

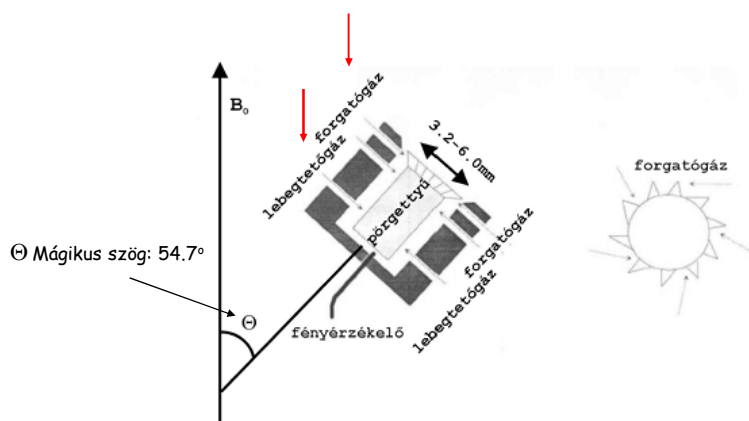
NMR szilárd fázisban

Igen széles jelek, mert a meghatározó kölcsönhatások a „solid state” NMR spektrumokban:

- **dipole-dipole** (homo-, heteronukleáris) csatolódás (direct, through space)
- kémiai eltolódás **anizotrópiája**
- **quadrupolar** kölcsönhatások (csak quadrupolar magoknál)

A kémiai eltolódások irányfüggésének ($\Delta\sigma$ anizotrópia) valamint a téren keresztüli homo- és heteronukleáris dipoláris csatolások jelkiszélesítő hatásának elnyomása

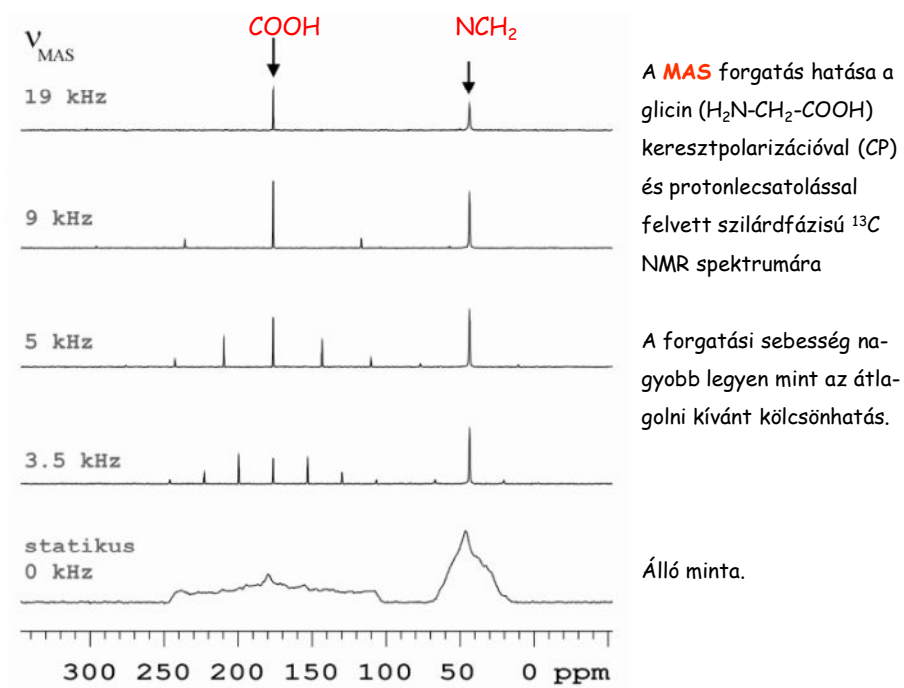
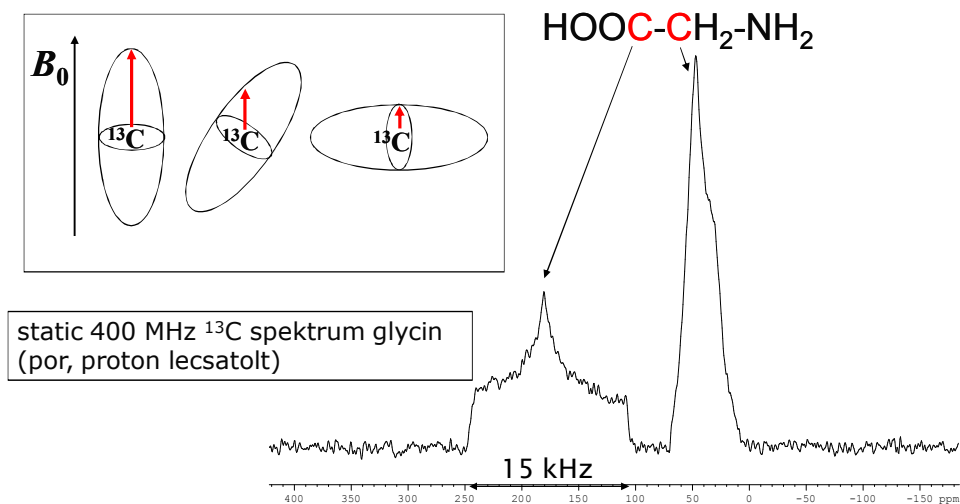
McConnell egyenlet: $\Delta\sigma \propto (\chi_{||} - \chi_{\perp}) (1 - 3\cos^2\Theta) / R^3$; χ : mágneses szuszceptibilitás



A cirkónia mintatartó (rotor) elhelyezkedése a szilárdfázisú mérőfejben

Chemical Shift Anisotropy

Nagy kémiai eltolódás tartományú magok, spin 1/2



$^1\text{H} \rightarrow ^{13}\text{C}$ mágnesszettség átvitel keresztpolarizációval (Cross Polarisation)

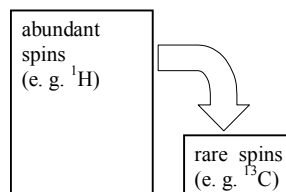
(Boltzmann)

$$\frac{N(\text{felső})}{N(\text{alsó})} = e^{\frac{-\Delta E}{kT}} \approx 1 - \frac{\Delta E}{kT} = 1 - \frac{h}{2\pi} \cdot \frac{\gamma B}{kT}$$

Azonos ^1H és ^{13}C betöltöttséghez eltérő (spin)-hőmérséklet tartozik: pl.:

$$e^{\frac{\gamma_H B_0}{kT_H}} = \frac{P_2}{P_1} = e^{\frac{\gamma_C B_0}{kT_C}}$$

$$T_C = \frac{\gamma_C}{\gamma_H} T_H \quad T_C = \frac{1}{4} 300\text{K} = 75\text{K}$$

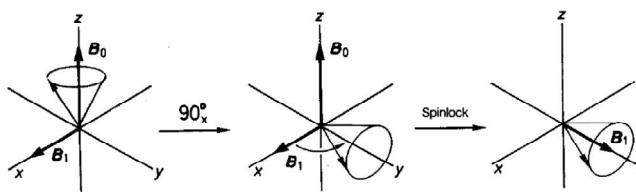


Meleg tartály \rightarrow hideg tartály

γ : giromágneses hányados, $\gamma_H/\gamma_C = 4/1$
 $\omega = \gamma \cdot B$ $\gamma_H \cdot B \neq \gamma_C \cdot B$

Hartmann-Hahn rezonancia feltétel:

$$\gamma_H \cdot B_1(^1\text{H}) = \gamma_C \cdot B_1(^{13}\text{C})$$



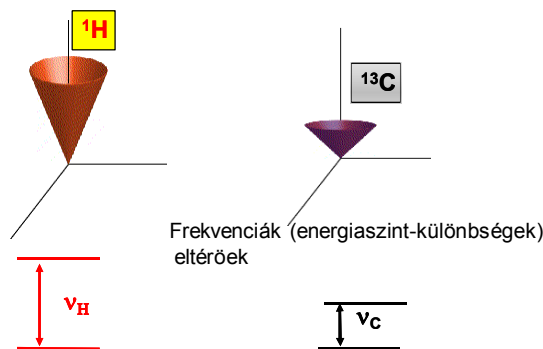
Hartmann-Hahn Spinlock Experiments

Keresztpolarizáció (CP)

Laboratóriumi koordináta-rendszerben

$$\omega = \gamma B_0$$

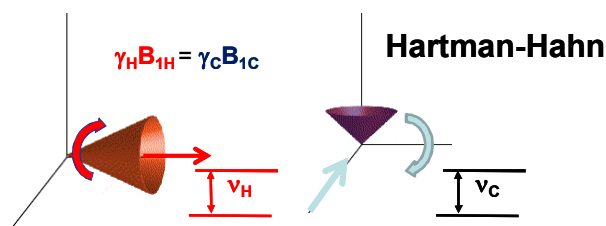
$$\gamma_H \sim 4 \gamma_C$$



Frekvenciák (energiaszint-különbségek) eltérőek

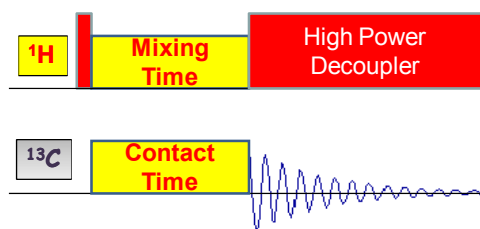
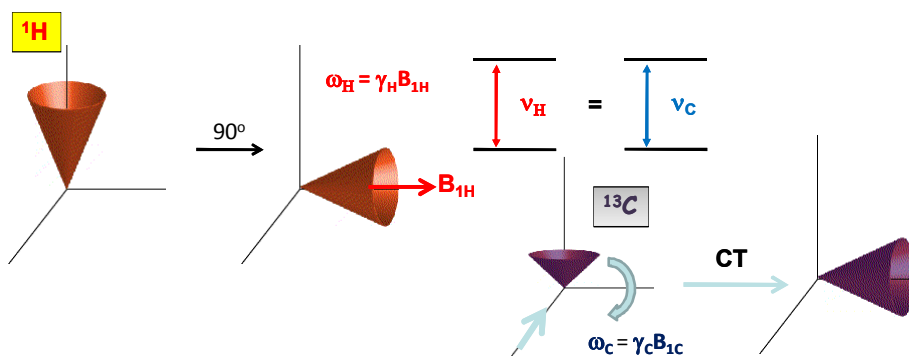
Forgó koordináta-rendszerben

