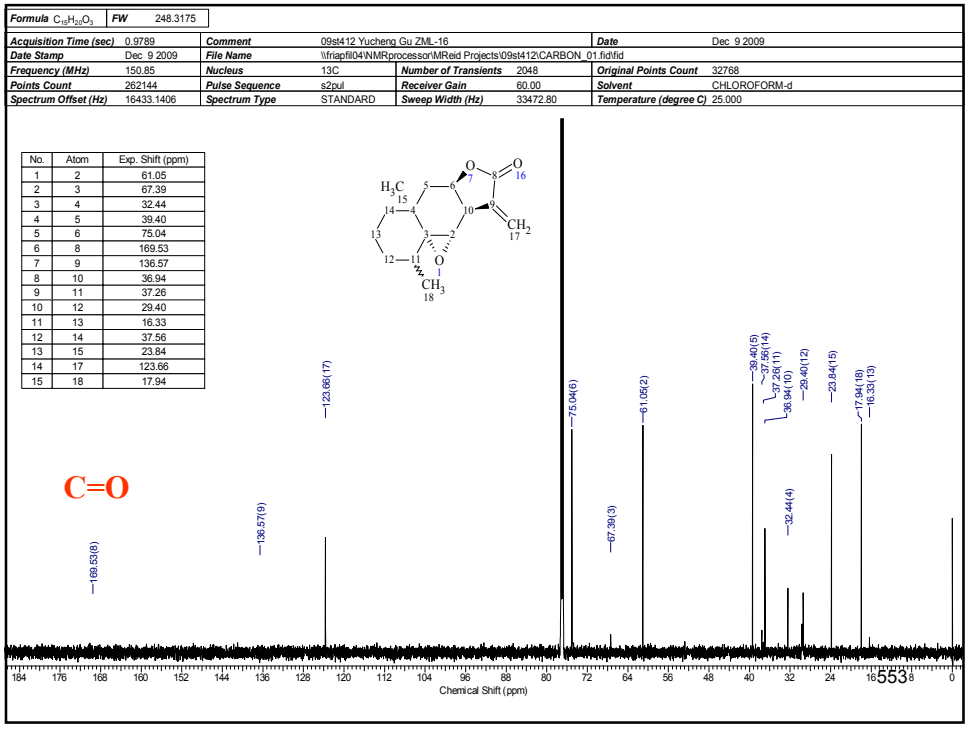


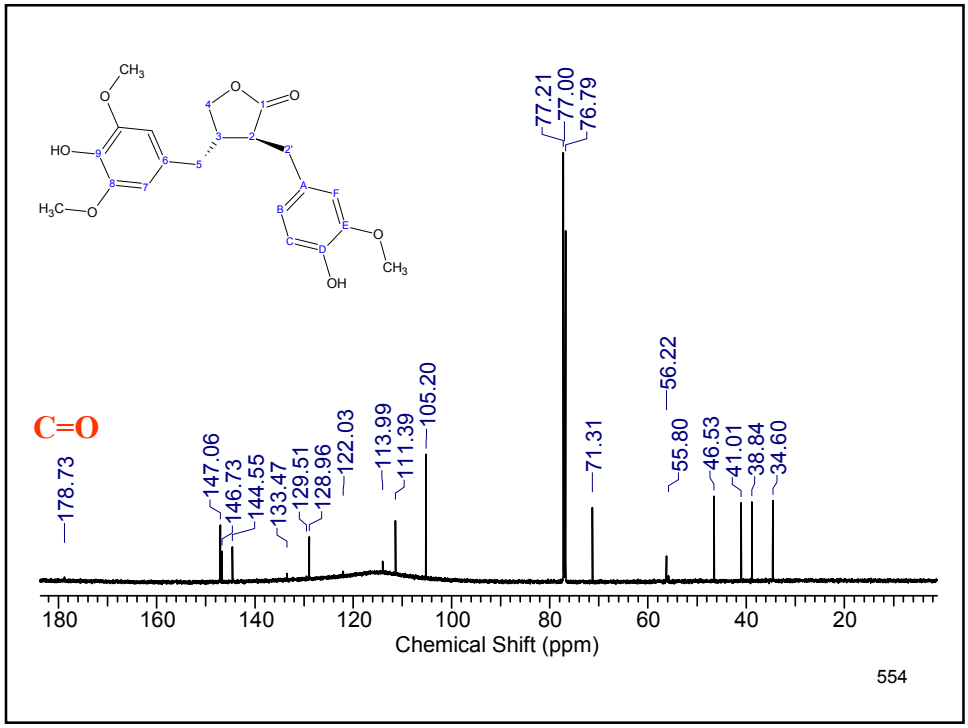
δ	6a	7
异构体1	35.9	38.7
异构体2	41.2	32.5

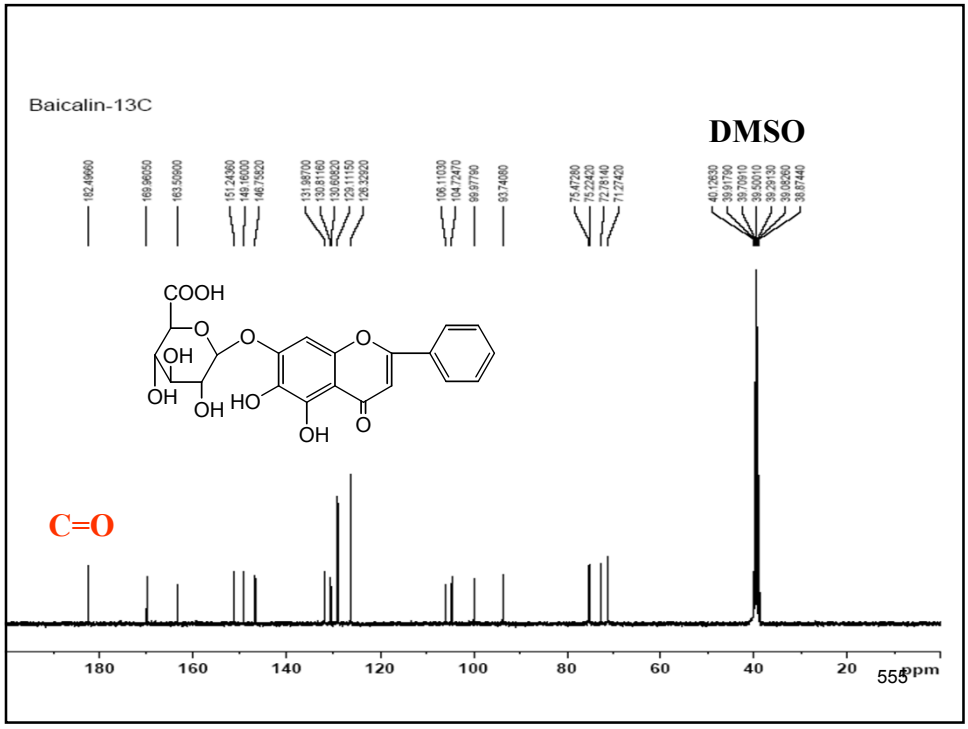
550


化学位移：SP², SP³， 含杂原子
OH
OH
O
O
77.21
77.00
76.79
76.64
77.00 76.25
Chemical S...
30.26
29.84
29.59
30.00
Chemical ...
C=O
179.32
144.91
112.40
81.69
76.64
71.71
45.39
44.51
41.19
30.26
29.84
29.59
22.76
13.20
12.43
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)
551

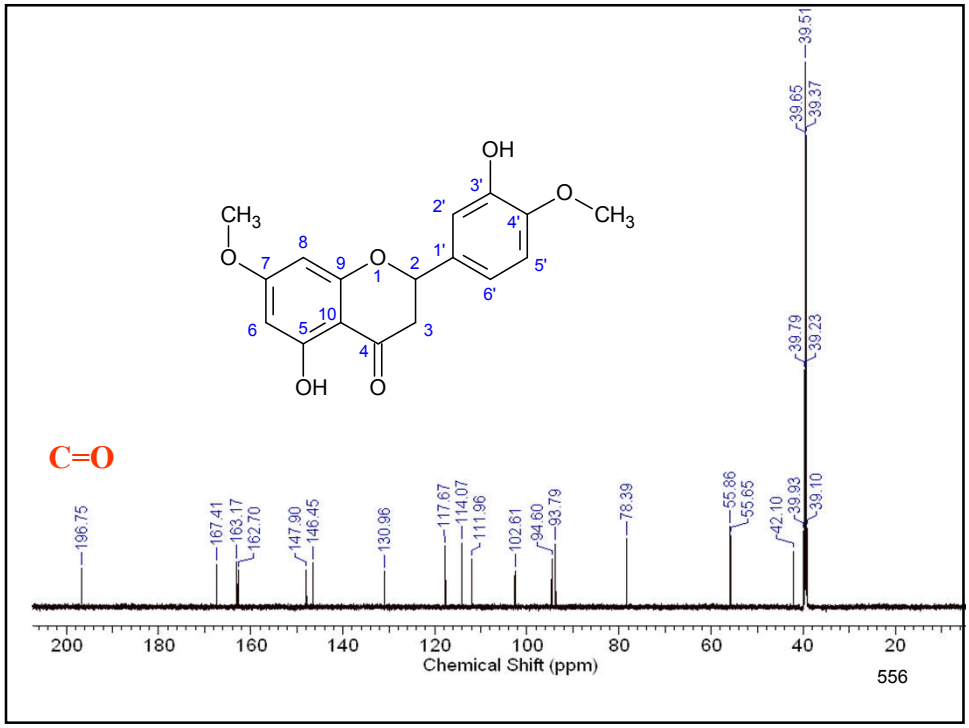

OH
OH
O
O
81.73
71.73
45.40
41.21
13.22
12.45
112.43
30.28
29.85
29.61
22.78
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)
552


Formula C15H20O3 FW 248.3175
Acquisition Time (sec) 0.9789 Comment 09st412 Yucheng Gu ZML-16 Date Dec 9 2009
Date Stamp Dec 9 2009 File Name \\friapfil04\NMRprocessor\MReid Projects\09st412\CARBON_01.fid\fid
Frequency (MHz) 150.85 Nucleus 13C Number of Transients 2048 Original Points Count 32768
Points Count 262144 Pulse Sequence s2pul Receiver Gain 60.00 Solvent CHLOROFORM-d
Spectrum Offset (Hz) 16433.1406 Spectrum Type STANDARD Sweep Width (Hz) 33472.80 Temperature (degree C) 25.000
No. Atom Exp. Shift (ppm)
1 2 61.05
2 3 67.39
3 4 32.44
4 5 39.40
5 6 75.04
6 8 169.53
7 9 136.57
8 10 36.94
9 11 37.26
10 12 29.40
11 13 16.33
12 14 37.56
13 15 23.84
14 17 123.66
15 18 17.94
C=O
169.53(8)
136.57(9)
123.66(17)
75.04(6)
67.39(3)
61.05(2)
39.40(5)
37.56(14)
37.26(11)
36.94(10)
32.44(4)
29.40(12)
23.84(15)
17.94(18)
16.33(13)
Chemical Shift (ppm)
553


C=O
178.73
147.06
146.73
144.55
133.47
129.51
128.96
122.03
113.99
111.39
105.20
77.21
77.00
76.79
71.31
56.22
55.80
46.53
41.01
38.84
34.60
Chemical Shift (ppm)
554


Baicalin-13C
DMSO
COOH
O
OH
OH
OH
HO
O
O
OH
O
C=O
180
160
140
120
100
80
60
40
20
ppm

555


OH
3'
2'
4'
O
CH3
CH3
O
8
7
9
O
1
2
1'
5'
6'
10
6
5
3
4
OH
O
C=O
196.75
167.41
163.17
162.70
147.90
146.45
130.96
117.67
114.07
111.96
102.61
94.60
93.79
78.39
55.86
55.65
42.10
39.93
39.10
39.79
39.23
39.65
39.37
39.51
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

556

核磁共振碳谱特点

优点：1) 掌握碳原子（特别是无氢原子连接时）的信息

2) 化学位移范围大（可超过200 ppm）

3) 可确定碳原子级数

4) 准确测定驰豫时间，可帮助指认碳原子

难点：灵敏度低、信噪比差

^{13}C天然丰度：1.1%；$S/N \propto \gamma 3$，$\gamma C3/\gamma H3 \approx 1/64$

（在同等实验条件下是氢谱的1/6000）

^{13}C谱中最重要的信息是化学位移δ

557

Obstacles needed to be overcome before carbon NMR emerged as a routine tool :

i) As noted, the abundance of ^{13}C in a sample is very low (1.1%), so higher sample concentrations are needed.

ii) The ^{13}C nucleus is over fifty times less sensitive than a proton in the NMR experiment, adding to the previous difficulty.

.

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Obstacles needed to be overcome before carbon NMR emerged as a routine tool :

iii) Hydrogen atoms bonded to a ^{13}C atom split its NMR signal by 130 to 270 Hz, further complicating the NMR spectrum.

iv) Unlike proton NMR spectroscopy, the relative strength of carbon NMR signals are not normally proportional to the number of atoms generating each one.

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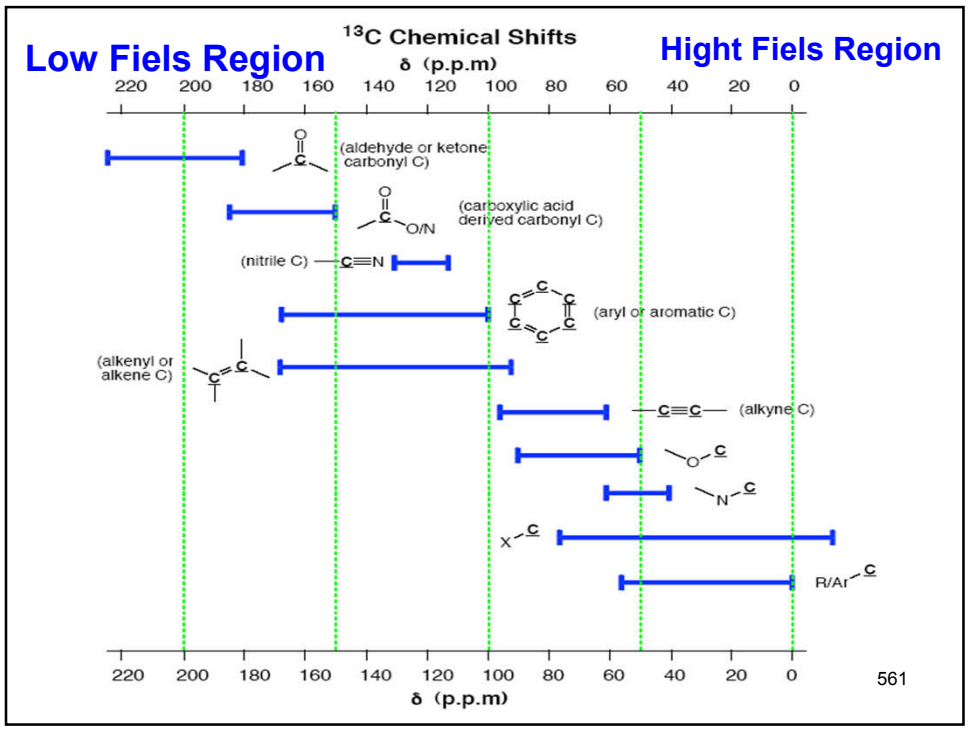
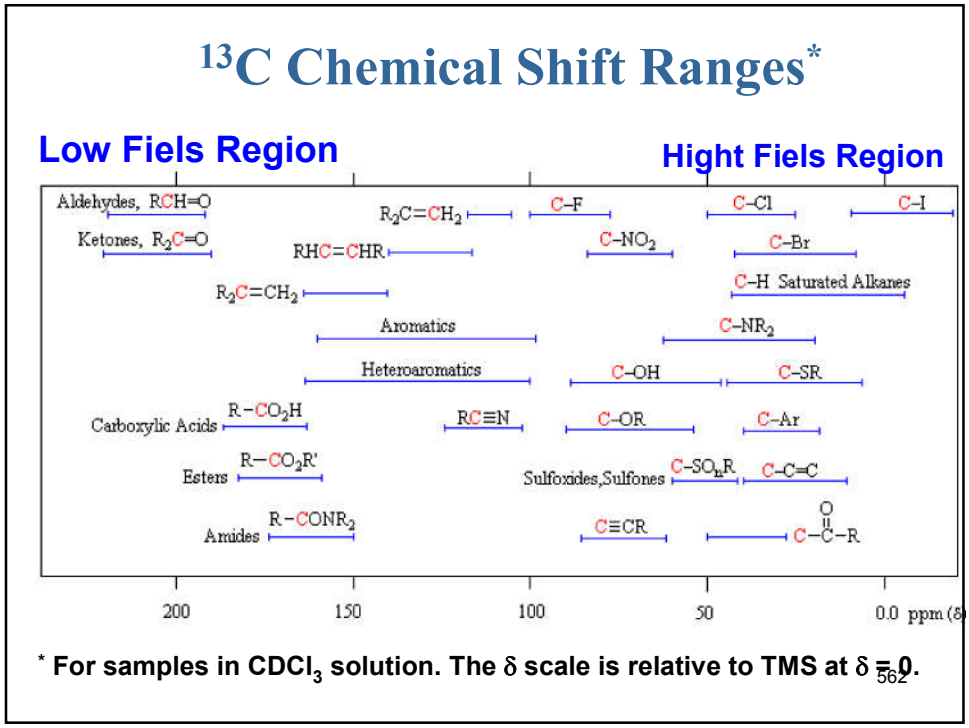
Chemical shift ranges utilized for disfunctionalization of the ^{13}C NMR data

Chemical Function	Multiplicity	Ranges
C=O	1	190.0–250.0
CHO	2	190.0–250.0
R–COO–R	1	165.5–190.0
C=C	1	113.0–165.5
	2	104.0–167.0
	3	100.0–167.0
C–OH	1	61.0–100.0
	2	54.0–90.0
	3	54.0–90.0
C(OR)2	1	100.0–113.0
CH(OR)2	2	90.0–104.0

560


Low Fiels Region
^{13}C Chemical Shifts
δ (p.p.m)
Hight Fiels Region
220 200 180 160 140 120 100 80 60 40 20 0
(aldehyde or ketone carbonyl C)
(carboxylic acid derived carbonyl C)
O/N
(nitrile C)
(aryl or aromatic C)
(alkenyl or alkene C)
(alkyne C)
R/Ar
561