Az energia állításával a ^{13}C rezonanciafrekvenciája az ^1H rezonanciafrekvenciájával egyenlővé tehető



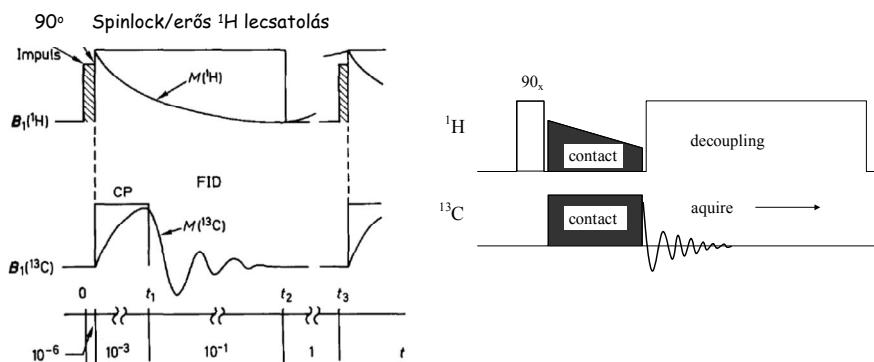
Hartman-Hahn

Keresztpolarizáció (CP)

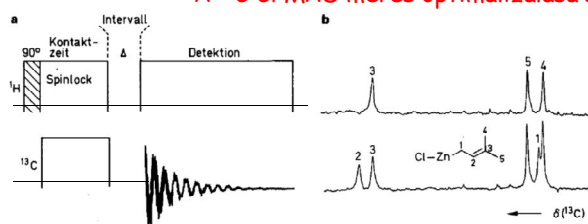


Hartman-Hahn
A keverési idő alatti kölcsönhatás (CT) folytán a ¹³C mágneszettség növekszik

Szilárdfázisú ¹³C mérés CPMAS technikával

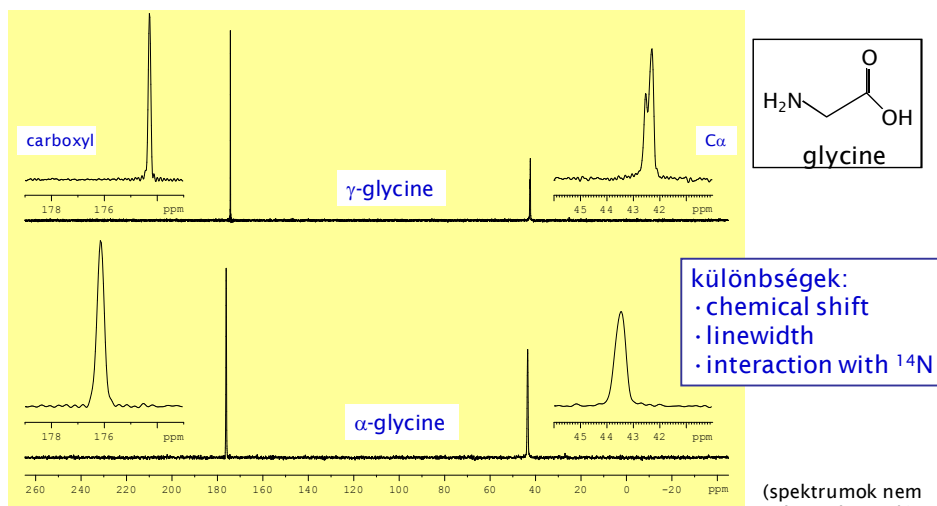


A ¹³C CPMAS mérés optimalizálása a CH₂ + CH / CH₃ + C jelek megkülönböztetésére



$\Delta \sim 30-100 \mu s$

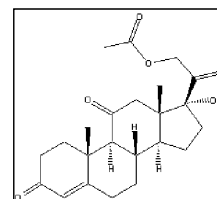
Glycin polimorfok ^{13}C CP/MAS spektruma



400MHz spectrometer, spinning speed 15 kHz
 α - and γ -glycine crystallised from water or 5% aqueous acetic acid, resp.

High Resolution NMR in the Solid State

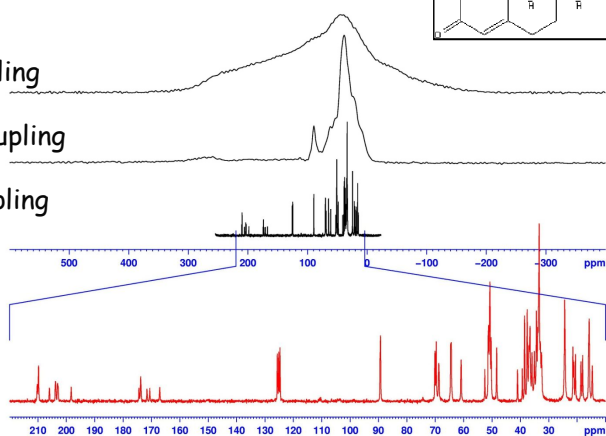
^{13}C CPMAS spectra of Cortisone acetate,
 500 MHz; $\text{C}_{23}\text{H}_{30}\text{O}_6$



Static no ^1H decoupling

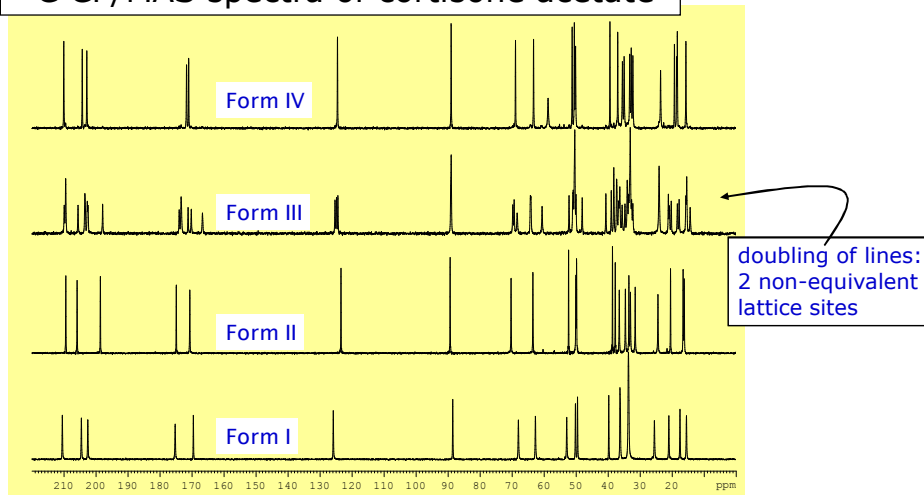
Static with ^1H decoupling

MAS with ^1H decoupling



Cortisone Acetate: Discrimination of Polymorphs

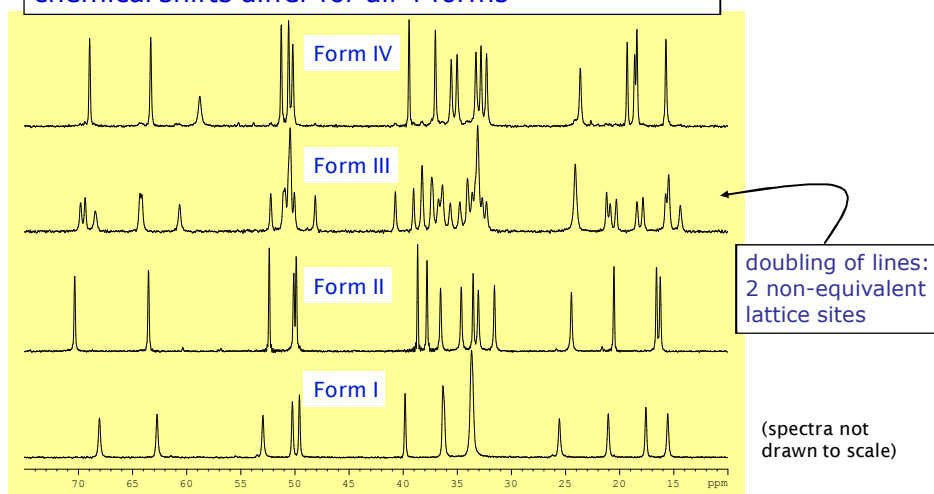
^{13}C CP/MAS spectra of cortisone acetate