^{13}C Chemical Shift Ranges*
Low Fiels Region
Hight Fiels Region
Aldehydes, RCH=O
Ketones, R2C=O
R2C=CH2
RHC=CHR
R2C=CH2
Aromatics
Heteroaromatics
Carboxylic Acids
R-CO2H
Esters
R-CO2R'
Amides
R-CONR2
RC≡N
C-F
C-NO2
C-OH
C-OR
C≡CR
C-Cl
C-Br
C-H Saturated Alkanes
C-NR2
C-SR
C-Ar
Sulfoxides,Sulfones
C-SO2R
C-C=C
C-C-R
200 150 100 50 0.0 ppm (δ)
* For samples in CDCl3 solution. The δ scale is relative to TMS at δ = 0.
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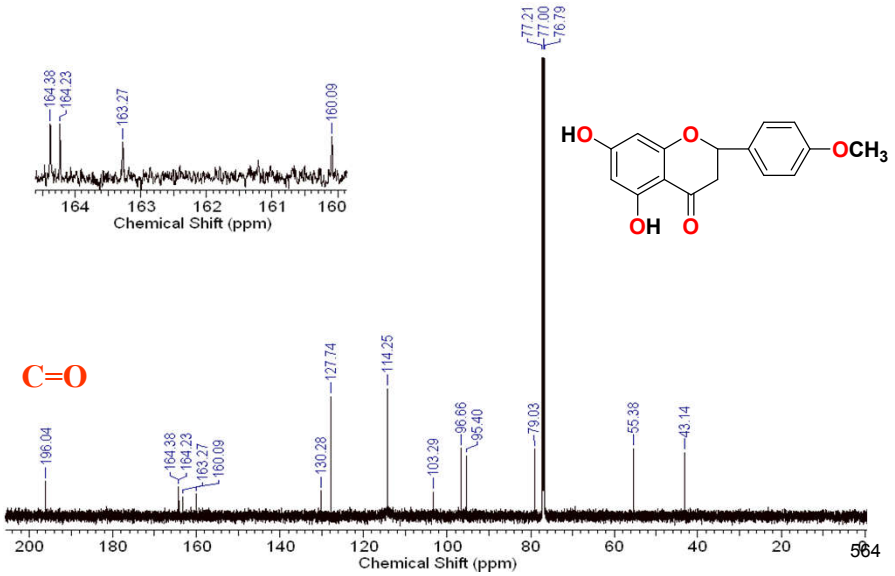
核磁共振碳谱例子

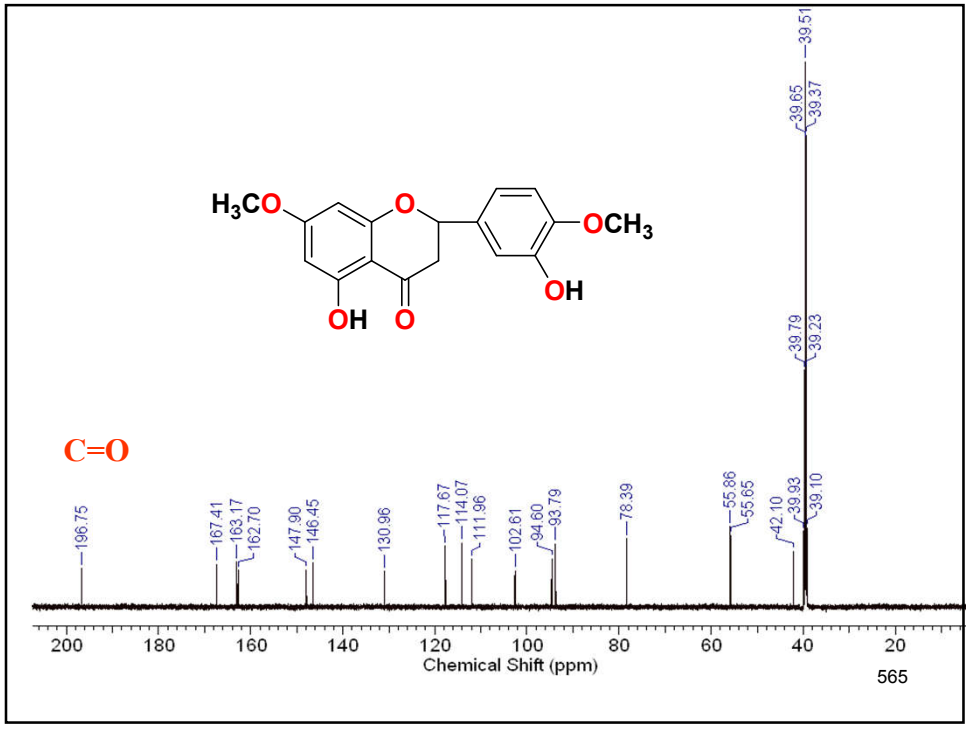
Examples of ^{13}C-NMR Spectra

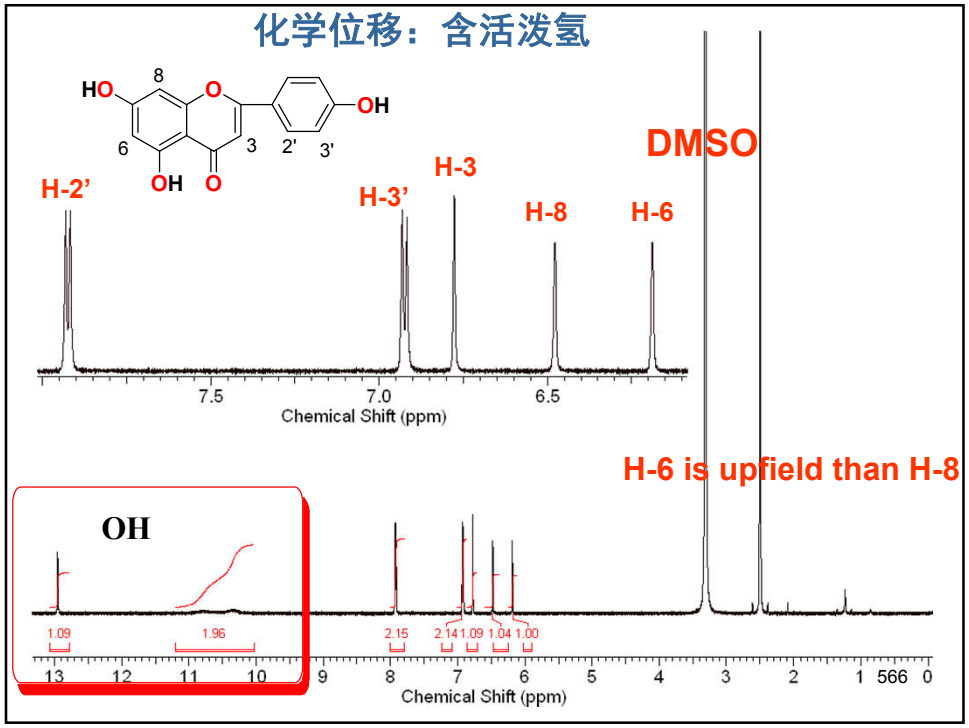
563

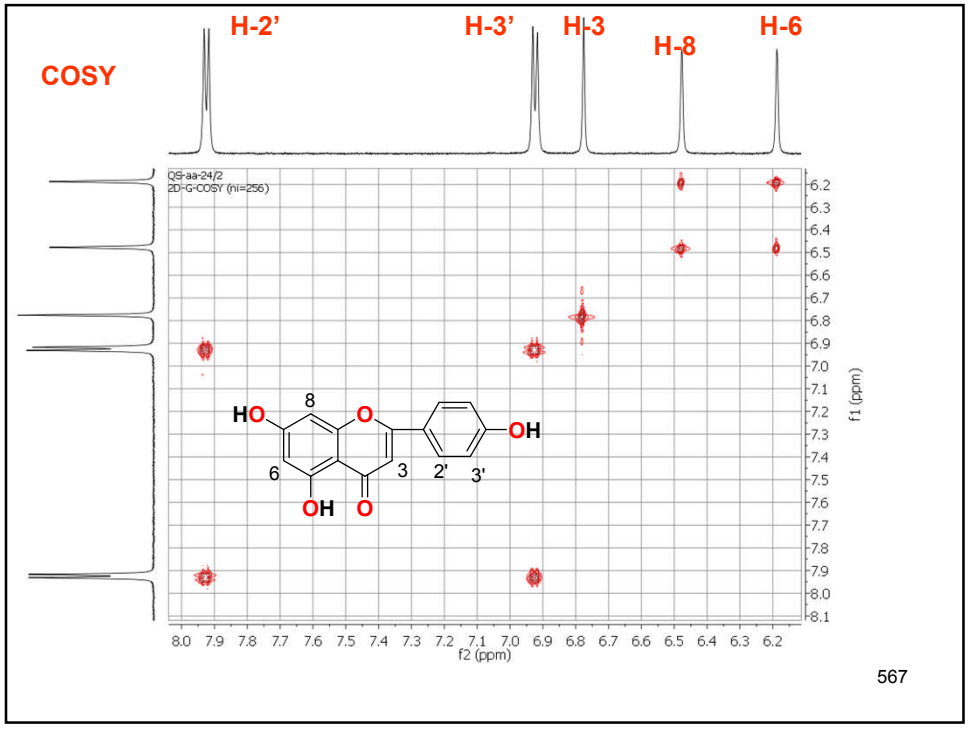
化学位移：SP^2, SP^3， 含杂原子

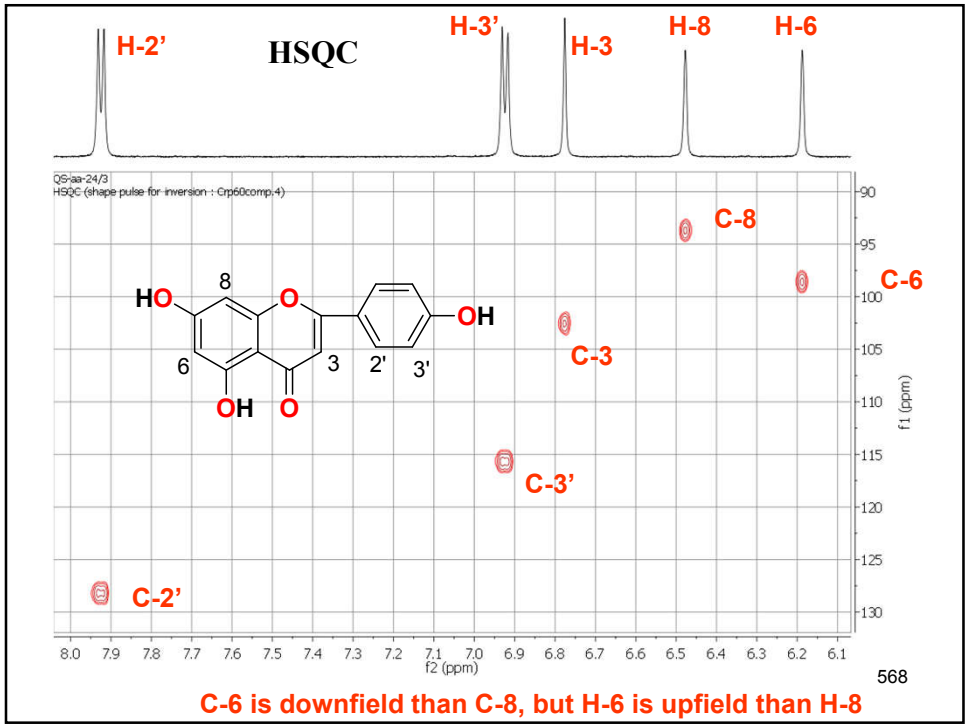


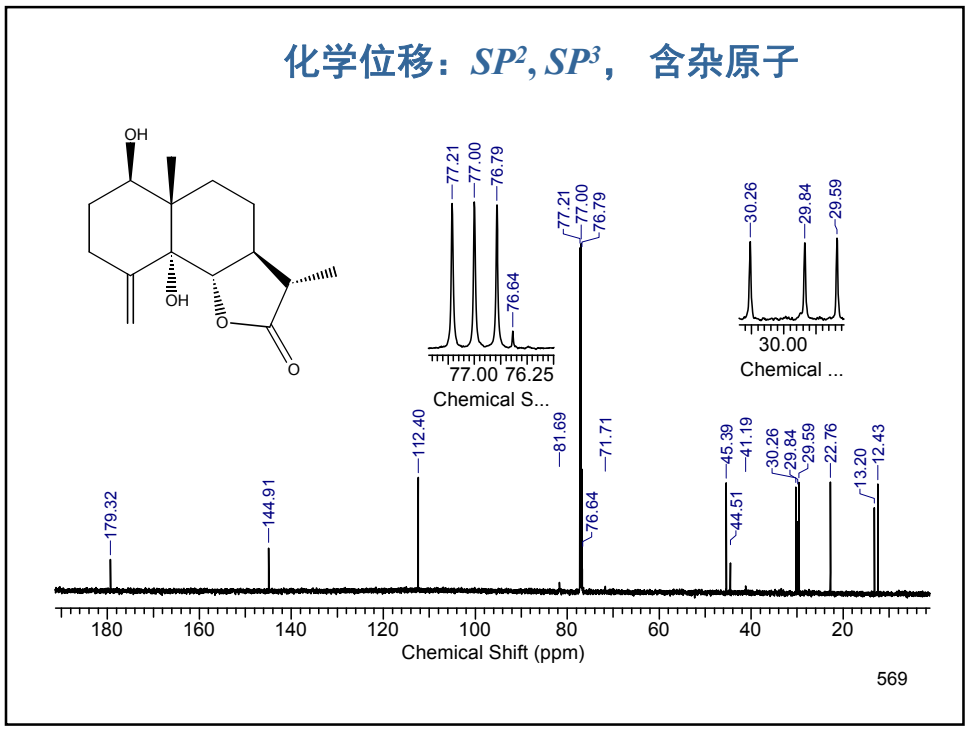
564

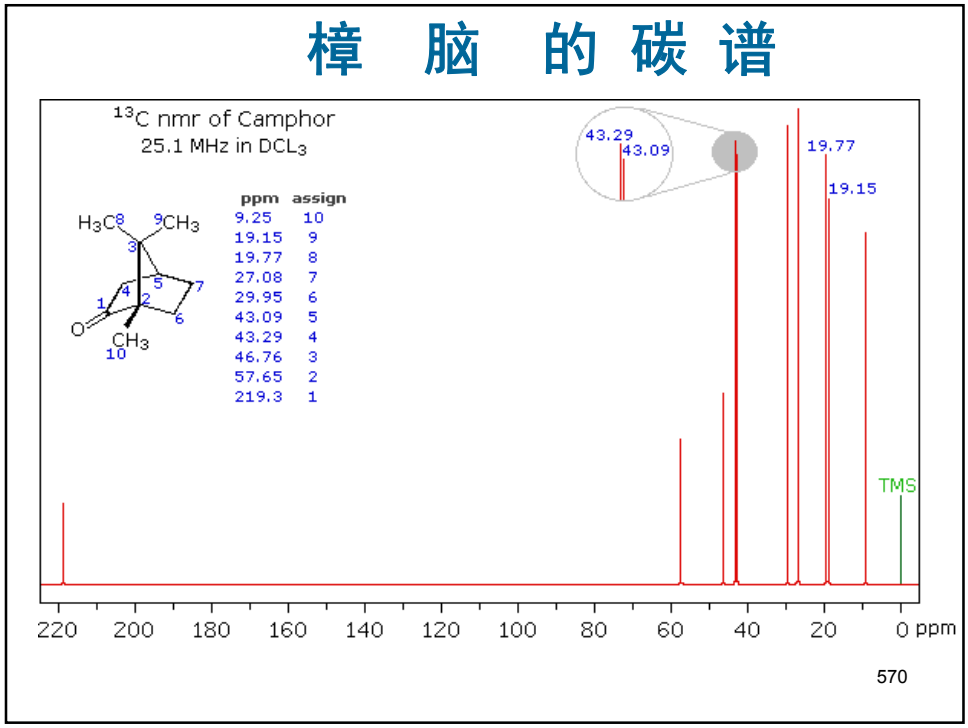

H3CO
O
OCH3
OH
OH
O
C=O
196.75
167.41
163.17
162.70
147.90
146.45
130.96
117.67
114.07
111.96
102.61
94.60
93.79
78.39
55.86
55.65
42.10
39.93
39.79
39.65
39.51
39.37
39.23
39.10
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)
565

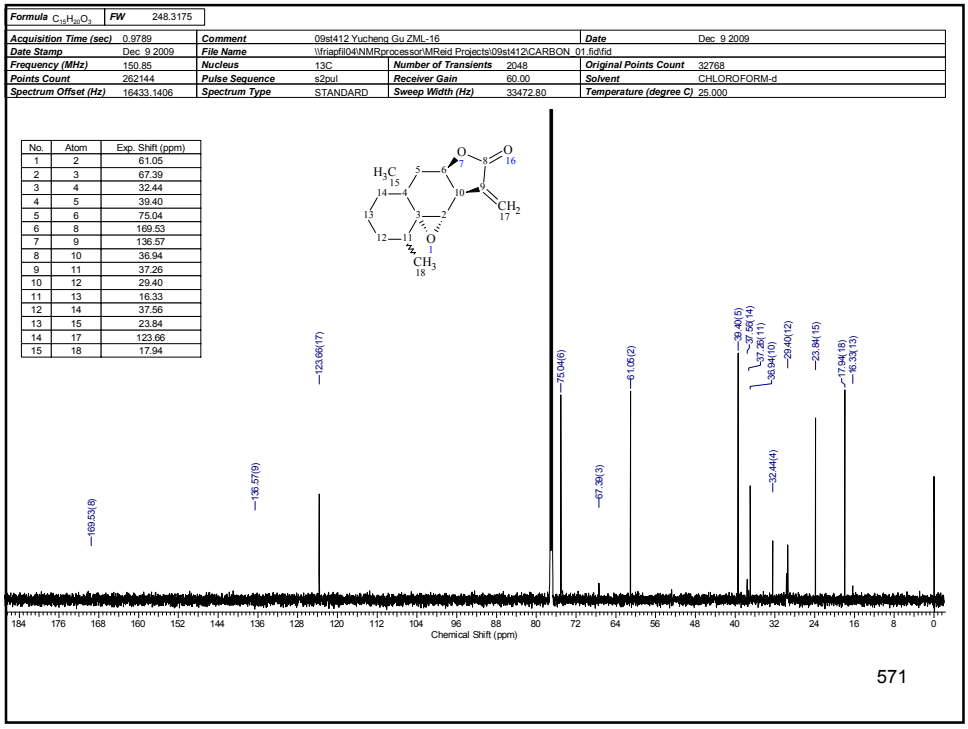

化学位移：含活泼氢
HO
8
O
OH
6
3
2'
3'
OH
O
H-2'
H-3'
H-3
H-8
H-6
DMSO
7.5
7.0
6.5
Chemical Shift (ppm)
H-6 is upfield than H-8
OH
1.09
1.96
2.15
2.14
1.09
1.04
1.00
13
12
11
10
9
8
7
6
5
4
3
2
1
566
0
Chemical Shift (ppm)