400 MHz spectrometer, spinning speed 15 kHz, measurement time \approx 40 min

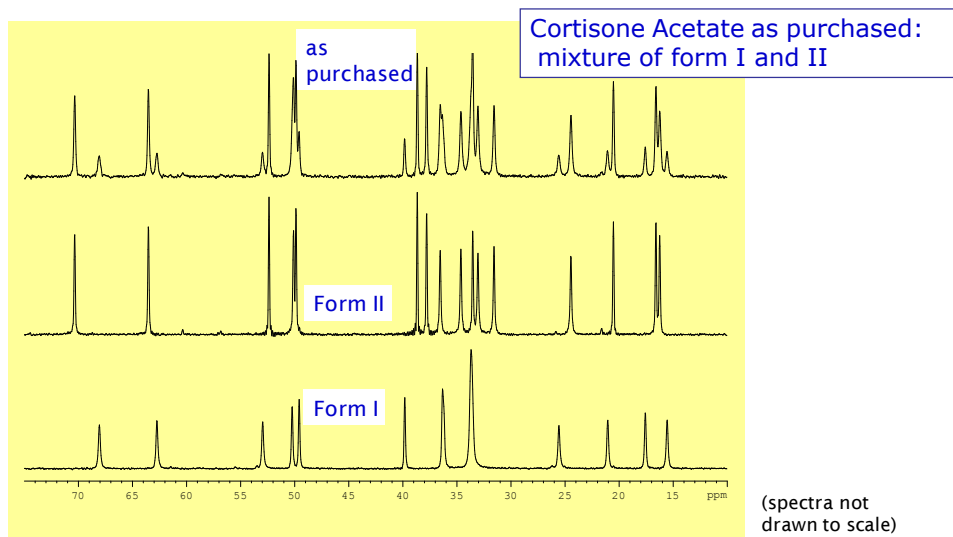
Cortisone Acetate: Discrimination of Polymorphs

chemical shifts differ for all 4 forms



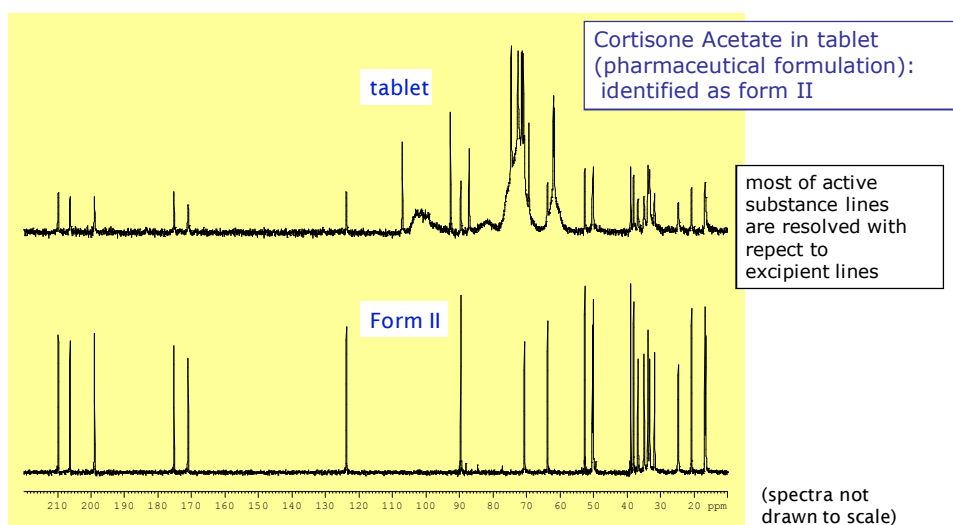
^{13}C CP/MAS spectra, expanded view on 75 - 10 ppm region

Cortisone Acetate: Identification of Polymorphs



^{13}C CP/MAS spectra, expanded view of 75 - 10 ppm region

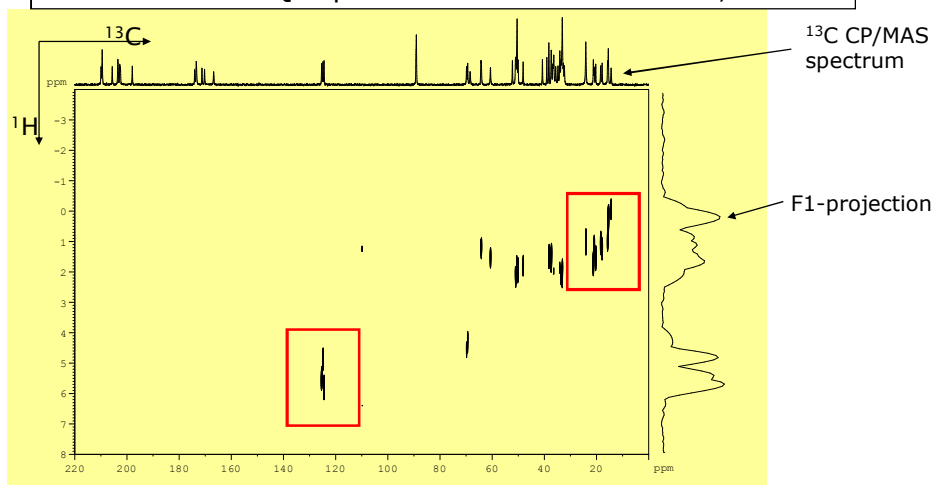
Cortisone Acetate: Identification of Polymorphs



^{13}C CP/MAS spectra, full view

Cortisone Acetate: Characterisation of Polymorphs

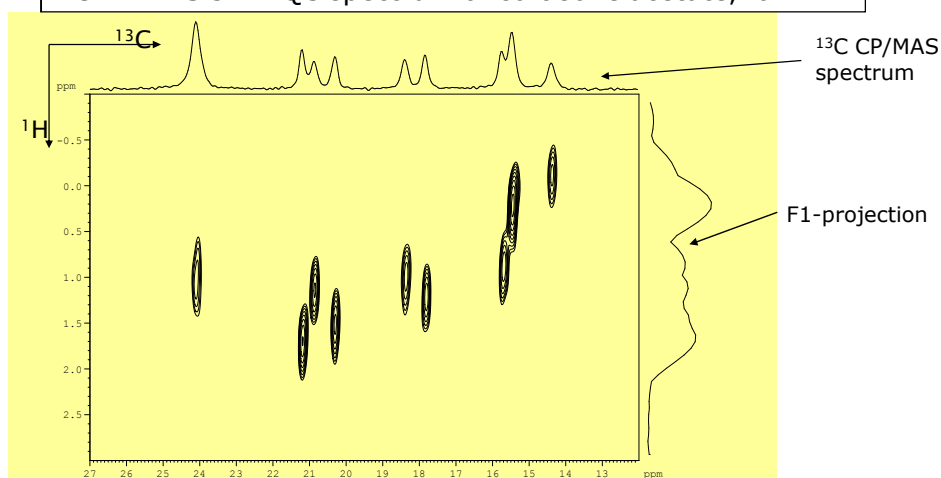
^{13}C - ^1H MAS-J-HMQC spectrum of cortisone acetate, form III



400 MHz spectrometer, spinning speed 13.717 kHz, contact time 400 μs

Cortisone Acetate: Characterisation of Polymorphs

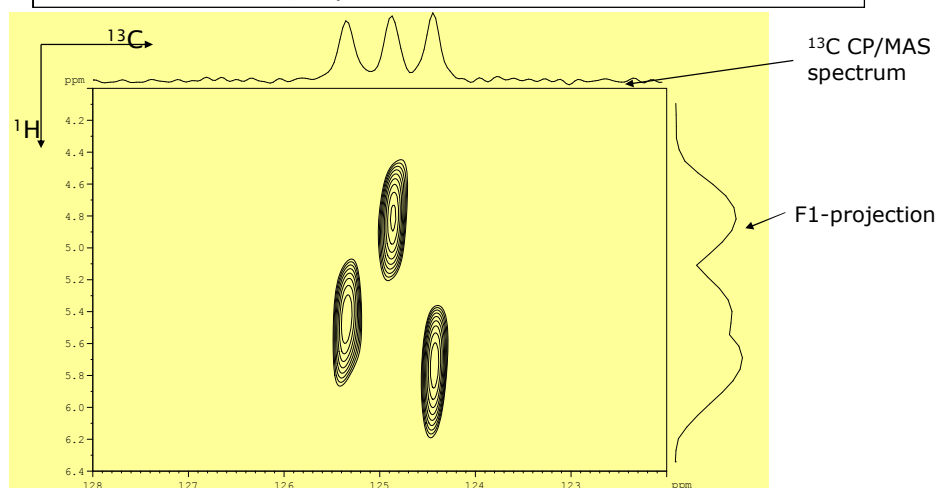
^{13}C - ^1H MAS-J-HMQC spectrum of cortisone acetate, form III



expanded view of ^{13}C 27 ppm - 12 ppm region

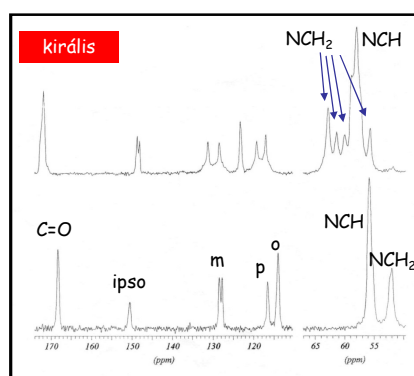
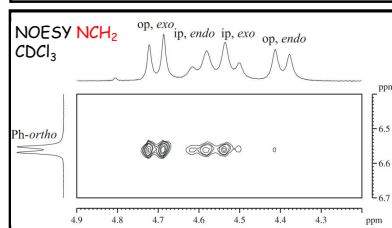
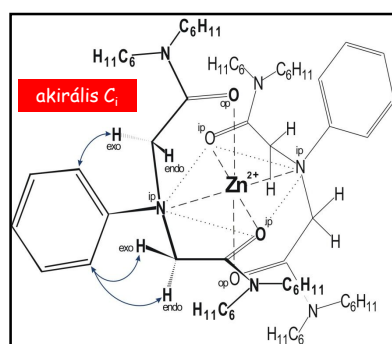
Cortisone Acetate: Characterisation of Polymorphs