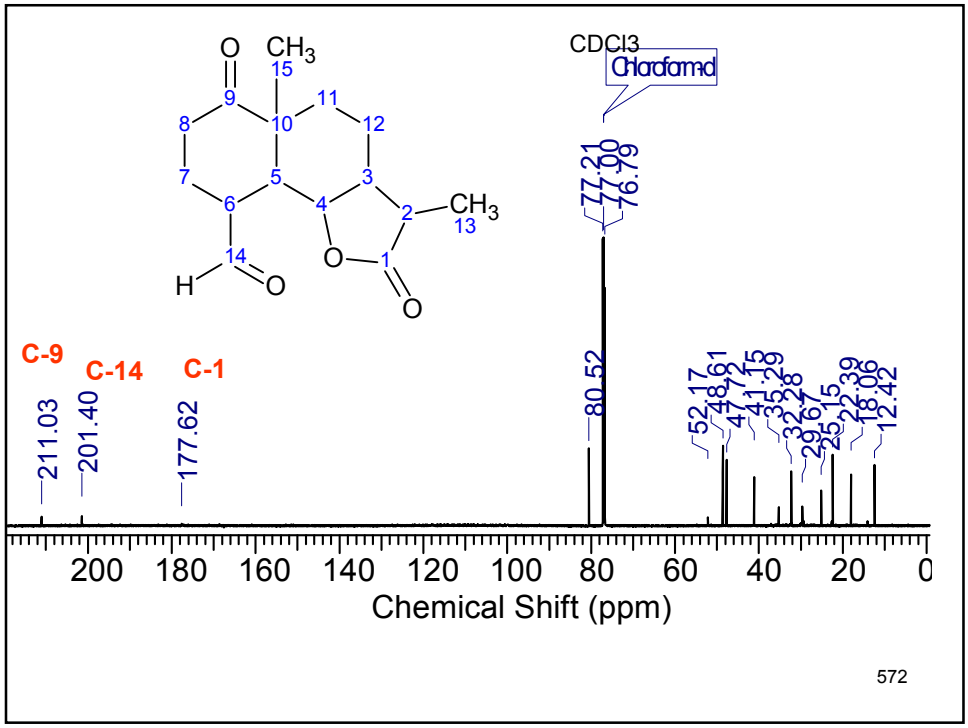

COSY
H-2'
H-3'
H-3
H-8
H-6
QS-aa-24/2
2D-G-COSY (ni=256)
f2 (ppm)
f1 (ppm)
HO
O
OH
OH
O
8
6
3
2'
3'
567

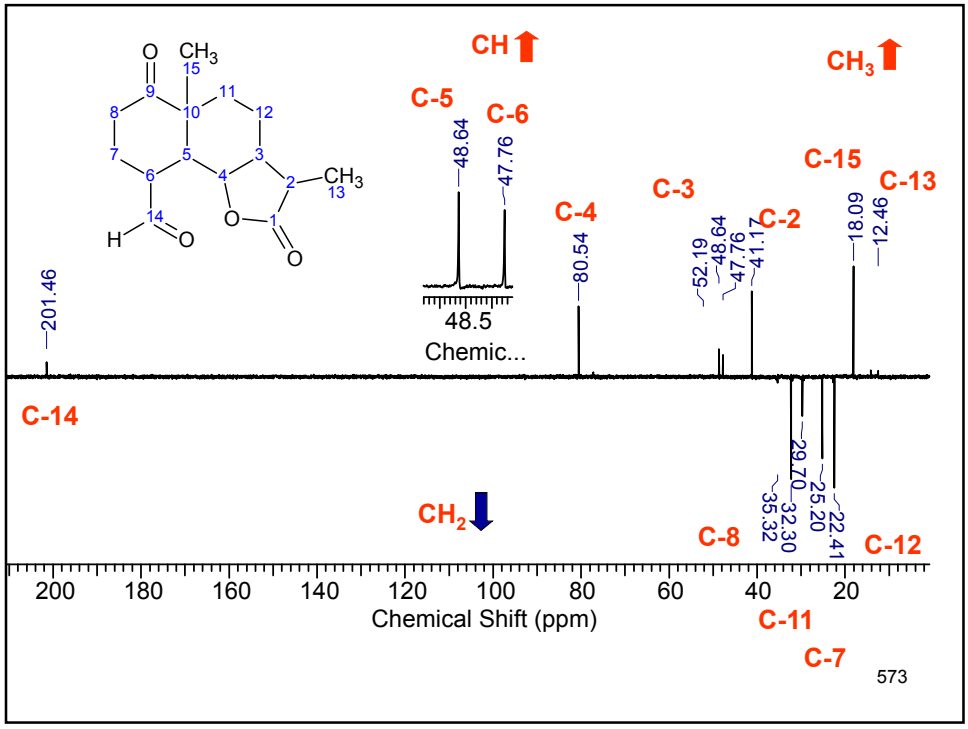

HSQC
H-2'
H-3'
H-3
H-8
H-6
QS-aa-24/3
HSQC (shape pulse for inversion : Crp60comp.4)
C-8
C-6
C-3
C-3'
C-2'
f2 (ppm)
f1 (ppm)
HO
O
OH
OH
O
8
6
3
2'
3'
568
C-6 is downfield than C-8, but H-6 is upfield than H-8

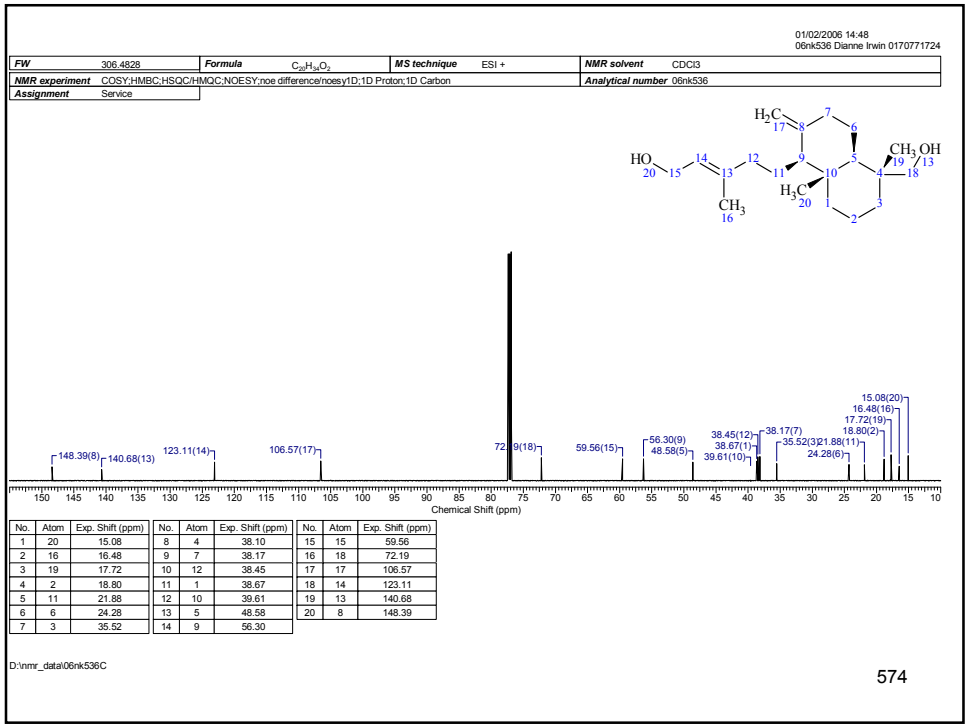

化学位移：SP², SP³， 含杂原子
OH
OH
O
O
77.21
77.00
76.79
76.64
77.00 76.25
Chemical S...
30.26
29.84
29.59
30.00
Chemical ...
179.32
144.91
112.40
81.69
77.21
77.00
76.79
76.64
71.71
45.39
41.19
30.26
29.84
29.59
22.76
13.20
12.43
44.51
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)
569

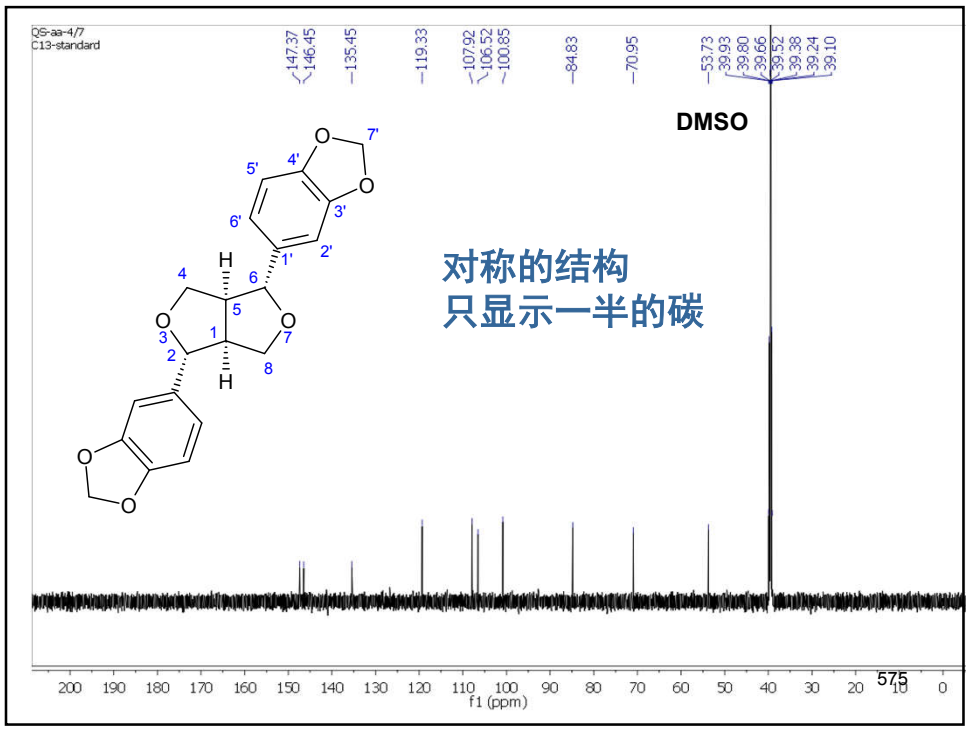

樟 脑 的 碳 谱
13C nmr of Camphor
25.1 MHz in DCL3
ppm assign
9.25 10
19.15 9
19.77 8
27.08 7
29.95 6
43.09 5
43.29 4
46.76 3
57.65 2
219.3 1
H3C
CH3
CH3
O
43.29
43.09
19.77
19.15
TMS
220
200
180
160
140
120
100
80
60
40
20
0 ppm
570

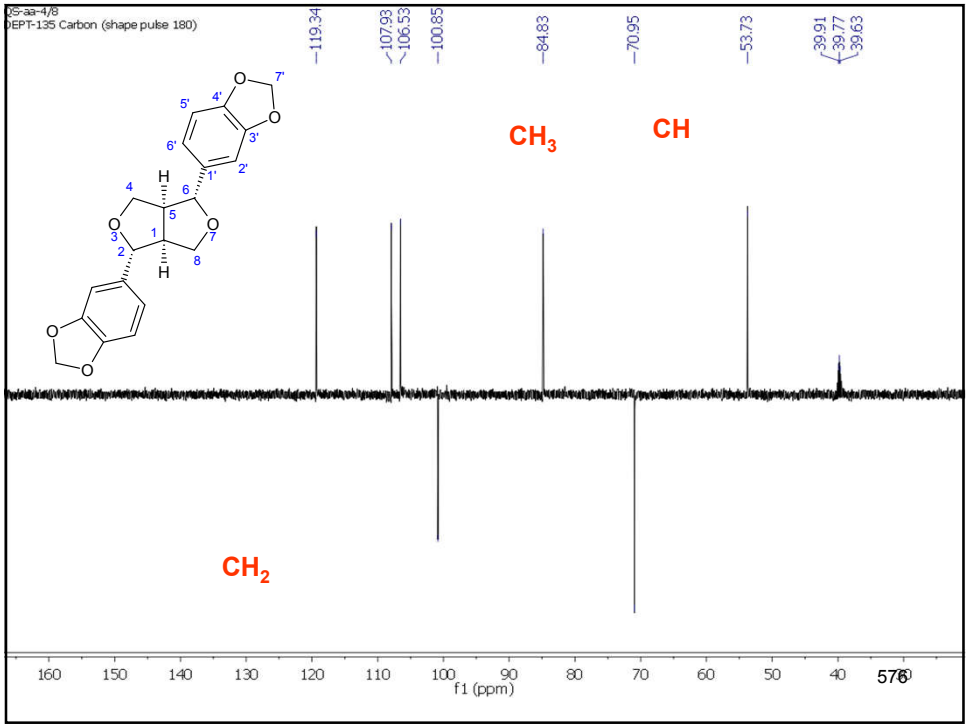

Formula C15H20O3 FW 248.3175
Acquisition Time (sec) 0.9789 Comment 09st412 Yucheng Gu ZML-16 Date Dec 9 2009
Date Stamp Dec 9 2009 File Name \\friapfil04\NMRprocessor\MReid Projects\09st412\CARBON_01.fid\fid
Frequency (MHz) 150.85 Nucleus 13C Number of Transients 2048 Original Points Count 32768
Points Count 262144 Pulse Sequence s2pul Receiver Gain 60.00 Solvent CHLOROFORM-d
Spectrum Offset (Hz) 16433.1406 Spectrum Type STANDARD Sweep Width (Hz) 33472.80 Temperature (degree C) 25.000
No. Atom Exp. Shift (ppm)
1 2 61.05
2 3 67.39
3 4 32.44
4 5 39.40
5 6 75.04
6 8 169.53
7 9 136.57
8 10 36.94
9 11 37.26
10 12 29.40
11 13 16.33
12 14 37.56
13 15 23.84
14 17 123.66
15 18 17.94
169.53(8)
136.57(9)
123.66(17)
75.04(6)
67.39(3)
61.05(2)
39.40(5)
37.56(14)
37.26(11)
36.94(10)
32.44(4)
29.40(12)
23.84(15)
17.94(18)
16.33(15)
Chemical Shift (ppm)
571

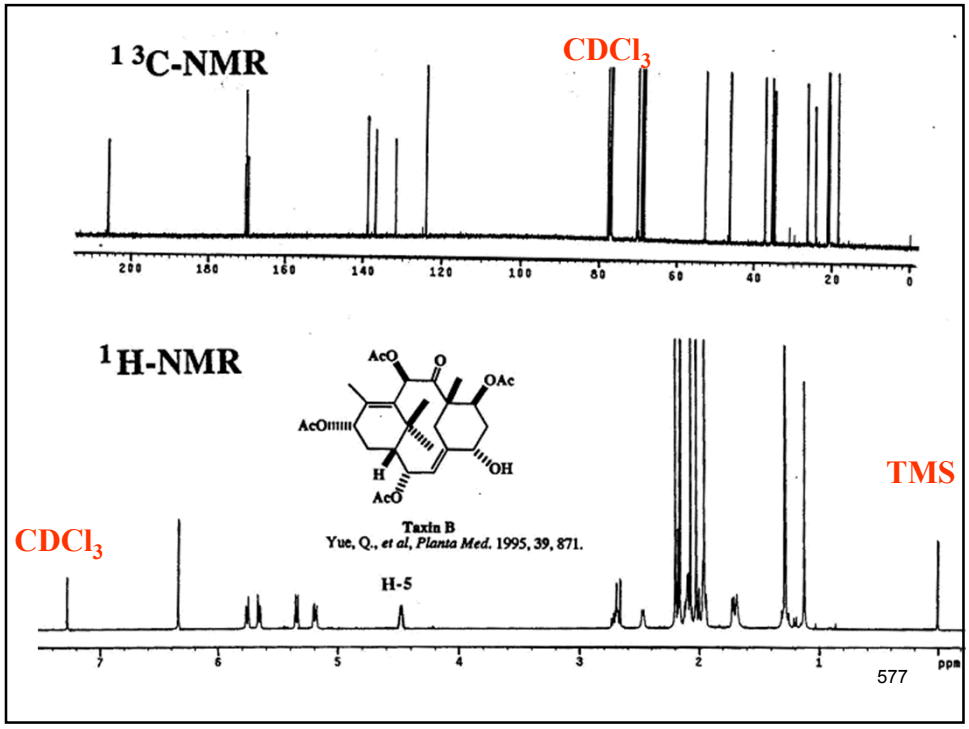

CDCl3
Chloroform-d
77.21
77.00
76.79
80.52
52.17
48.61
47.72
41.15
35.29
32.38
28.67
25.15
22.39
18.06
12.42
C-9
C-14
C-1
211.03
201.40
177.62
Chemical Shift (ppm)
572


CH
CH3
C-5
C-6
C-15
C-13
C-3
C-4
C-2
48.64
47.76
80.54
52.19
48.64
47.76
41.17
18.09
12.46
201.46
48.5
Chemic...
C-14
29.70
32.30
25.20
22.41
35.32
CH2
C-8
C-12
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)
C-11
C-7
573

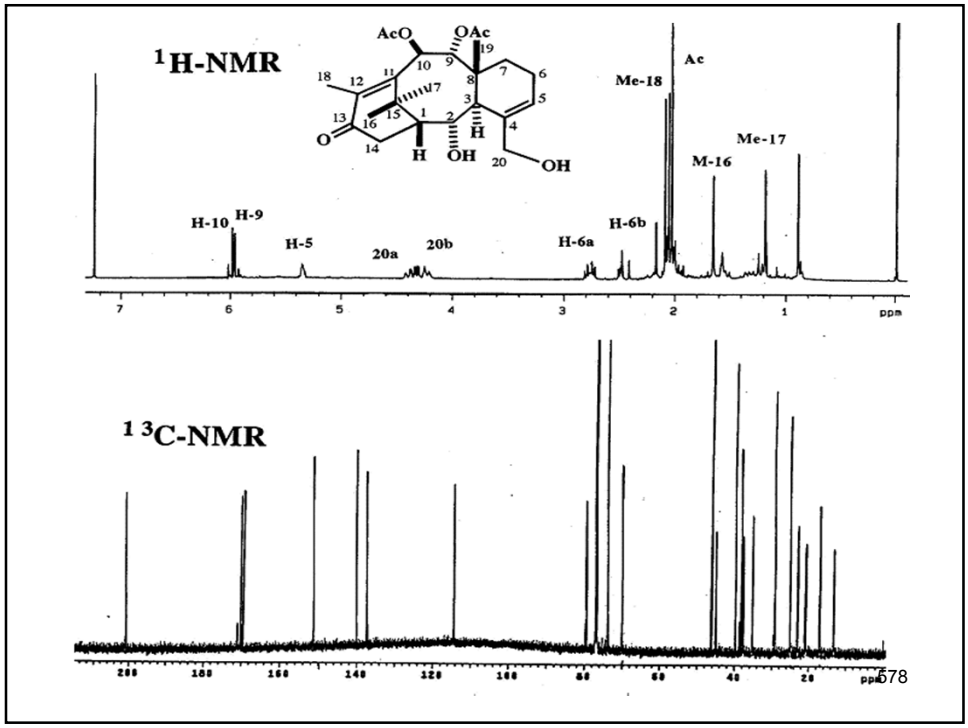

01/02/2006 14:48
06nk536 Dianne Irwin 0170771724
FW 306.4828
Formula C20H34O2
MS technique ESI +
NMR solvent CDCl3
NMR experiment COSY;HMBC;HSQC/HMQC;NOESY;noe difference/noesy1D;1D Proton;1D Carbon
Analytical number 06nk536
Assignment Service
148.39(8)
140.68(13)
123.11(14)
106.57(17)
72.19(18)
59.56(15)
56.30(9)
48.58(5)
38.45(12)
38.67(1)
39.61(10)
38.17(7)
35.52(3)
21.88(11)
24.28(6)
18.80(2)
17.72(19)
16.48(16)
15.08(20)
Chemical Shift (ppm)
No. Atom Exp. Shift (ppm)
1 20 15.08
2 16 16.48
3 19 17.72
4 2 18.80
5 11 21.88
6 6 24.28
7 3 35.52
8 4 38.10
9 7 38.17
10 12 38.45
11 1 38.67
12 10 39.61
13 5 48.58
14 9 56.30
15 15 59.56
16 18 72.19
17 17 106.57
18 14 123.11
19 13 140.68
20 8 148.39
D:\nmr_data\06nk536C
574