^{13}C - ^1H MAS-J-HMQC spectrum of Cortisone Acetate, form III



expanded view of ^{13}C 128 ppm - 122 ppm region

Iminodiacetamid Ph-N[CH₂CON(C₆H₁₁)₂]₂ ionofór cink komplexe

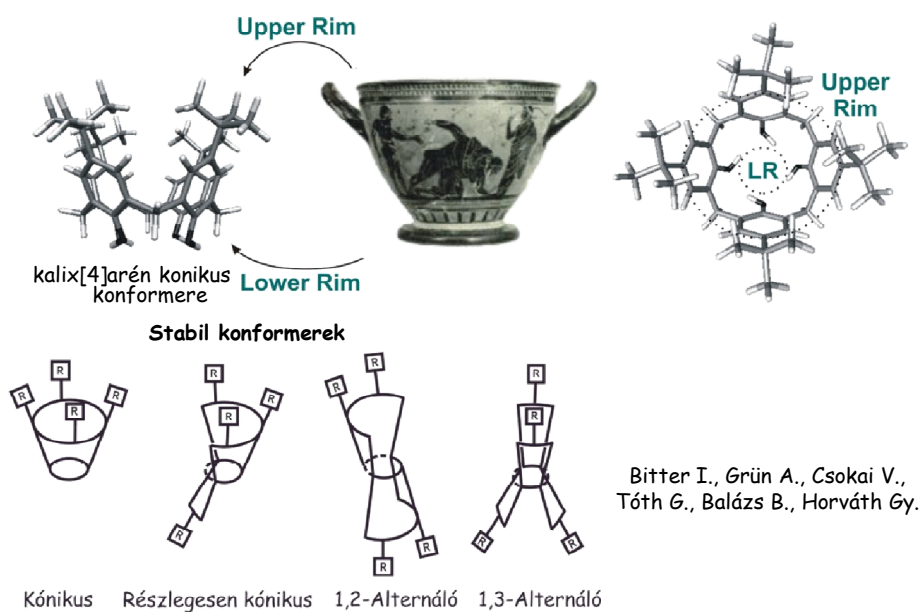


Komplex és szabad iminodiacetamid ionofór CP MAS ^{13}C NMR spektruma

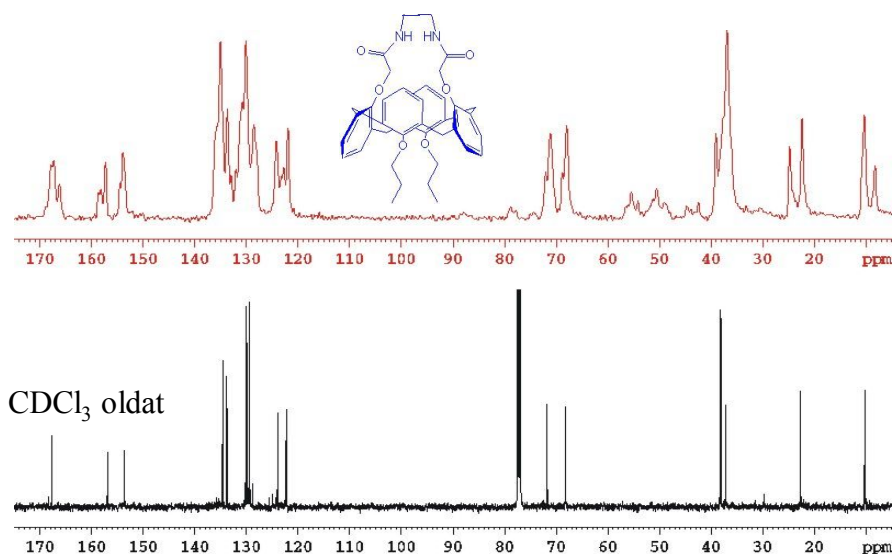
G. Tóth, B. Balázs, Gy. Horváth, D. Magjara, H. Duddeck, I. Bitter : J. Incl. Phen. Macr. Chem. 43, 145 (2002)

Kristályban deformáció folytán megszűnik a centrális szimmetria

Kalix[4]arének sztereokémiája

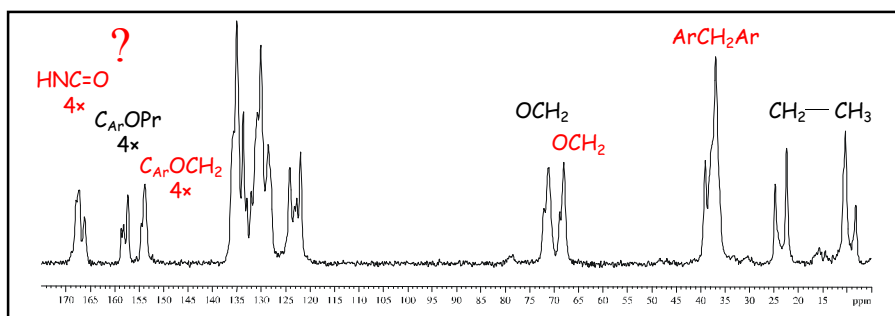
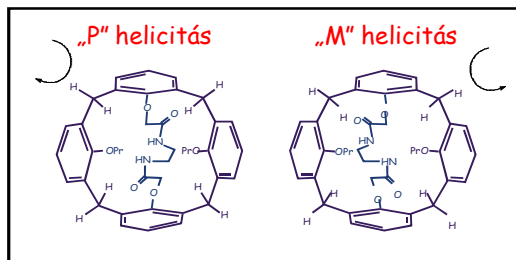


CP-MAS NMR Spektroszkópia (Cross-Polarisation-Magic-Angle-Spinning)



F.Benevelli, J.Klinowski, I.Bitter, A. Grün, B.Balázs, G.Tóth: J.Chem.Soc.,Perkin Trans. 2, 1187, (2002)

5 vegyület 1,3-alternáló konformerének ^{13}C CP MAS spektruma



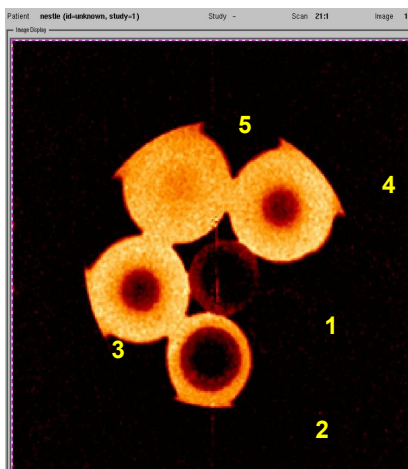
Control of Spagetti cooking by NMR

Art of Cuisine

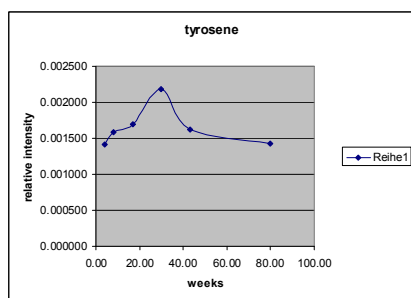
Effect of cooking time (Was ist al dente?)

- 1) dry
- 2) 1 min.
- 3) 3 min.
- 4) 5 min.
- 5) 10 min.

300 MHz 7 T
 Method: 3D Spin Echo MRI
 Data matrix: 128 x 128 x 32
 FOV: 5 x 5 x 15 mm
 Resolution: 39 x 39 x 468 μm
 TR: 200 ms
 TE: 2 ms
 SWH: 100 kHz
 Averages: 1
 Total time: 12 min



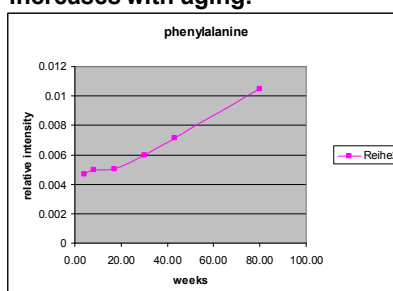
Control of Ripening process of cheeses by NMR



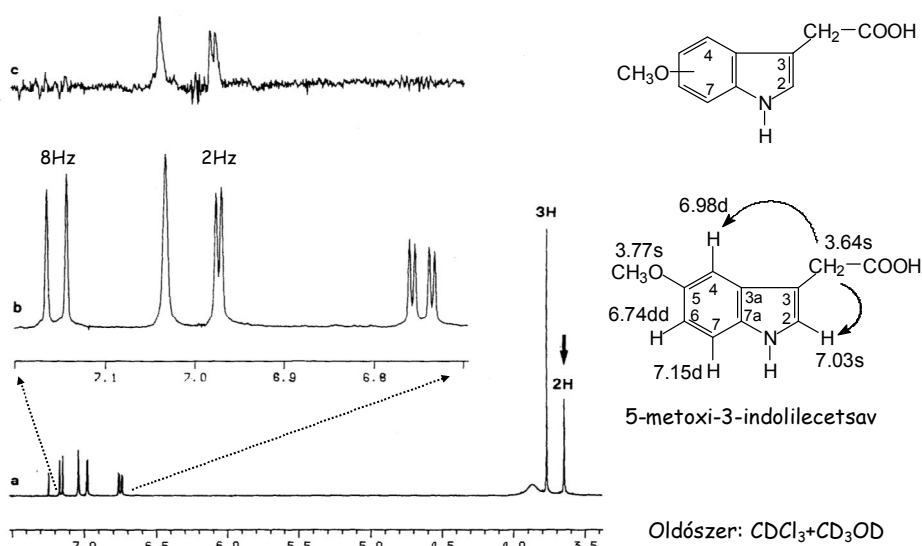
Beemster Gouda cheese
Different ripening stages