QS-aa-4/7
C13-standard
147.37
146.45
135.45
119.33
107.92
106.52
100.85
84.83
70.95
53.73
39.93
39.80
39.66
39.52
39.38
39.24
39.10
DMSO
对称的结构
只显示一半的碳
575
f1 (ppm)

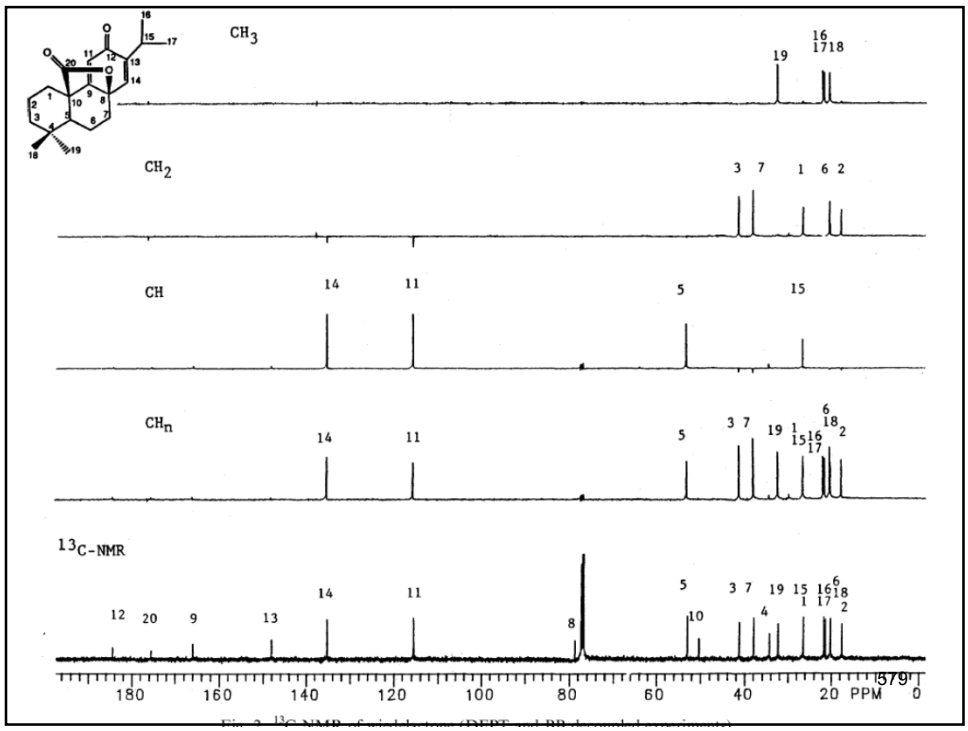

QS-aa-4/8
DEPT-135 Carbon (shape pulse 180)
119.34
107.93
106.53
100.85
84.83
70.95
53.73
39.91
39.77
39.63
CH3
CH
CH2
576
f1 (ppm)

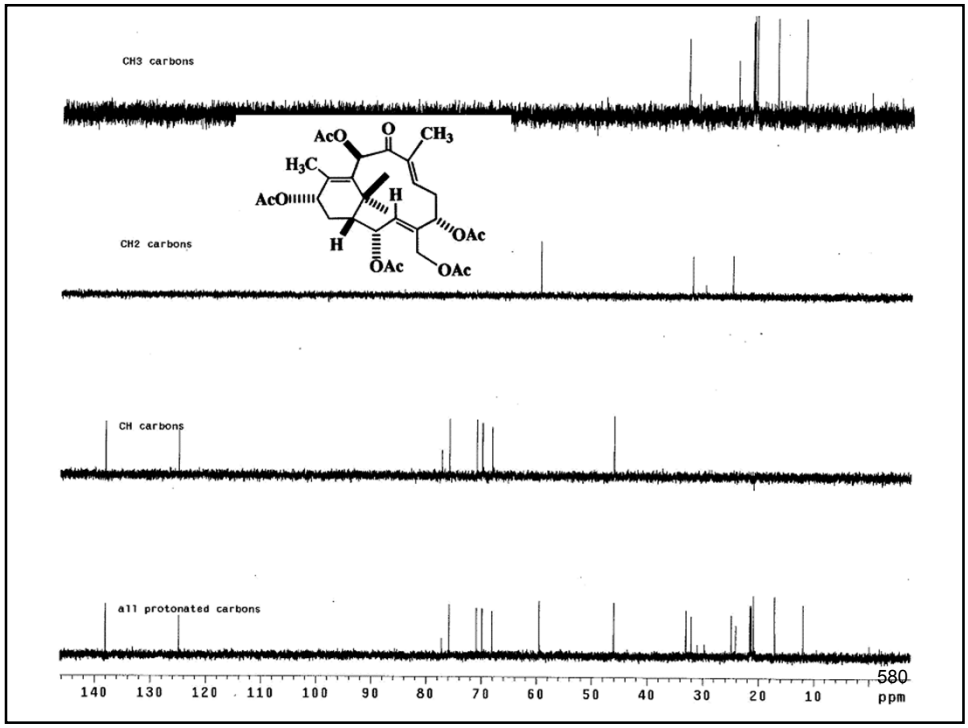

13C-NMR
CDCl3
1H-NMR
AcO
OAc
AcO
OH
H
AcO
Taxin B
Yue, Q., et al, Planta Med. 1995, 39, 871.
TMS
CDCl3
H-5
ppm

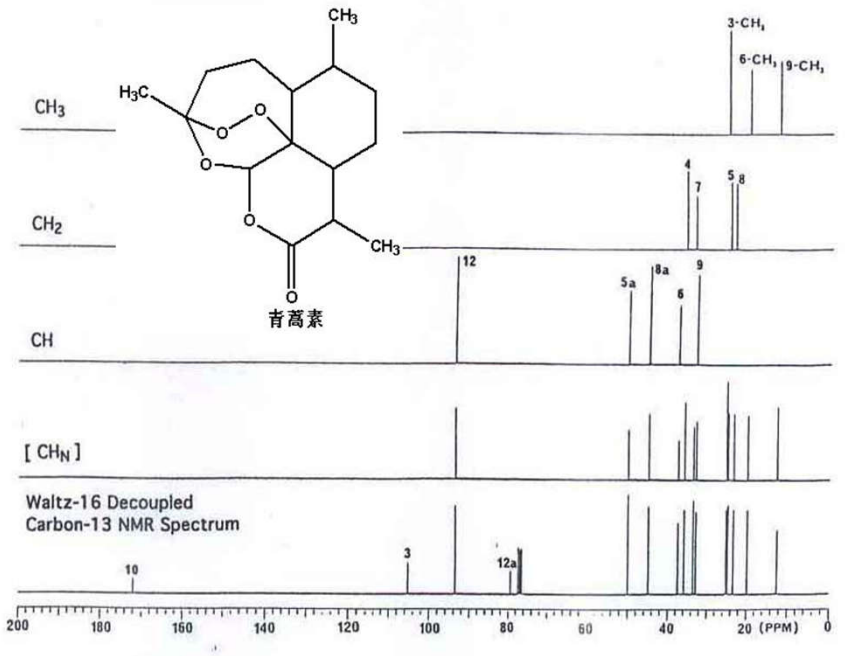
577


1H-NMR
AcO
OAc
OH
OH
Me-18
Ac
M-16
Me-17
H-10
H-9
H-5
20a
20b
H-6a
H-6b
ppm
13C-NMR
ppm

578

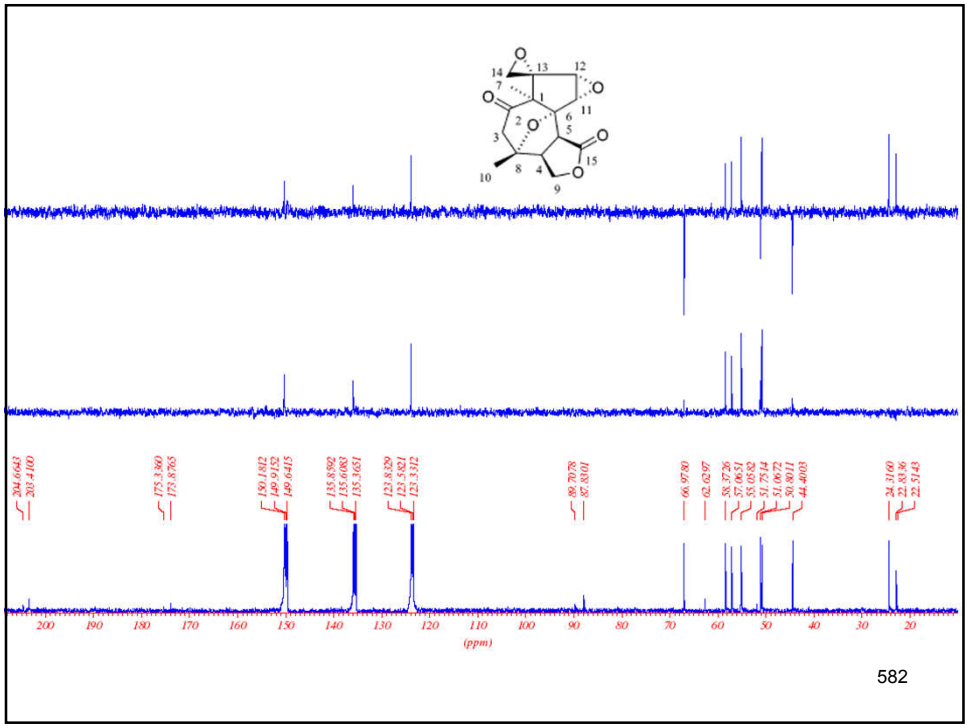

CH3
CH2
CH
CHn
13C-NMR
19
16 17 18
3 7 1 6 2
14 11 5 15
14 11 5 3 7 19 1 15 16 17 6 18 2
12 20 9 13 14 11 8 5 10 3 7 4 19 15 1 16 17 6 18 2
180 160 140 120 100 80 60 40 20 PPM 0
579


CH3 carbons
CH2 carbons
CH carbons
all protonated carbons
AcO
O
CH3
H3C
AcO
H
H
OAc
OAc
OAc
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
580



581

Figure 12.17. Edited DEPT ^{13}C spectrum of artemisinin. (Contributed by David Lankin and Geoffrey Cordell).



582

核磁共振碳谱的解析

解析步骤：

1）区分出杂质峰、溶剂峰，不要遗漏季碳的谱线；

2）计算不饱和度

3）分子对称性的分析：若谱线数目少于元素组成式中碳原子的数目，说明分子有一定的对称性；

4）碳原子级数的确定（活泼氢数目的确定）；

5）碳原子δ值的分区：饱和区、不饱和区、杂原子区、羰基区

6）推出结构单元，组合可能的结构式；

7）对推出的结构进行碳谱指认。

583

核磁共振碳谱的解析

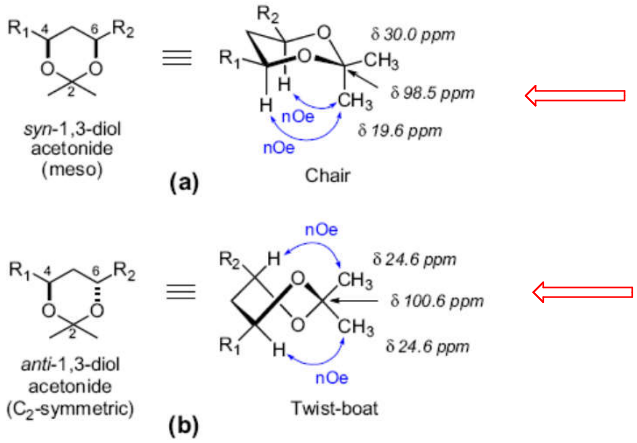


Fig. 1. Conformations, chemical shifts, and NOES for (a) syn-1,3-diol acetonide (SDA) and (b) anti-1,3-diol acetonide (ADA).

584

- **The meso-like syn-1,3-diol acetonide (SDA), adopts a chair 1,3-dioxolane conformation with axial and equatorial methyl groups. The anti-1,3-diol acetonide (ADA) with C2-like symmetry, prefers the twist-boat conformation to minimize 1,3-diaxial interactions; and the methyl groups are almost equivalent. In the SDA, the axial and equatorial methyl groups resonate atwd 30 ppm and wd 20 ppm, respectively. In the ADA case, the methyl group chemical shifts are almost identical to each other (wd 25 ppm). As the size difference of substituents at C4 and C6 increase, the 1,3-dioxane ring tends to adopt a chair conformation (Fig. 1). It should be noted that the symmetry elements in 1,2-diol acetonides are also useful for assignment purposes.**

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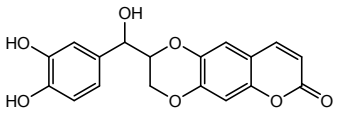
核磁共振二维谱

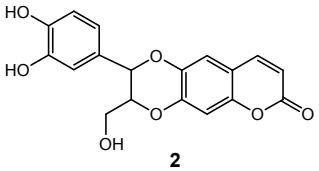
2D NMR Spectrum

586

如何区别下列两个化合物



1



2

猫眼草素-有第三中可能的结构吗？

猫眼大戟
Euphorbia lunulata

异核位移相关谱

- C—H COSY 是^{13}C 和^{1}H 核之间的位移相关谱。它反映了^{13}C 和^{1}H 核之间的关系。它又分为直接相关谱和远程相关谱，直接相关谱是把直接相连的^{13}C 和^{1}H 核关联起来，矩形的二维谱中间的峰称为交叉峰（ cross peak）或相关峰（correlated peak），反映了直接相连的^{13}C 和^{1}H 核，在此图谱中季碳无相关峰。
- 远程相关谱则是将相隔两至四根化学键的^{13}C 和^{1}H 核关联起来，甚至能跨越季碳、杂原子等，交叉峰或相关峰比直接相关谱中多得多，因而对于帮助推测和确定化合物的结构非常有用。

588

异核位移相关谱

- 在异核位移相关谱测试技术上又有两种方法，一种是对异核（非氢核）进行采样，这在以前是常用的方法，所测得的图谱称为“C，H COSY”或长程“C，H COSY”、COLOC（远程^{13}C—^{1}H化学位移相关谱，Correlation Spectroscopy Via Long Rang Coupling）。
- 因是对异核进行采样，故灵敏度低，要想得到较好的信噪比必须加入较多的样品，累加较长的时间。

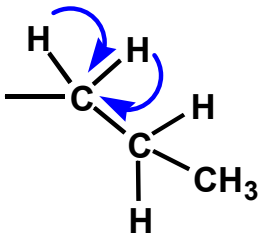
589

单键的异核位移相关谱

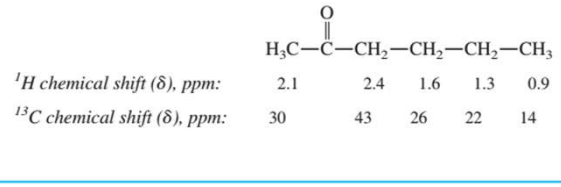
- 另一种是对氢核进行采样，这种方法是目前常用的方法，所得的图谱为：
- HMQC（^{1}H 检测的异核多量子相干实验，^{1}H Detected Heteronuclear Muliple Quantum Coherence）
- HSQC（^{1}H 检测的异核单量子相干实验，^{1}H Detected Heteronuclear Single Quantum Coherence）谱。
- 由于是对氢核采样，故对减少样品用量和缩短累加时间很有效果。
- 皂苷分子中含有多个糖时，除糖的端基碳氢信号外，糖的其他碳氢信号均出现在同一区域，重叠严重，归属困难。

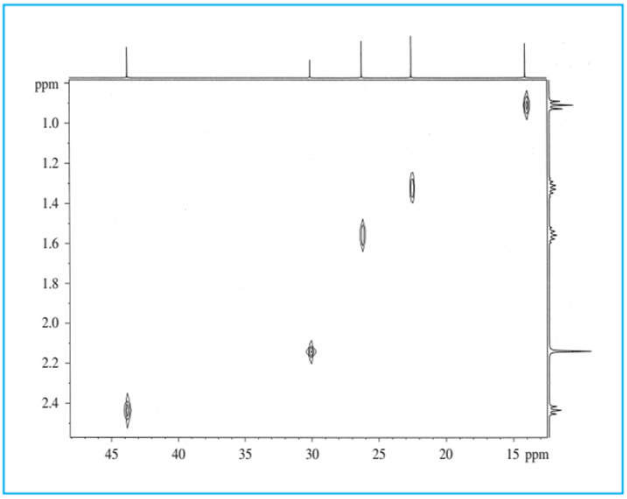
590

HMQC (Heteronuclear Multiple Quantum Coherence) Direct proton-carbon coupling: 1*J* assign CH, CH_2 and CH_3 carbon signals