HR-MAS spectra NOESY-presat
400MHz spin rate 4.5 KHz
≈ 5 minutes per sample

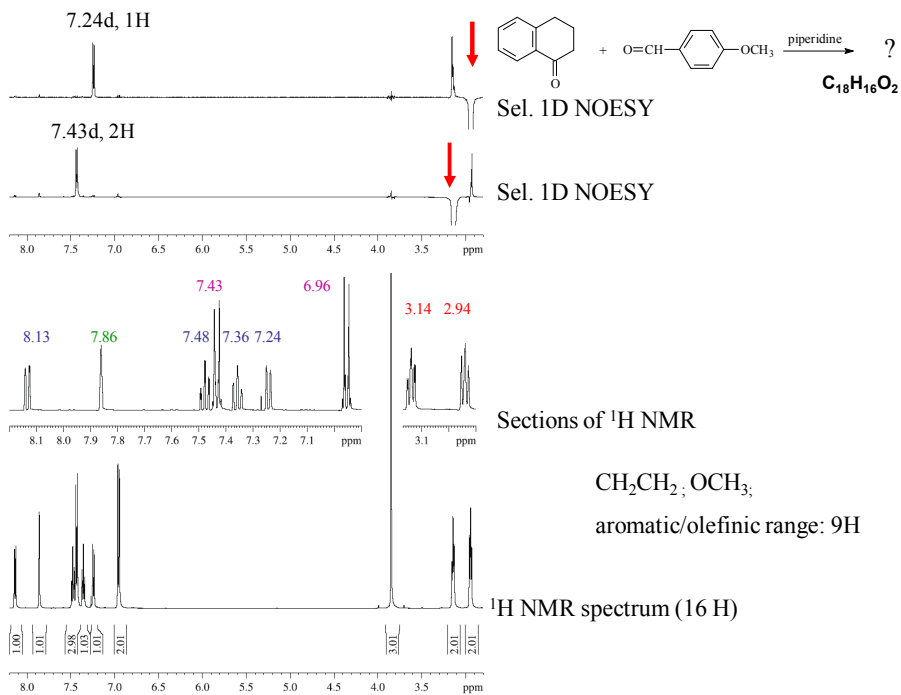
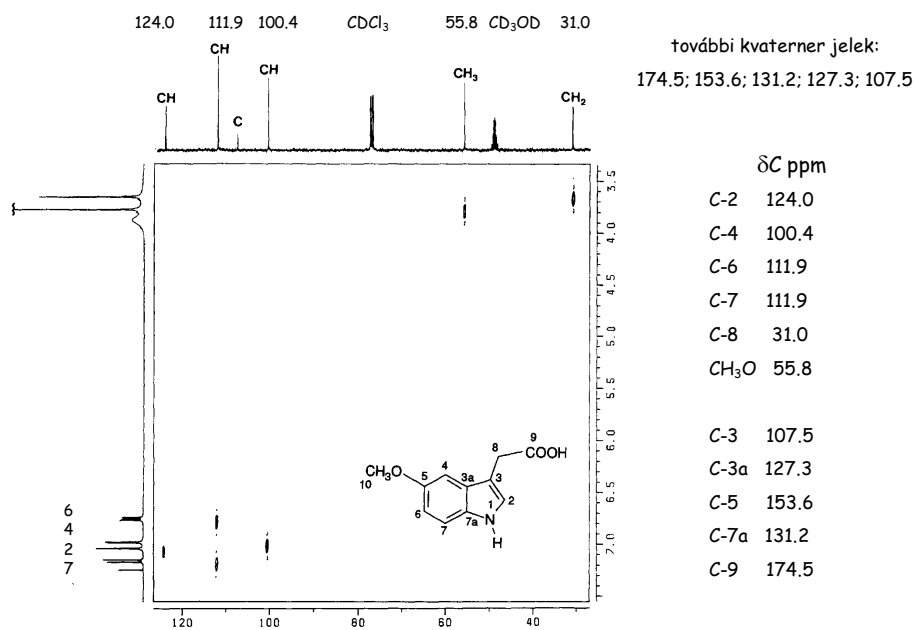
Tyrosine is converted to phenylic acids determining the taste of the cheese. Phenylalanine is not converted, Concentration increases with aging.

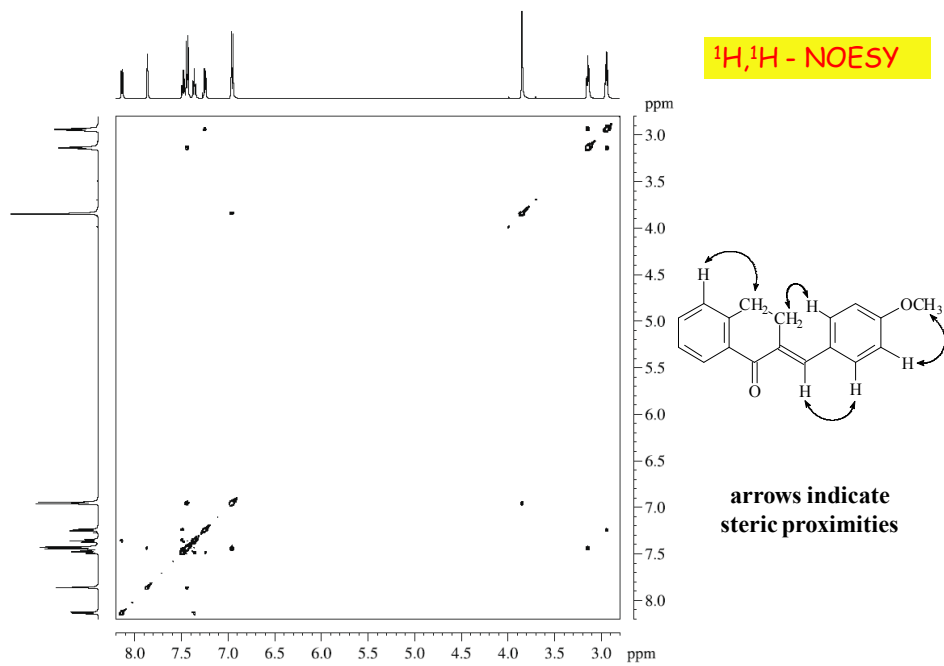
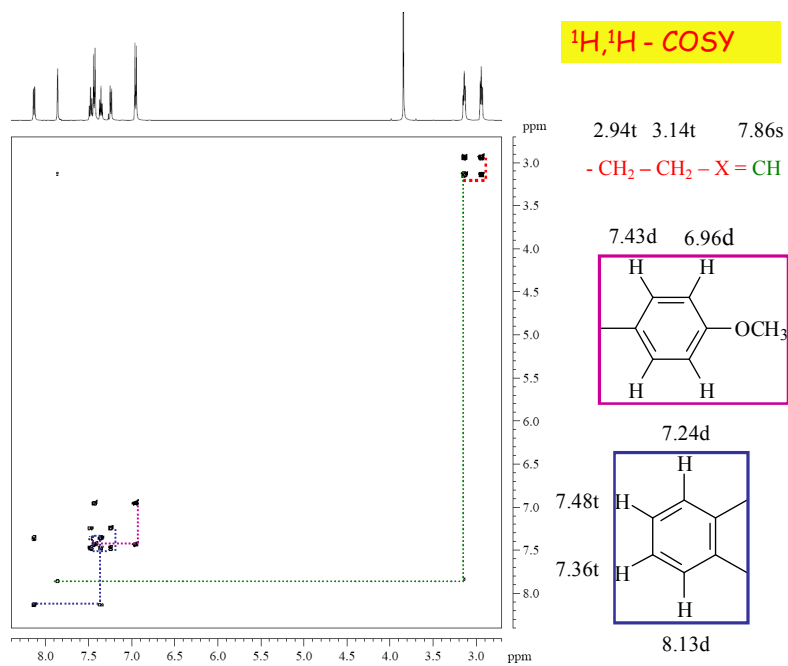


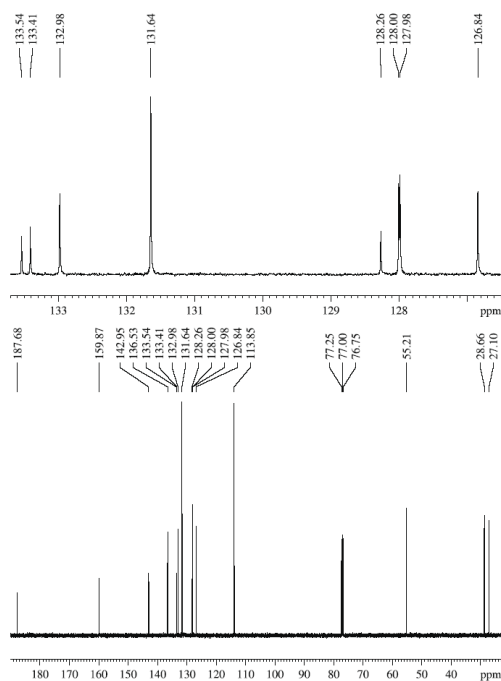
Határozza meg a CH_3O csoport helyét a 3.64 ppm-nél besugárzott NOE differencia spektrum (c) alapján!



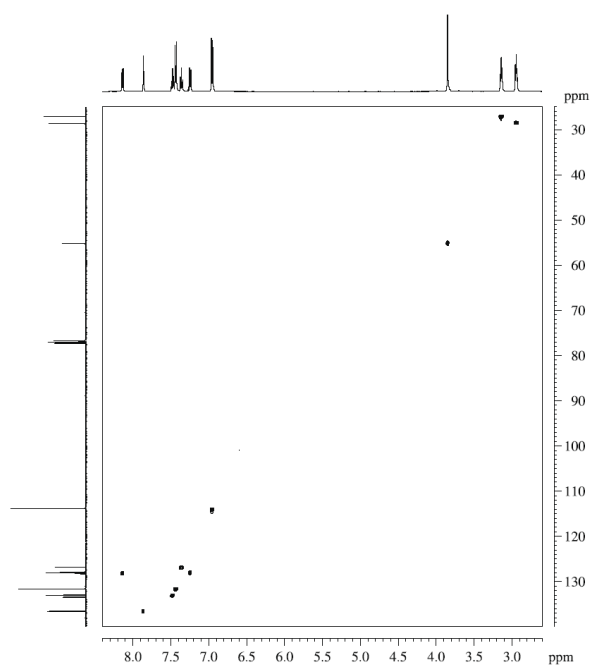
Végezze el a ^{13}C jelhozzárendelést a C,H-COSY spektrum alapján!





Section of ^{13}C NMR spectrum

16 Signals corresponding to C_{18} atoms
 3 (sp^3C); 1 $\text{C}=\text{O}$; 7 $=\text{CH}$; 5 $=\text{C}<$

 ^{13}C NMR spectrum $^1\text{H}, ^{13}\text{C}$ - HSQC

with section of $\text{sp}^2 =\text{CH}$ range

Compound **34** has been isolated from the phenolic fraction of the plant *Polygala arvensis*. Its molecular formula – determined by high-resolution mass spectrometry – is $C_{21}H_{20}O_5$. What is its structure?

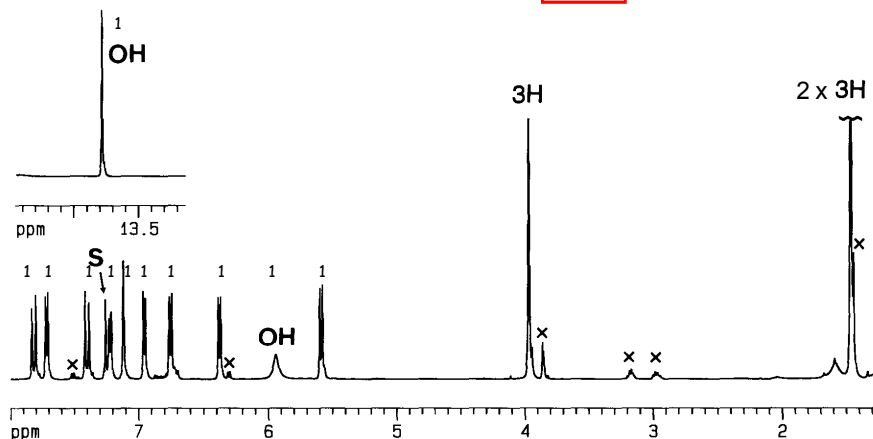


Fig. 4.25.1. 500 MHz 1H NMR spectrum of **34**, in $CDCl_3$; impurity signals are marked by "x"; S: solvent. The following signal splittings (doublets) have been determined: $\delta = 7.82, 15.3$ Hz; $\delta = 7.72, 8.8$ Hz; $\delta = 7.40, 15.3$ Hz; $\delta = 7.23, 8.2$ Hz; $\delta = 6.96, 8.2$ Hz; $\delta = 6.76, 10.0$ Hz; $\delta = 6.38, 8.8$ Hz; $\delta = 5.59, 10.0$ Hz. For an expansion see 1D spectra in Fig. 4.25.3.

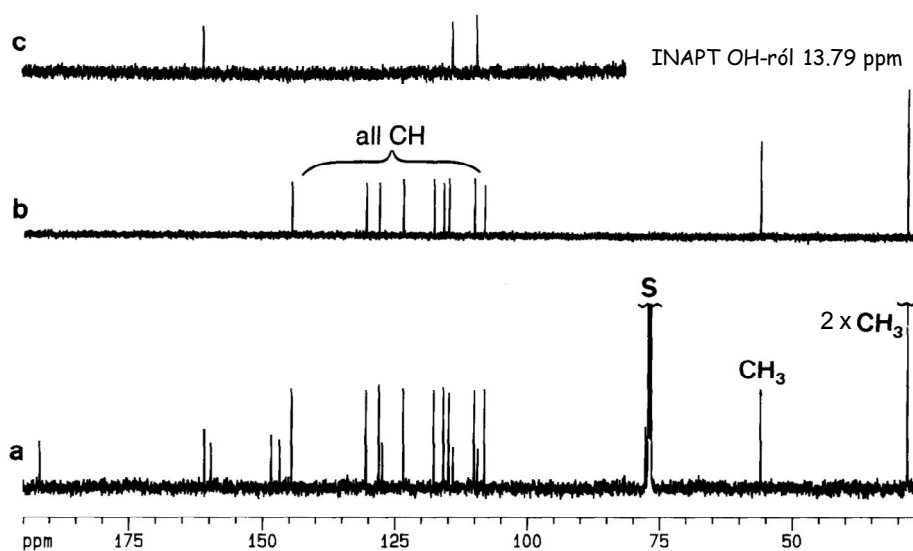


Fig. 4.25.2. a) 125.7 MHz ^{13}C NMR spectrum of **34**, in $CDCl_3$; b) DEPT135 spectrum; c) selective INEPT spectrum, irradiation at the signal at $\delta = 13.79$. The exact values of the ^{13}C chemical shifts are: $\delta = 191.9, 160.9, 159.7, 148.4, 146.8, 144.6, 130.5, 128.1, 127.4, 123.5, 117.7, 115.9, 114.9, 114.1, 110.1, 109.4, 108.2, 77.8, 56.0,$ and 28.4 .

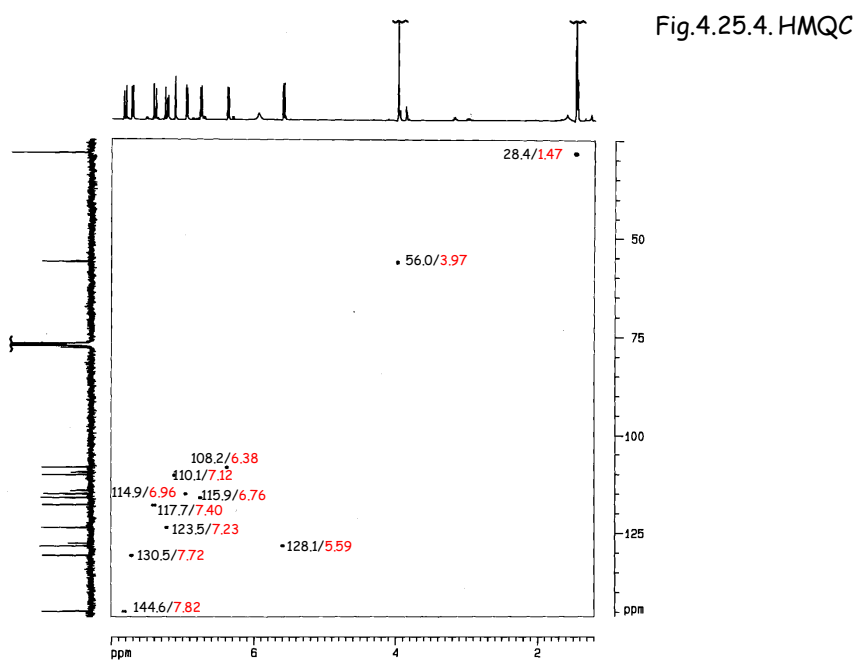
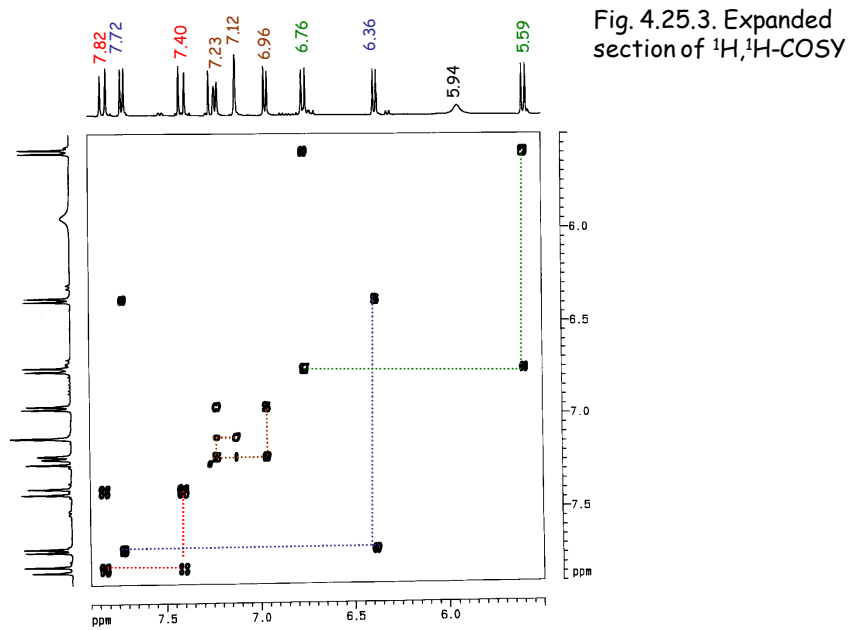