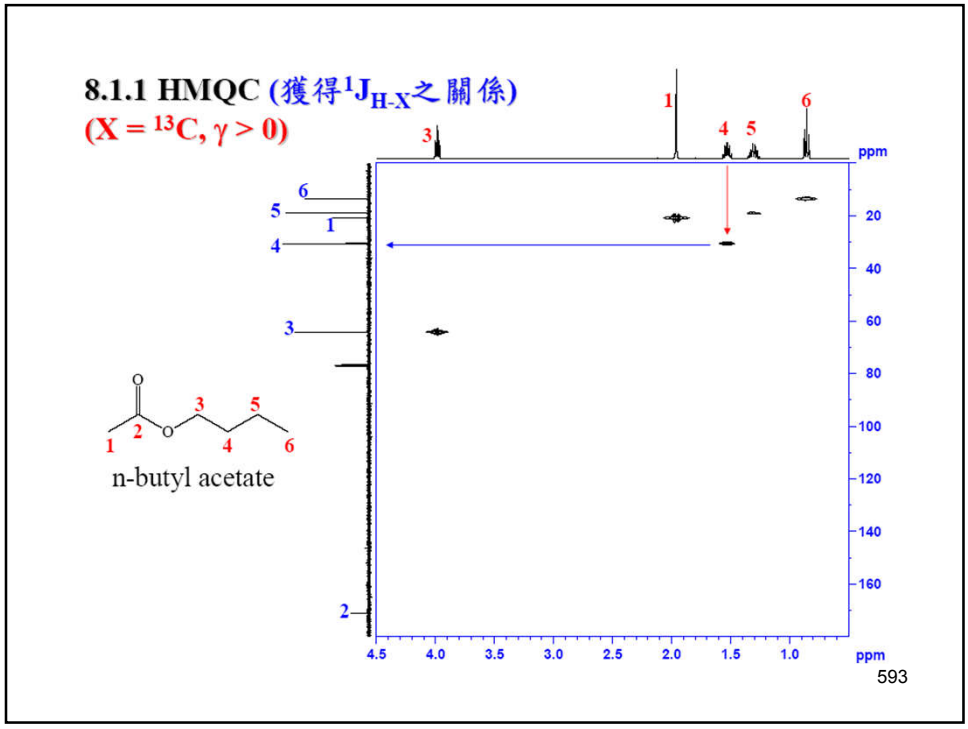


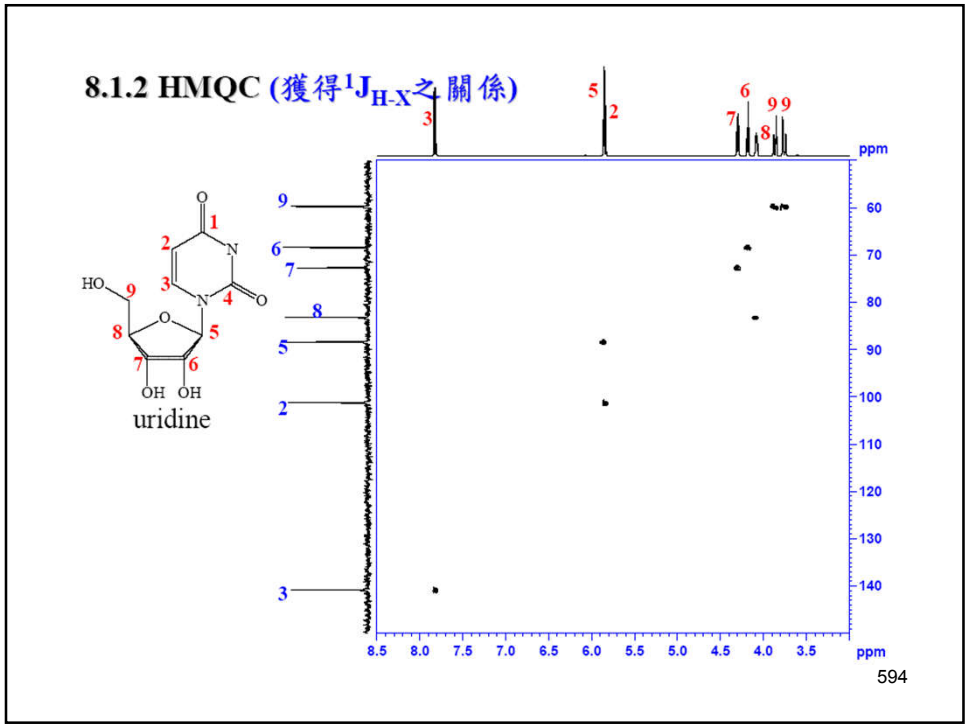
591

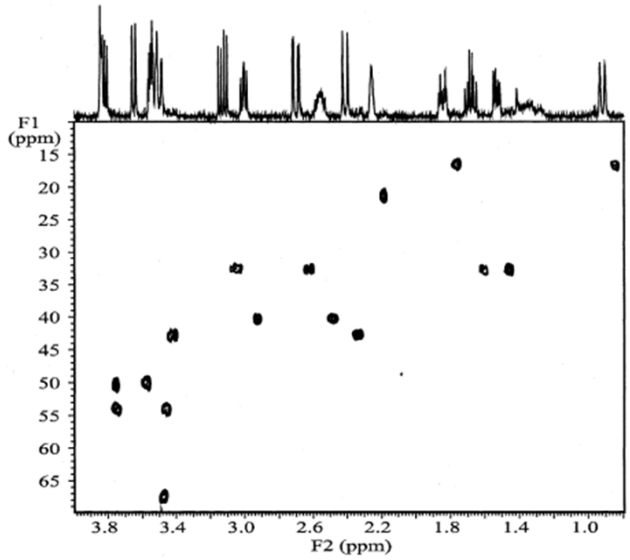




592


8.1.1 HMQC (獲得$^1J_{H-X}$之關係)
(X = ^{13}C, γ > 0)
n-butyl acetate
ppm
593

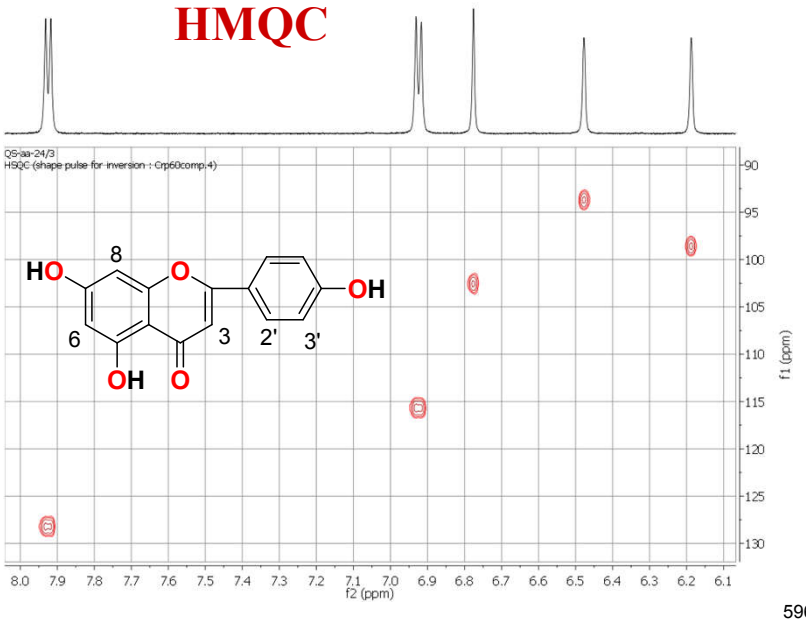

8.1.2 HMQC (獲得$^1J_{H-X}$之關係)
uridine
ppm
594



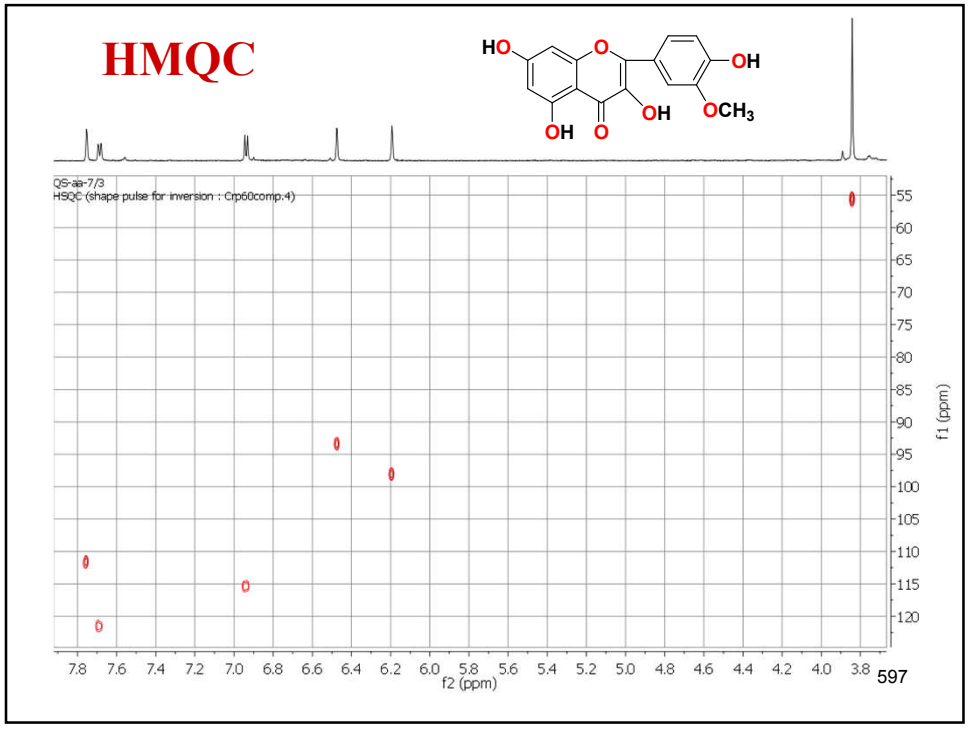
HMQC of 40 µg of Strychnine in 160 µl benzene 500 MHz

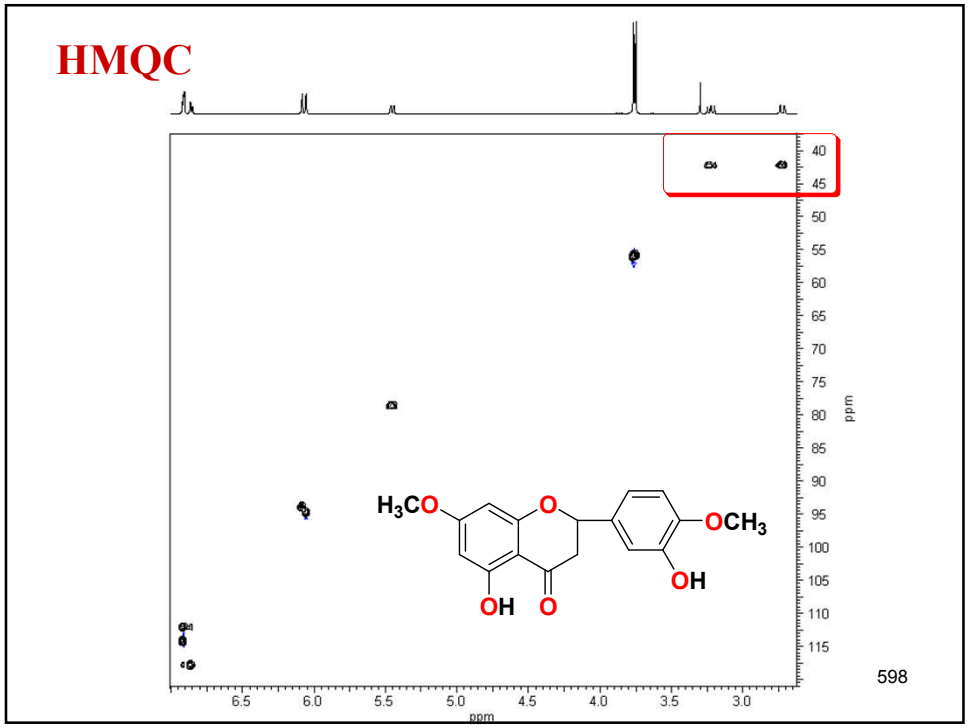
595

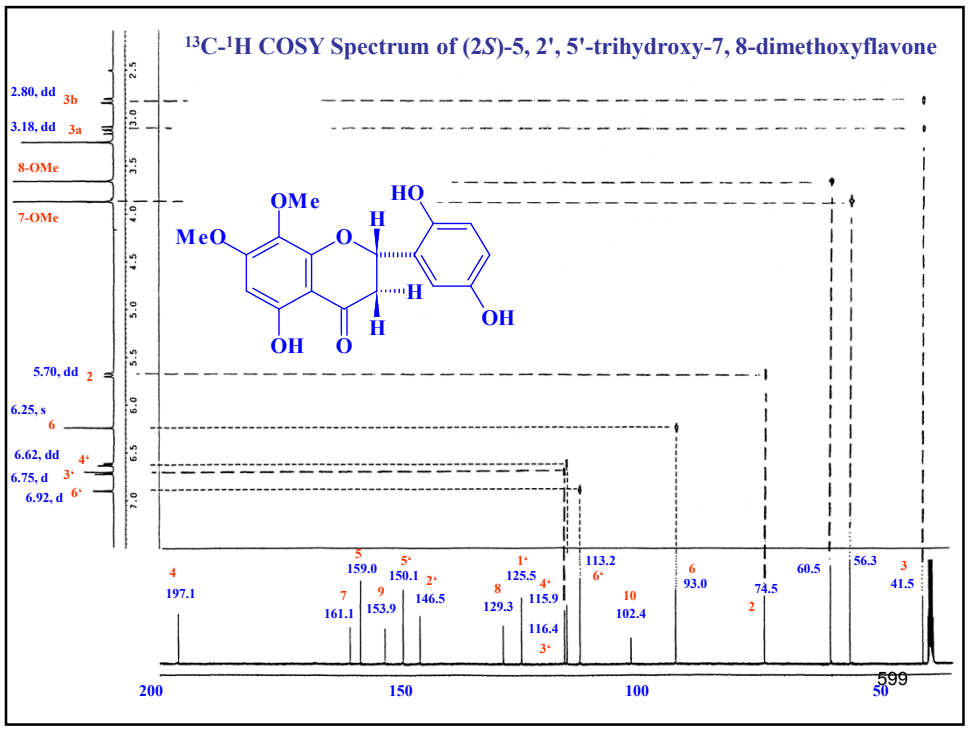
HMQC

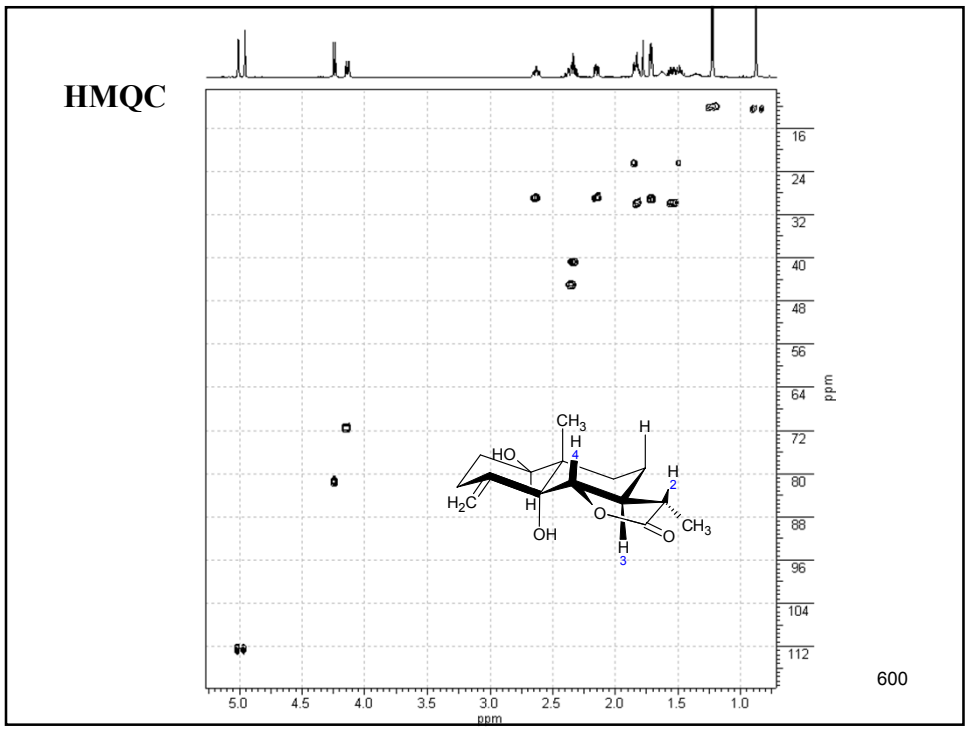


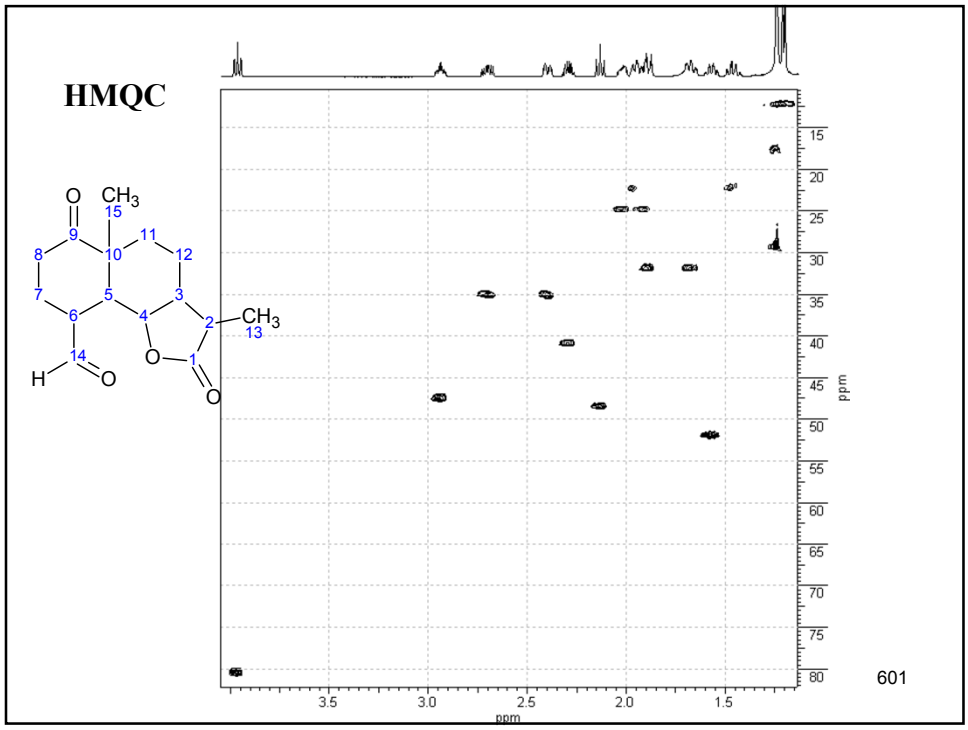
596

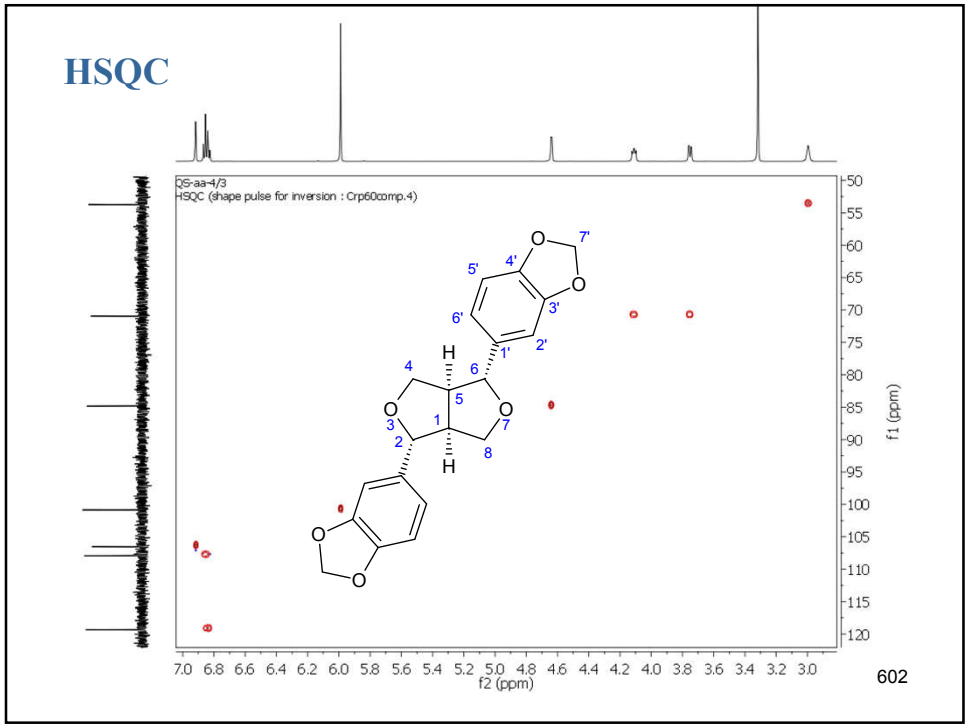

HMQC
HO
O
OH
OH
OH
O
OCH3
QS-aa-7/3
HSQC (shape pulse for inversion : Cmp60comp:4)
f1 (ppm)
f2 (ppm)
597

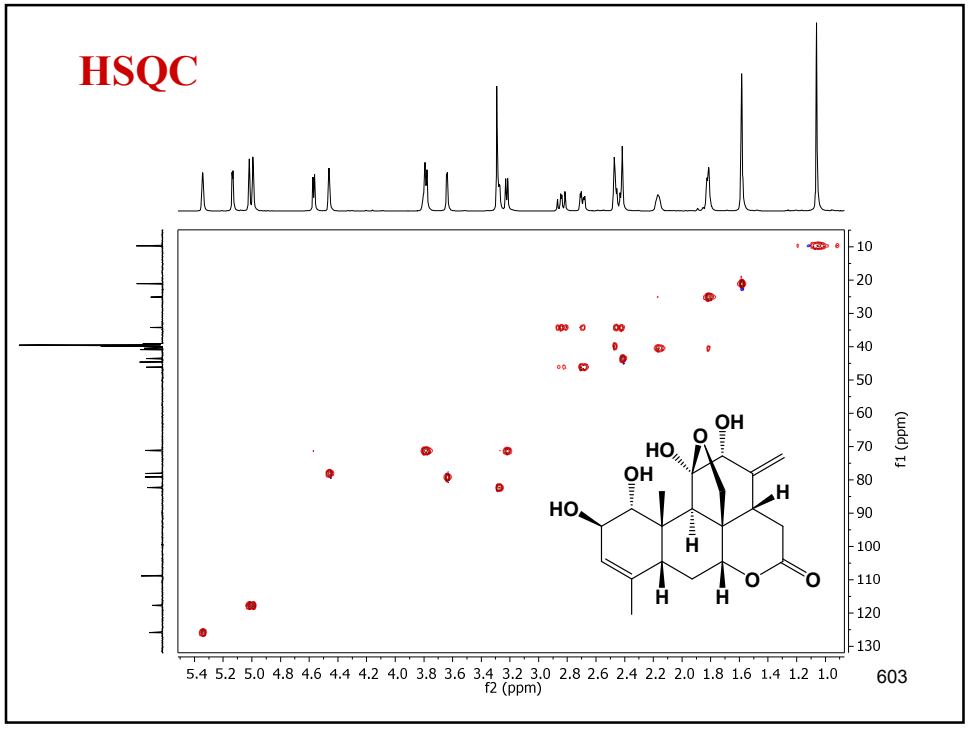

HMQC
H3CO
O
OCH3
OH
OH
O
ppm
598

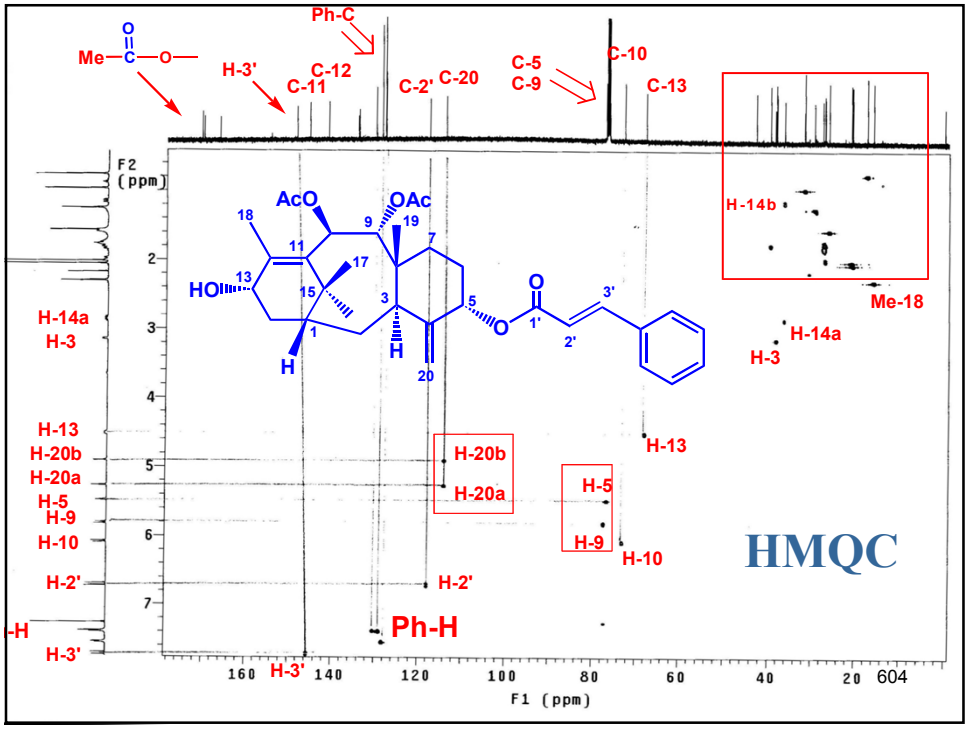

^{13}C-^{1}H COSY Spectrum of (2*S*)-5, 2', 5'-trihydroxy-7, 8-dimethoxyflavone
2.80, dd 3b
3.18, dd 3a
8-OMe
7-OMe
5.70, dd 2
6.25, s 6
6.62, dd 4'
6.75, d 3'
6.92, d 6'
OMe
MeO
O
H
HO
OH
OH
O
4 197.1
5 159.0
7 161.1
9 153.9
5' 150.1
2' 146.5
8 129.3
1' 125.5
4' 115.9
116.4 3'
113.2 6'
10 102.4
6 93.0
74.5 2
60.5
56.3
3 41.5
200
150
100
50
599

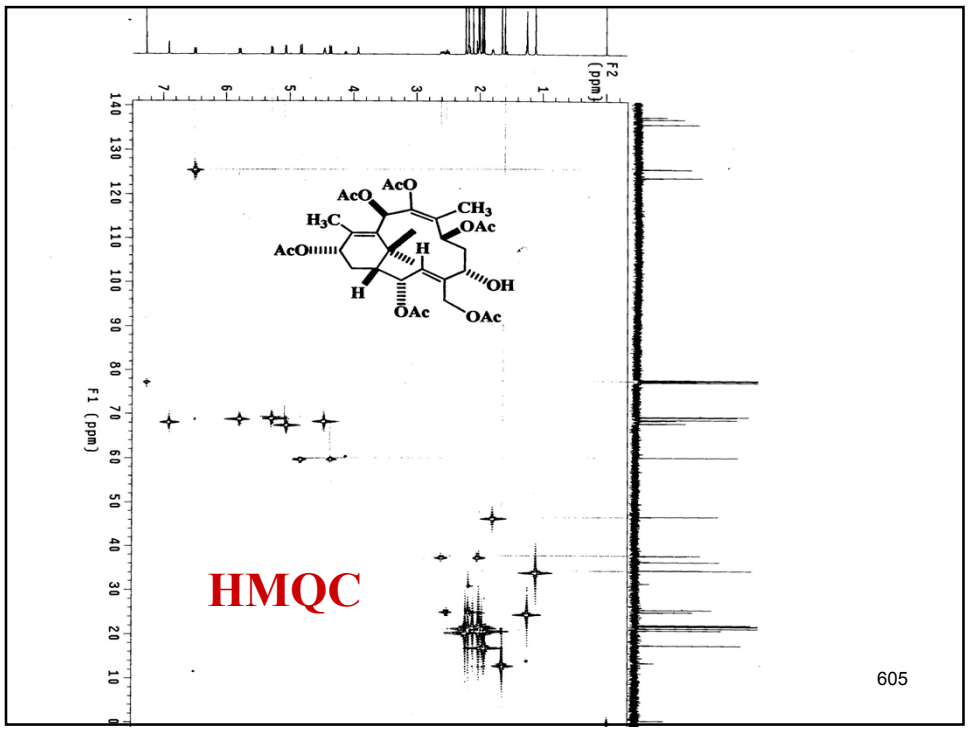

HMQC
16
24
32
40
48
56
64
72
80
88
96
104
112
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
CH3
H
HO
4
H2C
H
OH
H
2
O
CH3
O
H
3
600

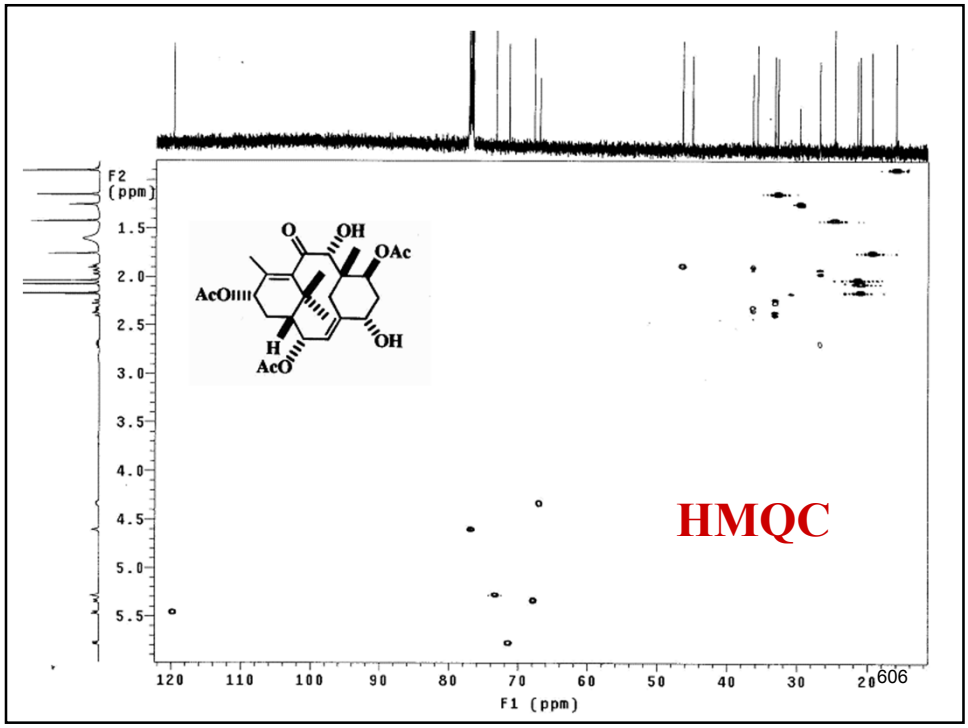

HMQC
O
CH3
15
9
11
8
10
12
7
5
3
6
4
2
CH3
13
14
O
1
H
O
O
ppm
3.5
3.0
2.5
2.0
1.5
ppm
601

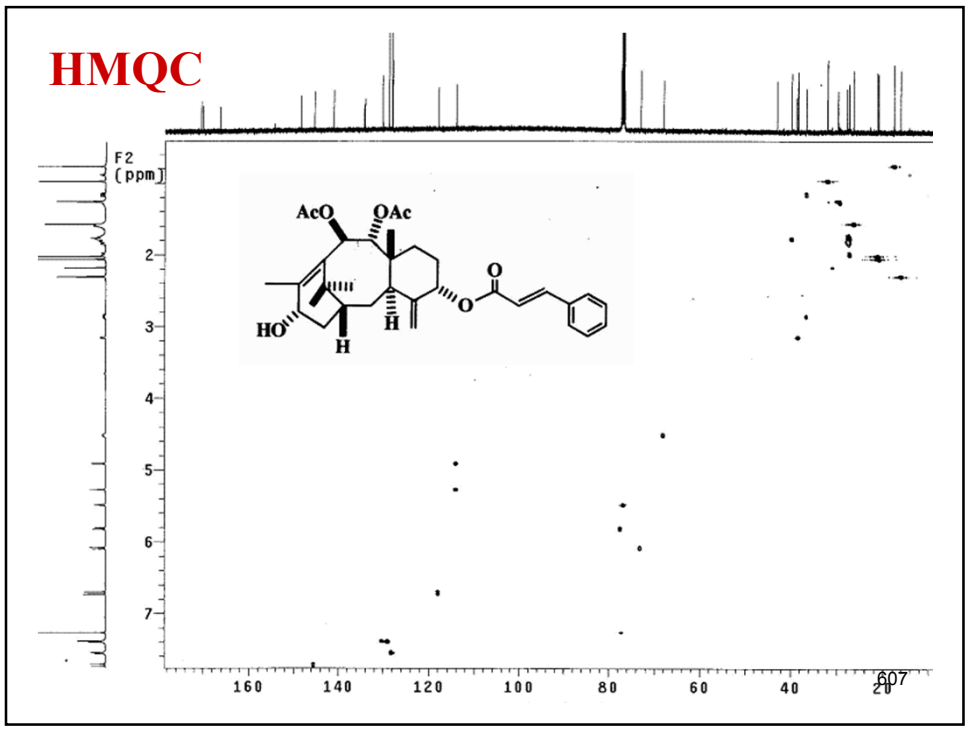

HSQC
QS-aa-4/3
HSQC (shape pulse for inversion : Crp60comp.4)
O
7'
5'
4'
O
6'
3'
2'
1'
H
4
6
5
O
3
1
O
7
2
8
H
O
O
f1 (ppm)
f2 (ppm)
7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
602


HSQC
f1 (ppm)
f2 (ppm)
603


Ph-C
Me—C—O
H-3'
C-12
C-11
C-2'
C-20
C-5
C-9
C-10
C-13
H-14b
Me-18
H-14a
H-3
AcO
OAc
HO
H-14a
H-3
H-13
H-20b
H-20a
H-5
H-9
H-10
H-2'
H-3'
H-20b
H-20a
H-5
H-9
H-10
H-13
H-2'
Ph-H
HMQC
F2 (ppm)
F1 (ppm)
604


HMQC
605


HMQC
606

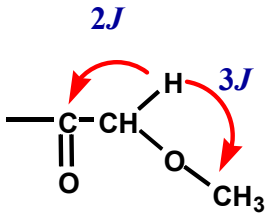


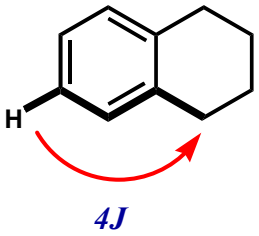
远程异核位移相关谱

- **HMBC**（^{1}H 检测的异核多键相关实验，^{1}H Detected Heteronuclear Muliple Bone Correlation 或 Long Range Heteronuclear Multiple Quantum Coherencel）谱：反映的是相隔2个和3个键的碳氢之间的相关信息，而中间隔的原子可以是碳，也可以是氧、氮等其他杂原子。应用HMBC谱可以较容易地确定苷分子中糖和糖以及糖和甘元之间的连接位置。
- 由于是对氢核采样，故对减少样品用量和缩短累加时间很有效果。

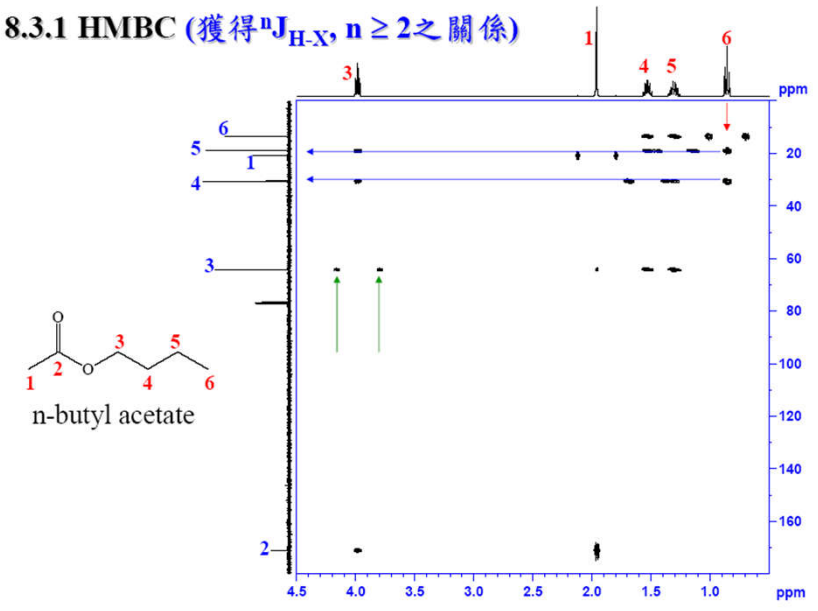
608

HMBC (Hetero-nuclear Multiple Bond Correlation) Coupling between protons and carbons that are more distant that one bond away assign quaternary carbons.