Fig. 4.25.5 HMBC

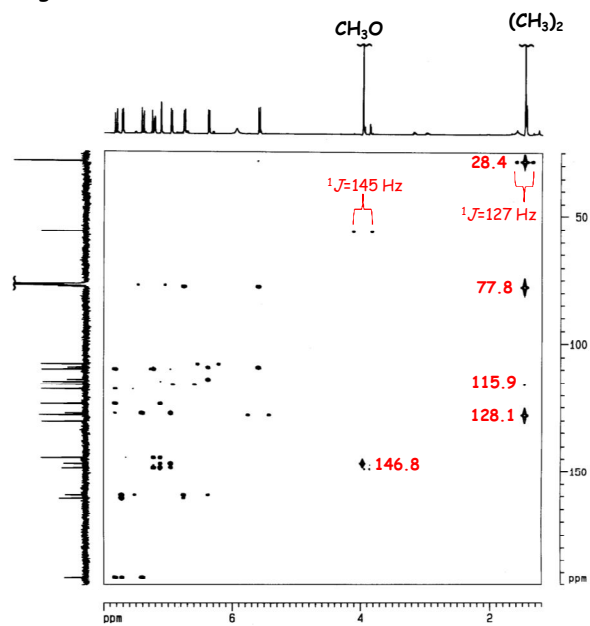


Fig. 4.25.6 HMBC széthúzás

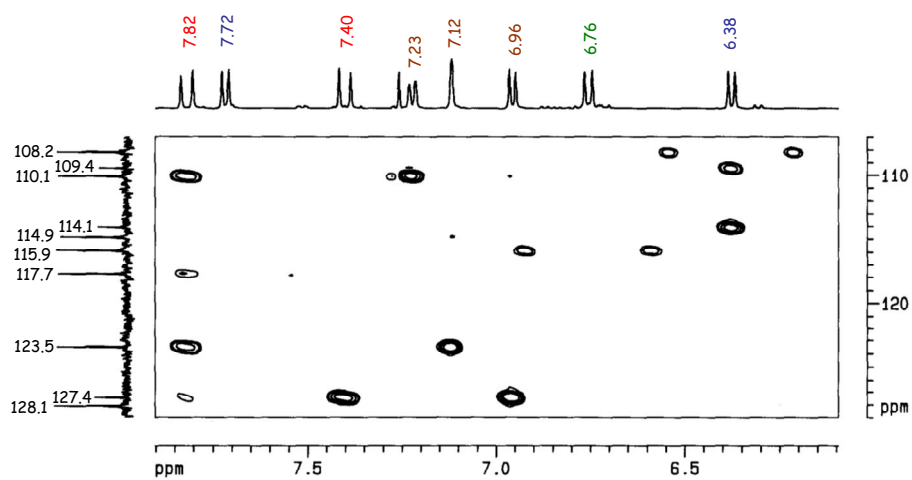
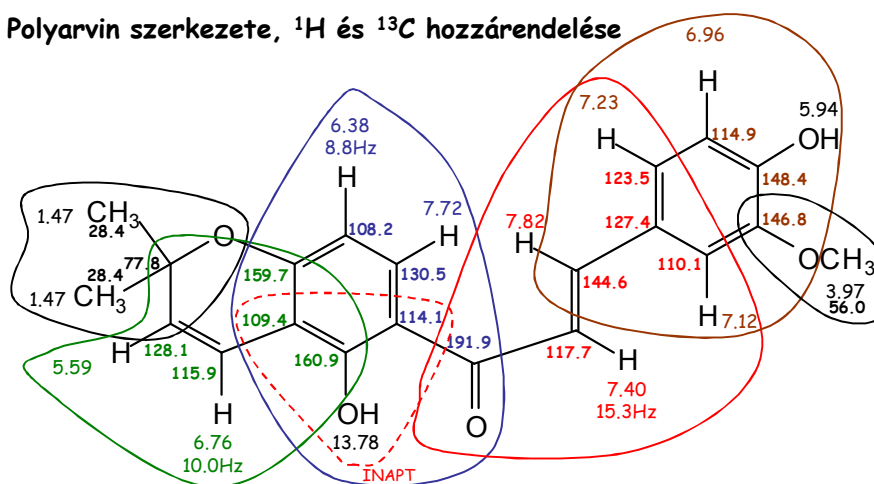


Table 6.25.1. Listing of ^1H correlations in the HMQC and HMBC spectra of **34**. $\text{C}_{21}\text{H}_{20}\text{O}_5$ DBE=12

^1H signals at $\delta =$	^{13}C signals at $\delta =$ (HMQC)	Long-range correlations at $\delta =$ (HMBC)
1.47		28.4
3.97		
5.59		
6.38		
6.76		
6.96		
7.12		
7.23		
7.40		
7.72		
7.82		
13.78	1D INAPT	109.4; 114.1; 160.9

Polyarvin szerkezete, ^1H és ^{13}C hozzárendelése

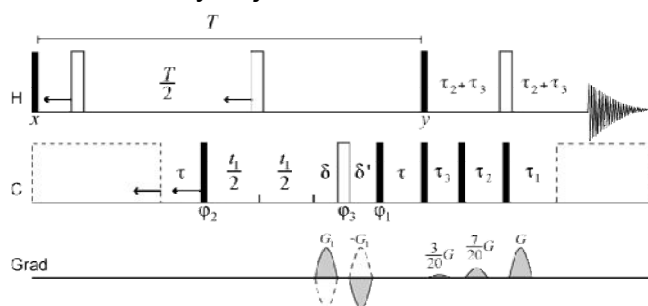


M. S. Rao, P. S. Rao, G. Tóth*, B. Balázs, H. Duddeck:
Isolation of Polyarvin, a Chalcone from *Polygala arvensis*.
Nat. Prod. Letters 12, 277-280 (1998)

A nice experiment: H2BC

Heteronuclear 2-Bond Correlations

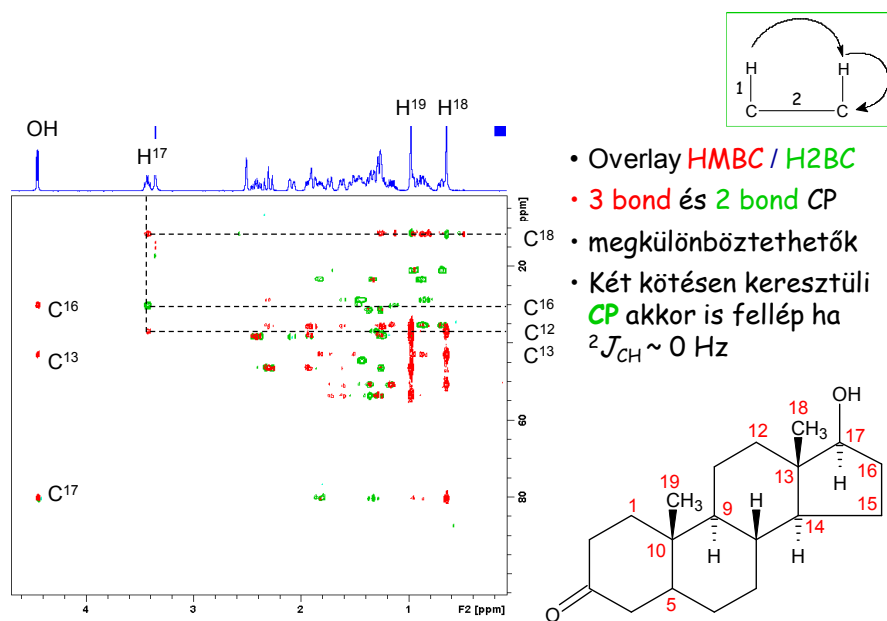
- felerősíti a 2 kötésen keresztüli korrelációt
- elnyomja a többkötésen keresztüli korrelációt



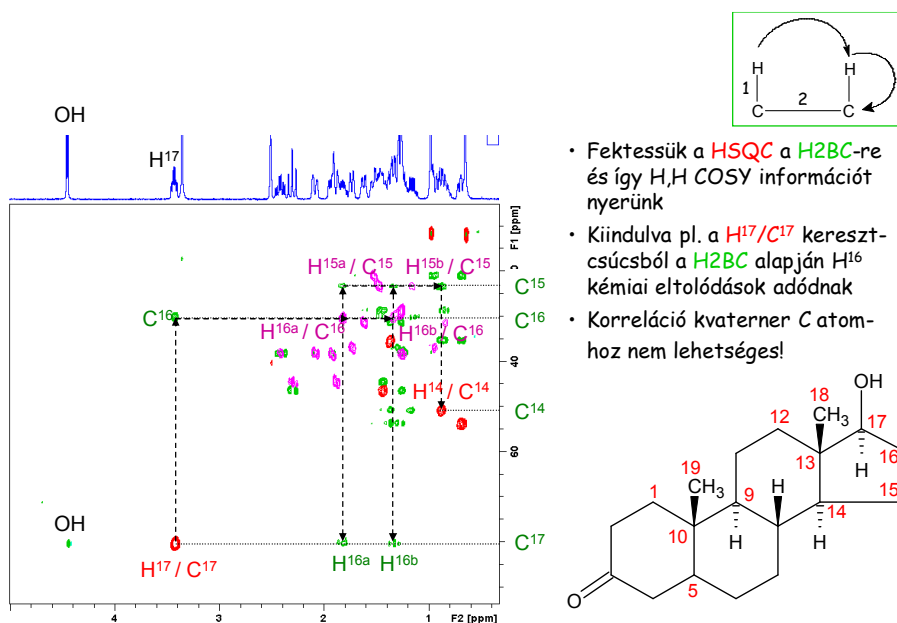
for more information:
www.crc.dk/nmr

3rd order low-pass J filter for correlating ^1H and ^{13}C nuclei
via $^1J_{\text{CH}}$ and $^1\text{H}-^1\text{H}$ couplings. **No $^2J_{\text{CH}}$ involved!**

Nils T. Nyberg, Jens Ø. Duus, Ole W. Sorensen *J. Am. Chem. Soc.* 127 6154-6155 (2005)



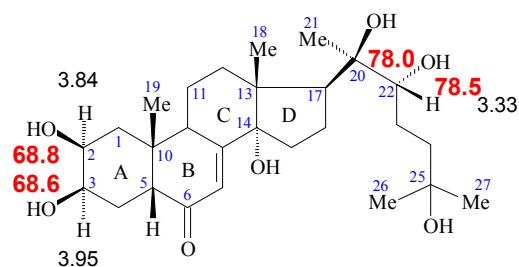
Nils T. Nyberg, Jens Ø. Duus, Ole W. Sorensen *J. Am. Chem. Soc.* 127 6154-6155 (2005)



- Fekessük a **HSQC** a **H2BC**-re és így **H,H COSY** információt nyerünk
- Kiindulva pl. a **H¹⁷/C¹⁷** kereszt-csúcsból a **H2BC** alapján **H¹⁶** kémiai eltolódások adódnak
- Korreláció kvaterner **C** atomhoz nem lehetséges!