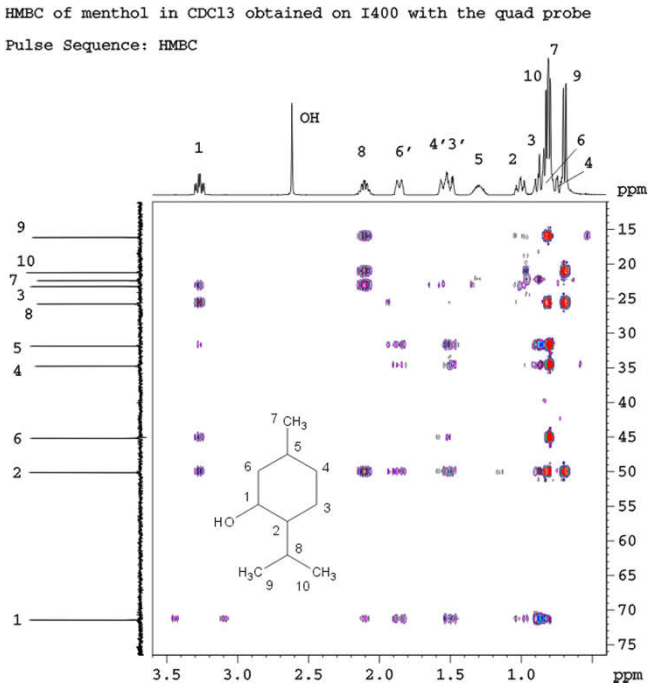




609

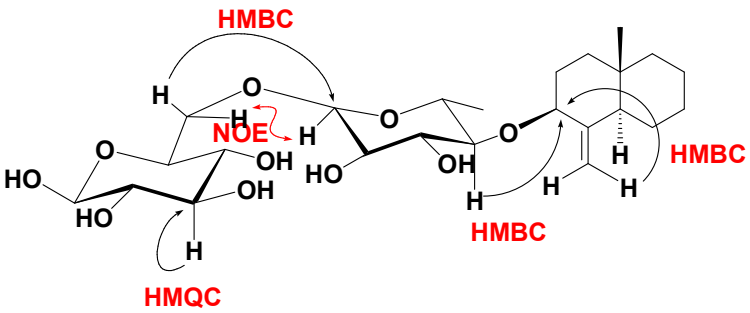


610

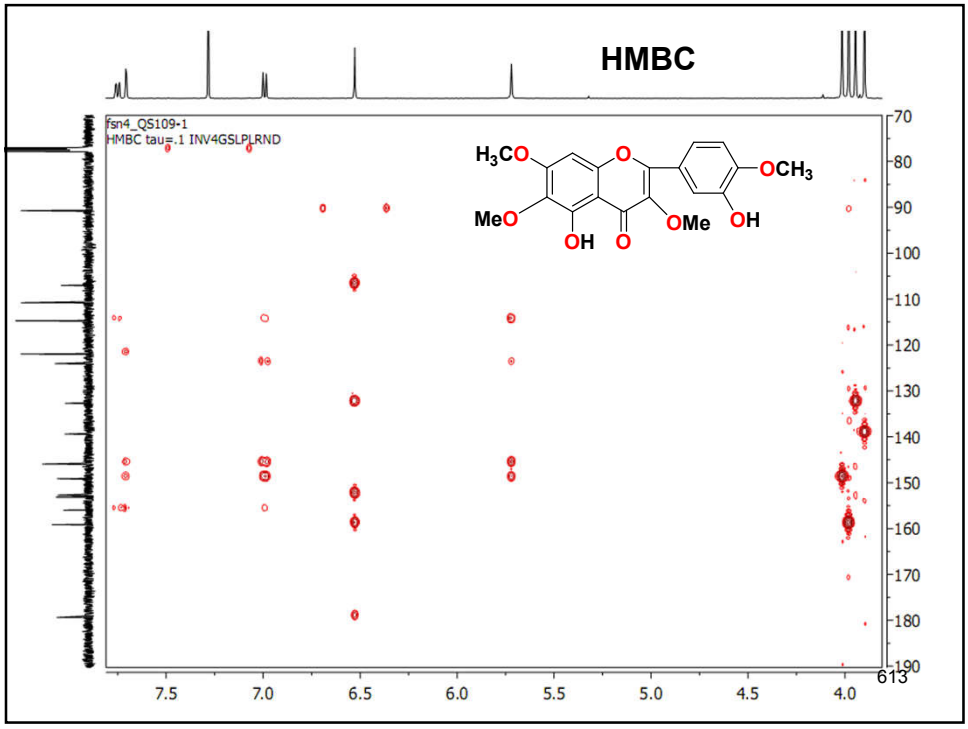


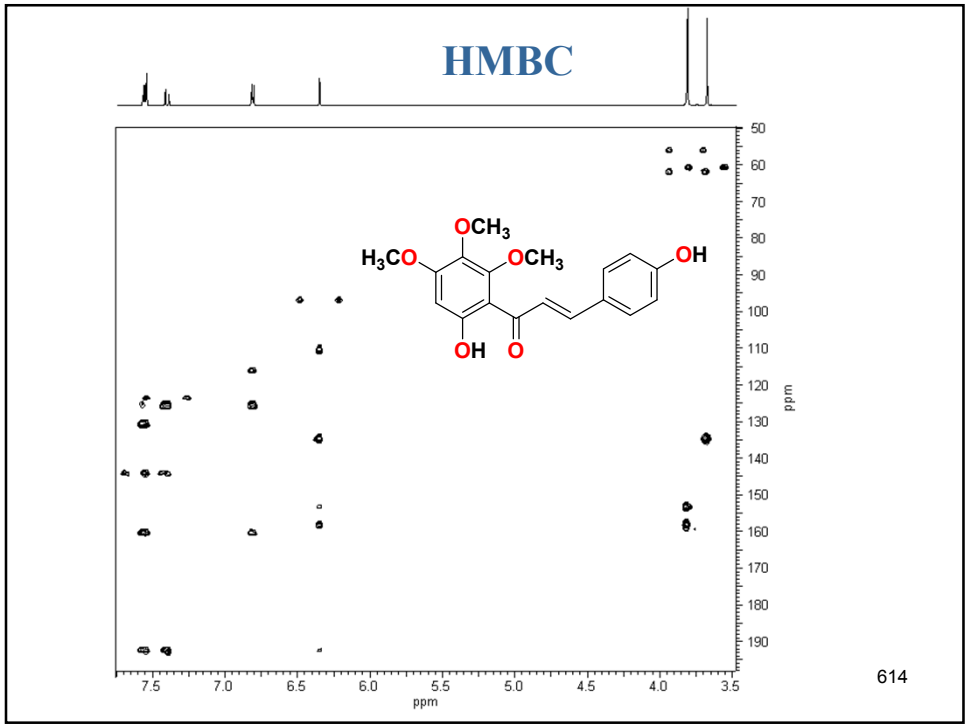
611

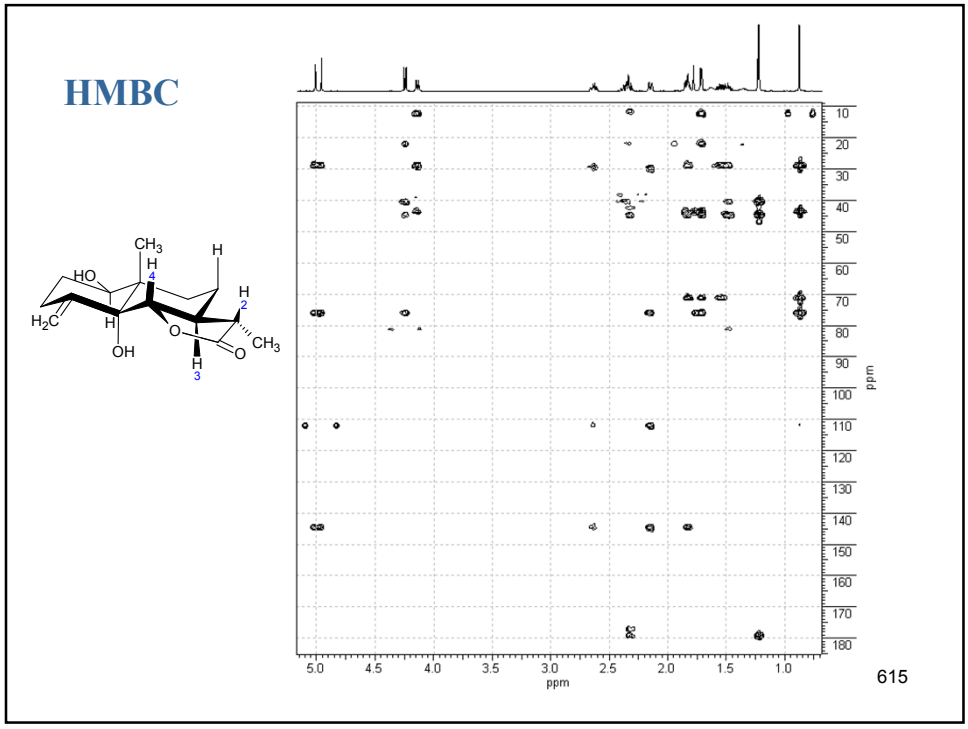
远程异核位移相关谱

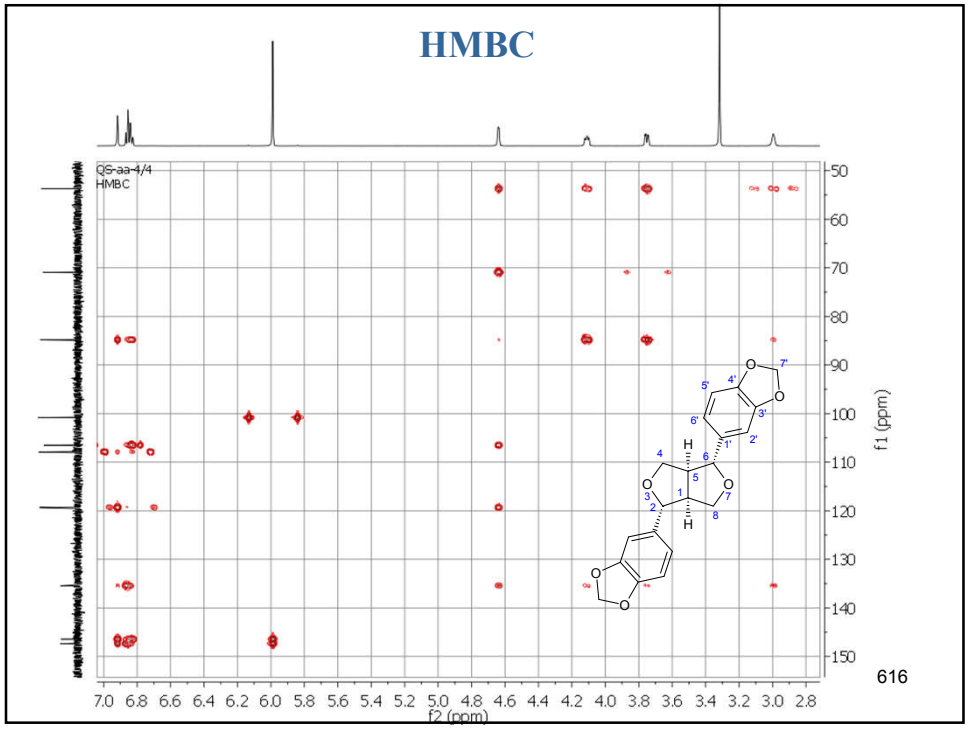


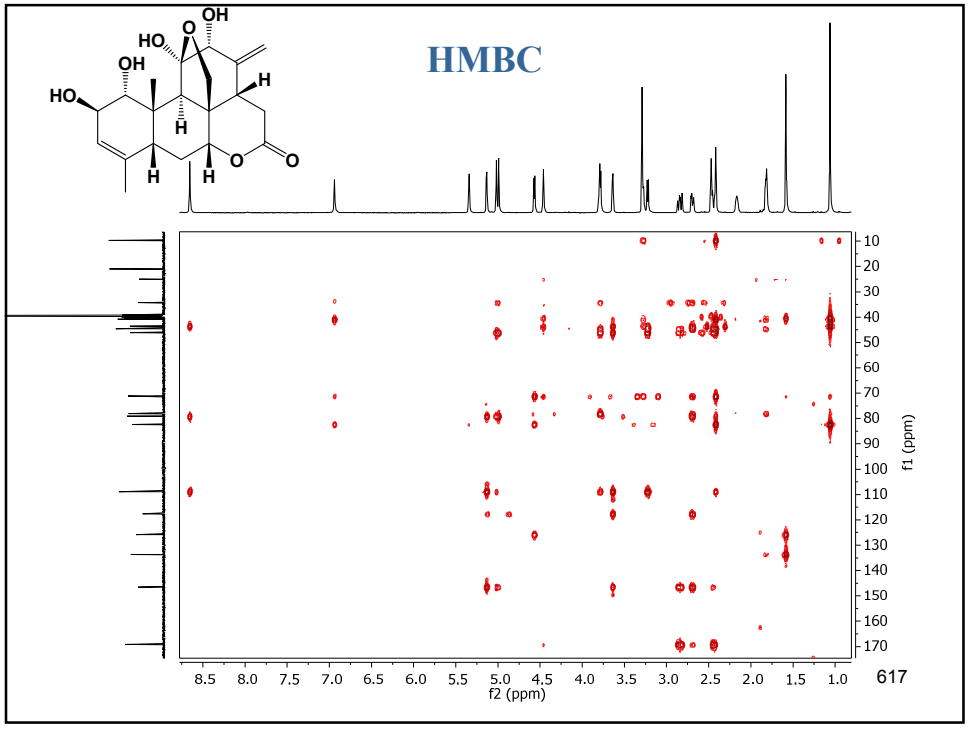
612

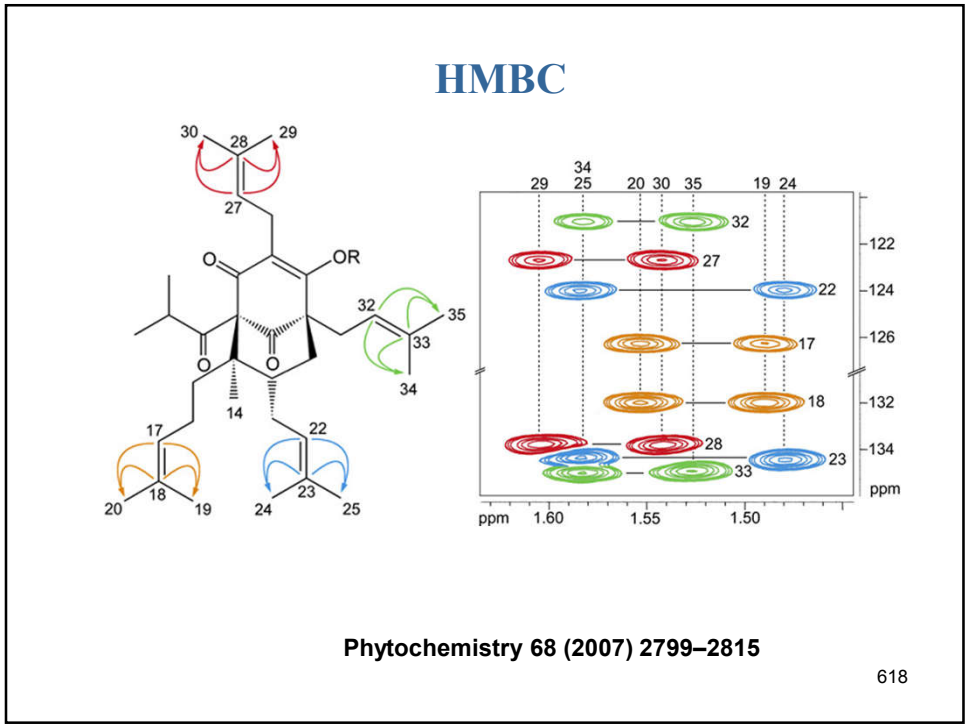

HMBC
fsn4_QS109-1
HMBC tau=.1 INV4GSLPLRND
H3CO
OCH3
MeO
OMe
OH
OH
O
O
613

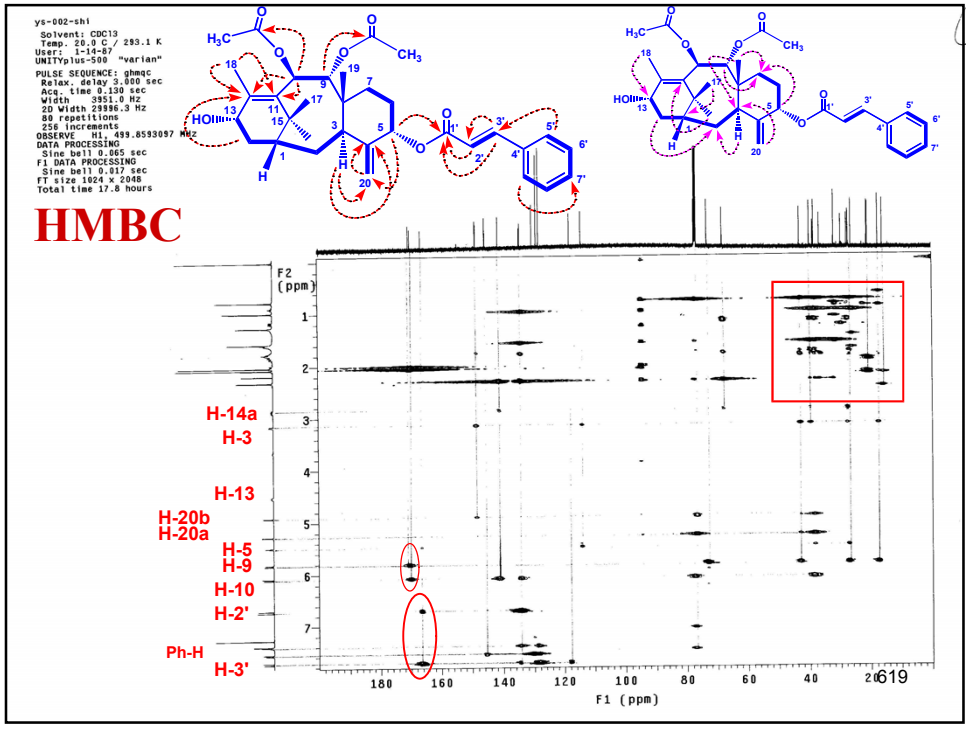

HMBC
OCH3
H3CO
OCH3
OH
OH
O
ppm
614

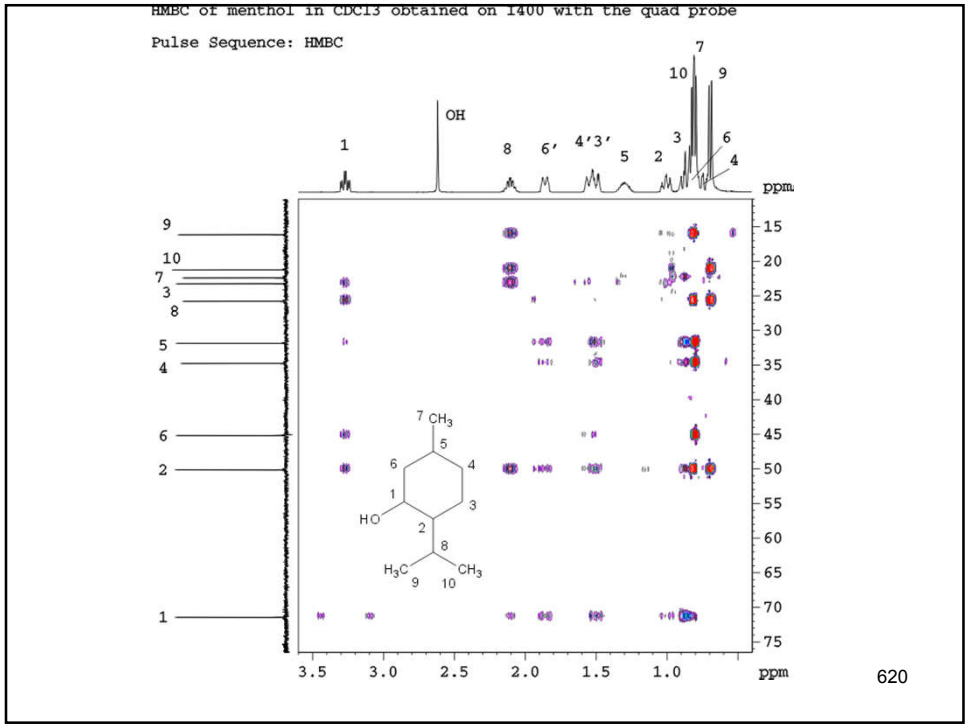

HMBC
CH3
H
HO
4
H
2
H2C
H
OH
O
O
CH3
H
3
ppm
615

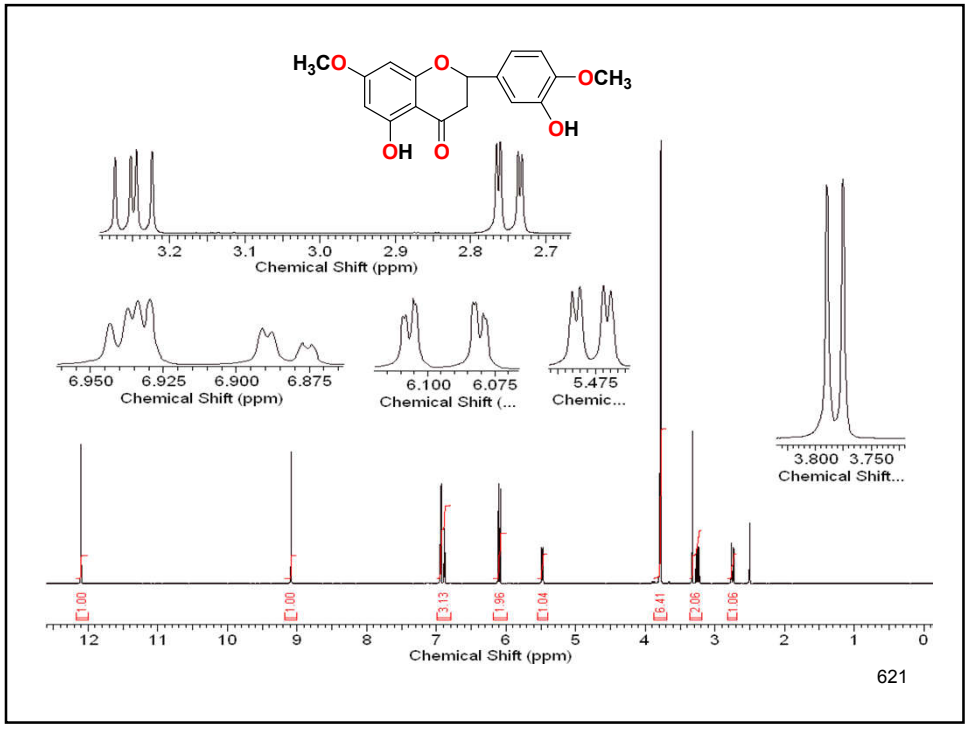

HMBC
QS-aa-4/4
HMBC
f2 (ppm)
f1 (ppm)
616

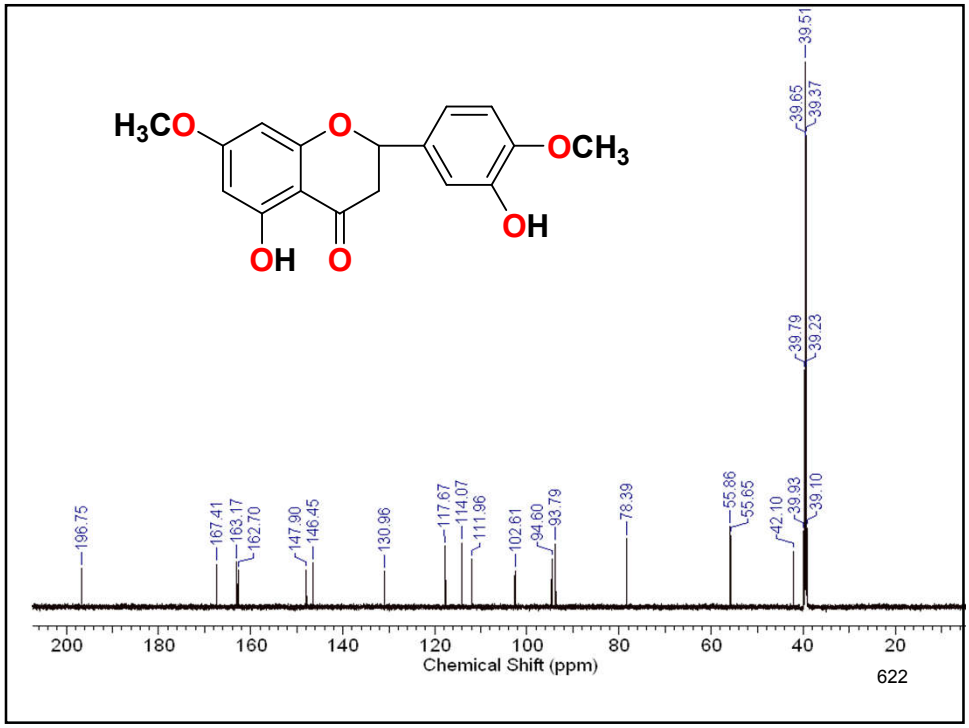

HMBC
OH
HO
O
OH
HO
H
H
H
H
O
O
f1 (ppm)
f2 (ppm)
617


HMBC
OR
O
O
O
14
27
30
28
29
32
33
34
35
17
18
19
20
22
23
24
25
ppm
1.60
1.55
1.50
Phytochemistry 68 (2007) 2799–2815
618

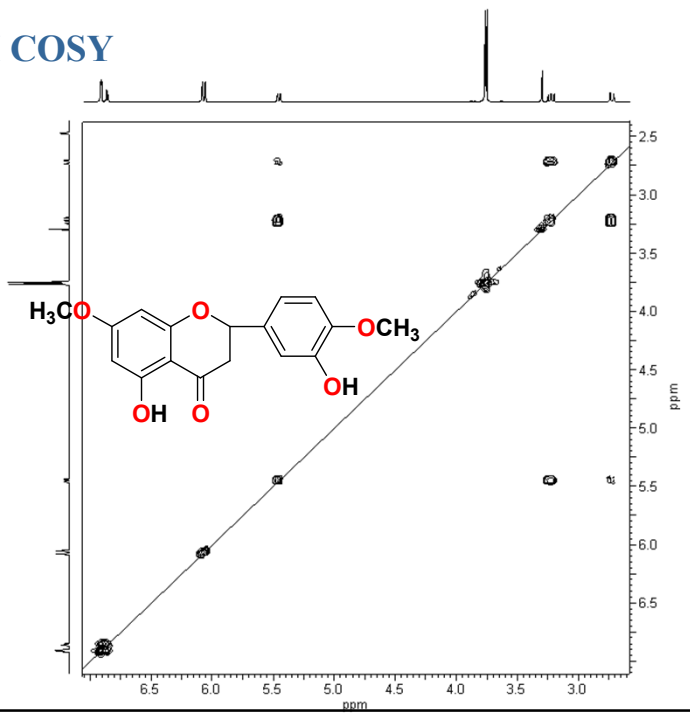

HMBC
H-14a
H-3
H-13
H-20b
H-20a
H-5
H-9
H-10
H-2'
Ph-H
H-3'
F2 (ppm)
F1 (ppm)
619


HMBC of menthol in CDCl3 obtained on 1400 with the quad probe
Pulse Sequence: HMBC
OH
ppm
620


H3CO
O
OCH3
OH
OH
O
3.2 3.1 3.0 2.9 2.8 2.7
Chemical Shift (ppm)
6.950 6.925 6.900 6.875
Chemical Shift (ppm)
6.100 6.075
Chemical Shift (...
5.475
Chemic...
3.800 3.750
Chemical Shift...
1.00 1.00 3.13 1.96 1.04 6.41 2.06 1.06
12 11 10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
621

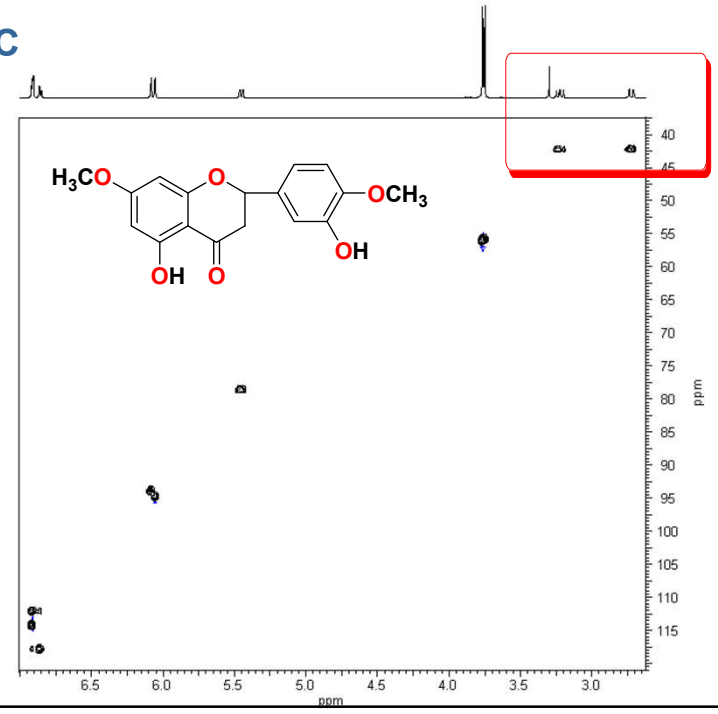

H3CO
O
OCH3
OH
OH
O
196.75
167.41
163.17
162.70
147.90
146.45
130.96
117.67
114.07
111.96
102.61
94.60
93.79
78.39
55.86
55.65
42.10
39.93
39.79
39.65
39.51
39.37
39.23
39.10
200 180 160 140 120 100 80 60 40 20
Chemical Shift (ppm)
622

^1H-^1H COSY



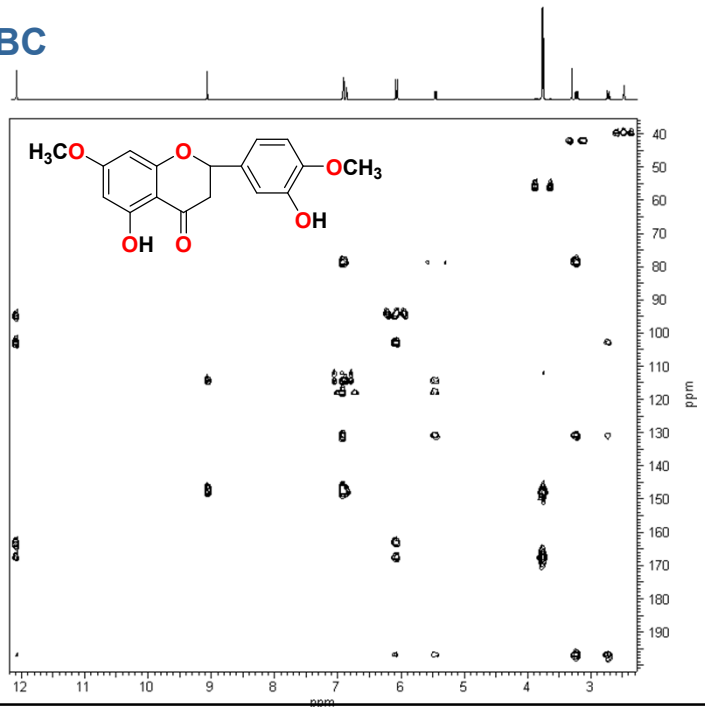
623

HMQC



624

HMBC



625

谱图的解析

- 化学位移值 δ
- 耦合（包括耦合常数 *J* 和自旋裂分峰形）
- 各峰面积之比（积分曲线高度比）

具体分析和综合利用这三种信息来推测化合物中所含的基团以及基团之间的连接顺序、空间排布等，最后提出分子的可能结构并加以验证

626

^{1}H-NMR 谱图解析时的注意事项

- 注意区分杂质峰、溶剂峰和旋转边带等非样品峰。
- 注意分子中活泼氢产生的信号。OH、NH、SH等活泼氢的核磁共振信号比较特殊，在解析时应注意。
  - 活泼氢多数能形成氢键，其化学位移值不固定，随测定条件在一定区域内变动；

627

^{1}H-NMR 谱图解析时的注意事项

活泼氢在溶液中会发生交换反应。当交换反应速度很快时，体系中存在的多种活泼氢(如样品中既含羧基，又含胺基、羟基或者含有几个不同化学环境的羟基，样品和溶剂中含活泼氢等)在核磁共振谱图上只显示一个平均的活泼氢信号，而且它们与相邻含氢基团的谱峰不再产生耦合裂分现象。如果使用二甲基亚砜$(CH_3)_2SO$ 为溶剂，因羟基能与它强烈缔合而使交换速度大大降低，此时可以观察到样品中不同羟基的信号以及羟基与邻碳上的质子耦合裂分的信息。根据裂分峰的个数可以区分伯、仲、叔醇。

628

^{1}H-NMR 谱图解析时的注意事项

- 正是因为活泼氢有以上特点，通过实验可以将它们与其他氢的信号区别开来。一种方法是改变实验条件，如样品浓度、测量温度等，吸收峰位置发生变化的就是活泼氢；另一种方法是利用重水交换反应。具体做法为，先测绘正常的氢谱，然后在样品溶液中滴加 1-2 滴重水并振荡，再测绘一氢谱。由于活泼氢与重水中的氘快速交换，原来由活泼氢产生的吸收峰消失。

629

核磁共振谱图综合解析

- 识别氢谱与碳谱中的溶剂峰与杂质峰。
- 初步分析谱图，找出特征峰并确定各谱线的大致归属。
  - 分析一维^{1}H 谱，根据谱图中化学位移值、耦合常数值、峰形和峰面积找出一些特征峰，获得一些最明显的结论。
  - 对照^{13}C 质子噪声去偶谱以及各个 DEPT 碳谱，确定各碳原子的级数。HMQC， HSQC
  - 按照化学位移分区的规律，大致确定各谱线所属的区域，如在饱和区还是在不饱和区，是否含杂原子、羰基以及活泼氢等。

630

核磁共振谱图综合解析

- 借助二维核磁共振谱对图谱作进一步的指认。
  - 解析^{1}H -^{1}H COSY 谱，从一维谱中已经确定的氢谱线出发找到与之相关的其它谱线。
  - 解析^{13}C -^{1}H COSY（或 HMQC、HSQC）谱，同样从已知的氢谱线出发找到各相关的碳谱线，以此推断出这些碳谱线的归属。
  - 解析^{13}C -^{1}H 远程相关谱（COLOC 或 HMBC），从已确定的碳谱线出发，找到与之相关的各氢谱线或从已知的氢谱线出发找到各相关的碳谱线，由此完成对一些未知谱线的指认。在二维谱中由于一些相关峰的强度较弱，在实验中常常未被检测到，另外在图谱中还常常会出现假峰，这些在二维谱的解析中应特别注意。

631

综合解析谱图的一般程序

1．确定样品的纯度。

2．确定分子式。确定分子式的方法有：

(1) 质谱法测定未知物的分子量，结合元素分析结果可以计算出化合物的分子式。

(2) 根据高分辨质谱给出的分子离子的精确质量数，查Beynon表或Lederberg表计算得出，也可根据低分辨质谱中的分子离子峰和M+1，M+2同位素峰的相对丰度比，查Beynon表来推算分子式。

632

(3) 由核磁共振^{13}C-NMR宽带去偶谱的峰数和峰的强度估算碳原子数，结合分子量，判断分子对称性。由偏共振去偶谱或DEPT谱得到与各碳相连的氢原子数，由^{1}H-NMR的积分曲线高度比也可认别各基团含氢数目比，确定化合物分子式。

可通过元素定性分析确定分子中是否含有杂原子，如含有N、S、X（卤素）等元素，还需测定其含量。分子是否含氧，可从红外光谱含氧基团（OH、C=O、C-O等）的吸收峰判断。

633

3．计算化合物的不饱和度。计算不饱和度对判断化合物类型很有必要。如不饱和度在1～3之间，分子中可能含有C=C、C=O或环，如不饱和度≥4，分子中可能有苯环。

4．结构单元的确定。

5．可能结构式的推导。

6．化合物的确定。

7． **验证：推出的结构和任何一个数据有矛盾说明结论都很可能是错误的。**

634

小　　结

- 化学位移：NMR 信号组的数目代表了分子中的等价质子的数目。
- NMR 信号组的位置告诉我们分子中每一种等价质子的化学环境。
- 峰强度：峰面积积分比对应于分子中各等价质子的数目比。
- 裂分：裂分的峰数与相邻的另一组等价质子的数目。
- 根据偶合常数可判别哪两组等价质子为相邻关系。
- 氘-氢交换：判别活泼氢的常用方法。

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Comparing UV, IR, MS and NMR

1. **Cost: NMR > MS > IR > UV**
2. **Ease of Usage: UV > IR > NMR > MS**
3. **Scope and Information Provided:**

   NMR > MS > IR > UV
4. **Theoretical background:**

   NMR >> MS > UV = IR
5. **Sensitivity MS > UV > IR > ^{1}H-NMR > ^{13}C-NMR**

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