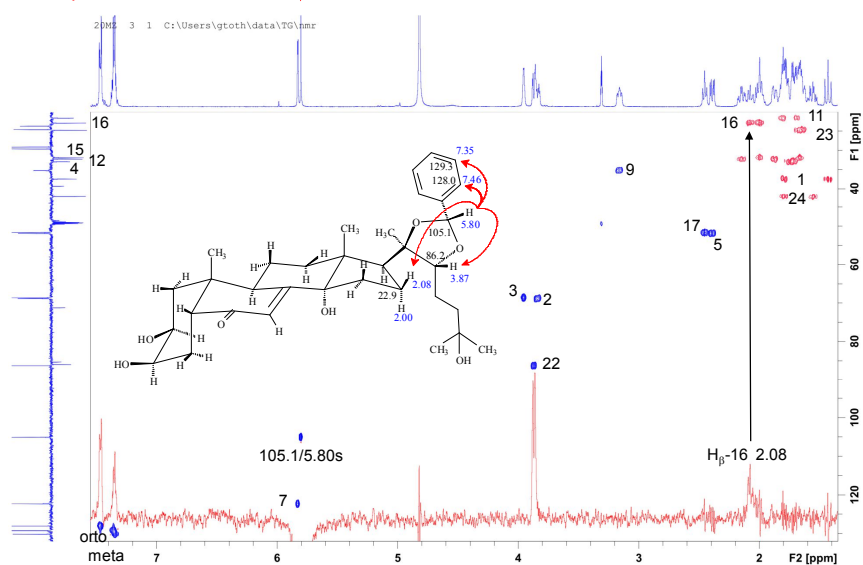
Nils T. Nyberg, Jens Ø. Duus, Ole W. Sorensen *J. Am. Chem. Soc.* 127 6154-6155 (2005)

20-Hidroxiiekdizon dioxolánok NMR vizsgálata

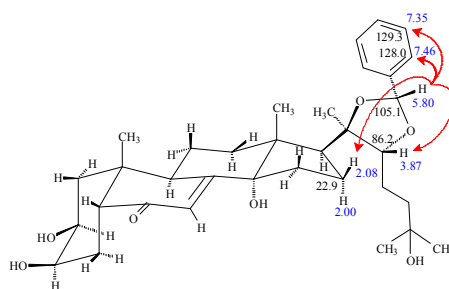


20-Hidroxiiekdizon ($\delta^1\text{H}$, $\delta^{13}\text{C}$)

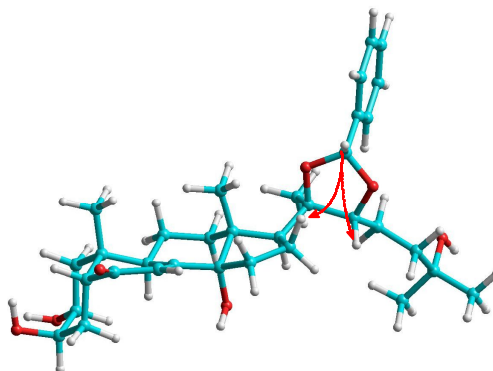
edHSQC + selROE 5.80s ↓

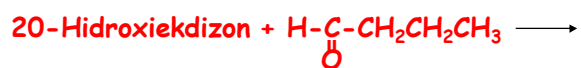


Sematikus térszerkezet
¹H kémiai eltolódások
 H-29 selROE térközeliségei

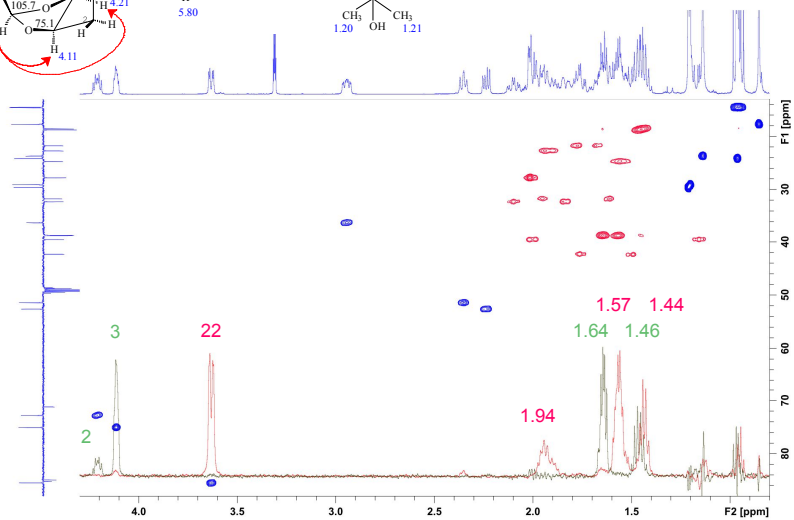
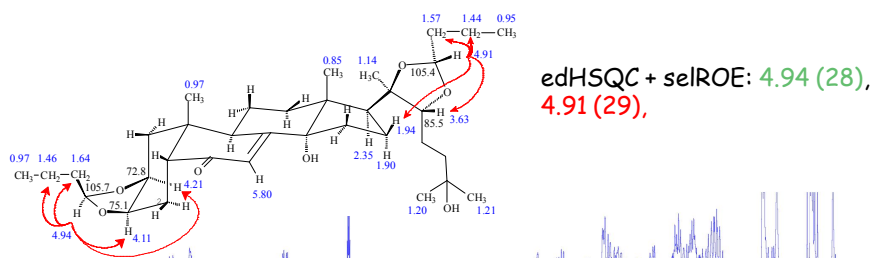
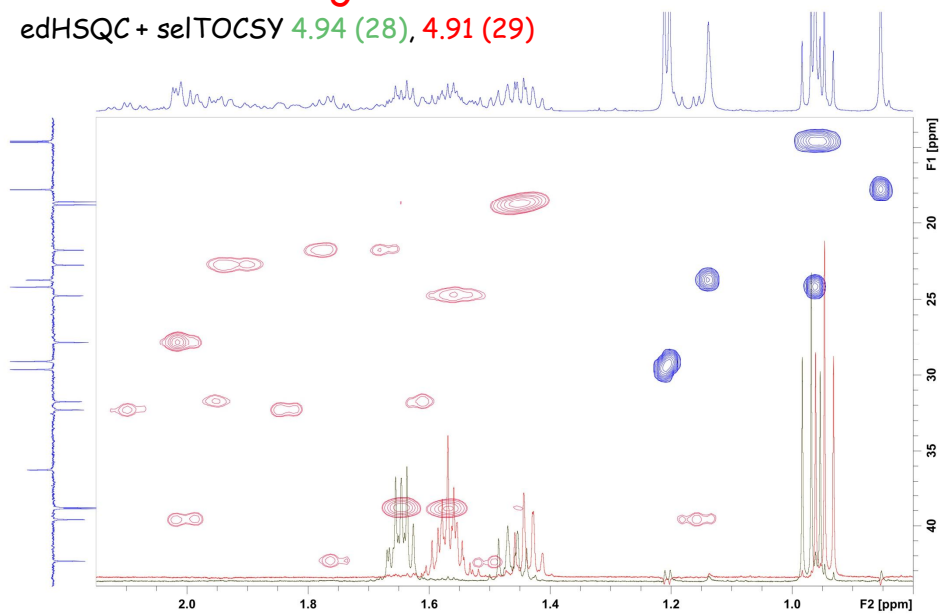


Hyperchem 8.0
 PM3 szemiempirikus
 finomított térszerkezet

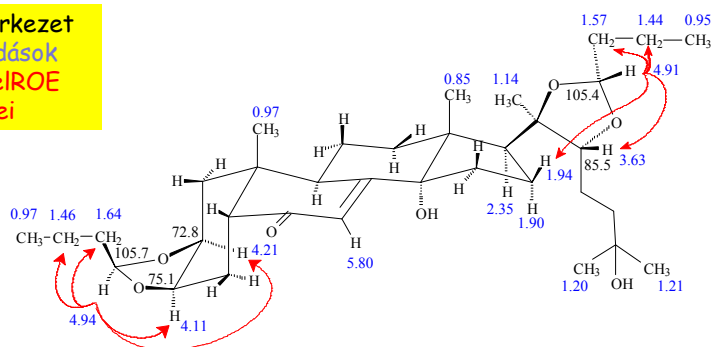




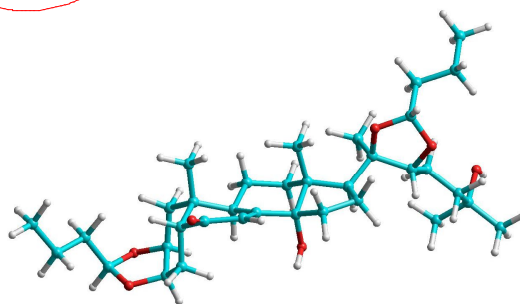
edHSQC + selTOCSY 4.94 (28), 4.91 (29)



Sematikus térszerkezet
 ^1H kémiai eltolódások
 H-28 és H-29 selROE
 térközelségei



Hyperchem 8.0
 PM3 szemempirikus
 finomított térszerkezet



Bruker Avance 500 (2002); 5mm BBO (direkt) mérőfej; S/N : ^1H = 350, ^{13}C = 230

MATCH tubes (mérőcsővek)

Átmérő: 1, 1.7, 2.0, **2.5**, 3.0, 4.25 and 5mm

térfogat \longrightarrow >0.1 ml

0.6 ml

edHSQC, HMBC mérésidő: **6 perc**, selROE ns=32 **>3 perc**

