

Spektrální metody NMR I

RNDr. Zdeněk Tošner, Ph.D.

Hlavova 8, místnost 020

tel. 22195 1323

tosner@natur.cuni.cz

www.natur.cuni.cz/nmr/vyuka.html

Literatura

Böhm, Smrčková-Voltrová: Strukturní analýza organických sloučenin

S. Voltrová: Příklady pro cvičení ze strukturní analýzy organických sloučenin

Buděšínský, Pelnář: UOCHB: Fyzikálně – chemické metody 3: Nukleární magnetická rezonance

Friebolin: Basic One- and Two-Dimensional NMR Spectroscopy

Günter: NMR Spectroscopy

Hore: Nuclear magnetic resonance

Hore, Jones, Wimperis: NMR: the toolkit

Claridge: High-resolution NMR techniques in organic chemistry

...

Odkazy na webu

M. Dračínský:

<http://www.uochb.cz/web/structure/671.html?lang=cz>

Databáze SDBS: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

Kurs: <http://www.chem.queensu.ca/FACILITIES/NMR/nmr/webcourse/index1.htm>

Kurs: <http://www.cis.rit.edu/htbooks/nmr/>

Kurs: http://tonga.usip.edu/gmoyna/NMR_lectures/NMR_lectures.html

Kurs: <http://www.vscht.cz/nmr/predmet/predmet.html#prednasky>

Kurs MRI: <http://www.cis.rit.edu/htbooks/mri/inside.htm>

NMR meets musicians: <http://www.chemie.uni-erlangen.de/oc/research/NMR/music.html>

Linky: <http://www.ebyte.it/library/StansNmrLinks.html>

http://nmr1.ioc.ac.ru/li_links.htm

Řešení 1 D: http://www.nd.edu/~smithgrp/structure/pbm_table.html

Řešení 1 D: <http://www.vscht.cz/nmr/predmet/priklady/priklady.html>

Web spectra: <http://www.chem.ucla.edu/~webspectra/>

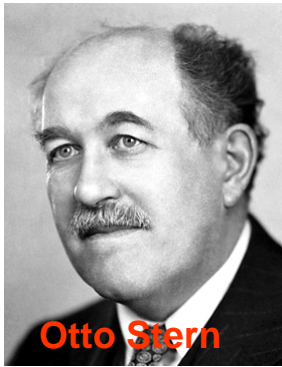
Využití NMR

Využití NMR

- určování chemické struktury – přírodní látky, organická syntéza
 - konstituce, konformace, konfigurace
 - ověření čistoty
- studium dynamických procesů
 - reakční kinetika
 - chemické a strukturní rovnováhy
- navrhování léčiv – drug design
 - Structure-Activity-Relationship
- určení prostorové struktury
 - peptidy a proteiny
 - oligonukleotidy a DNA, RNA
 - komplexy
 - polysacharidy
- lékařství
 - zobrazování měkkých tkání – anatomie, patologie
 - funkční zobrazování
 - in vivo spektroskopie
- fyzika – struktura materiálů
- potravinářství
 - quality control – spektroskopie, zobrazování
 - falšované potraviny (alkohol, džusy, med,...)
- metabolomika

Nobelovy ceny a NMR

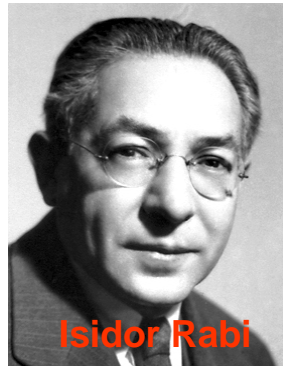
1943



Otto Stern

*magnetický moment
protonu*

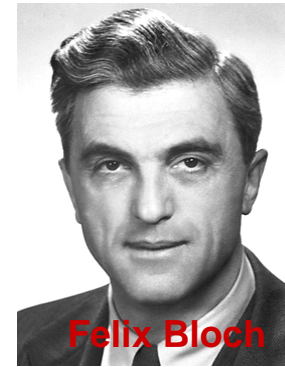
1944



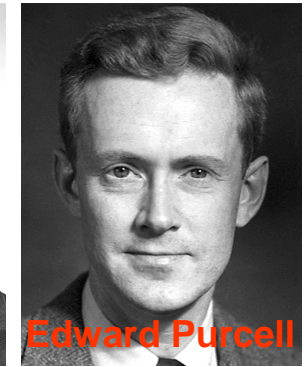
Isidor Rabi

*první měření magnetického
momentu atomového jádra*

1952



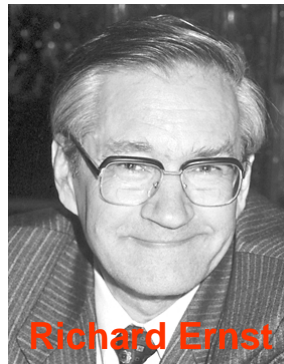
Felix Bloch



Edward Purcell

*rozvoj metod měření precese magnetického
momentu a objevů s tím spojených*

1991

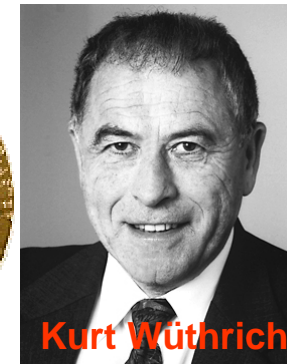


Richard Ernst

*metodologie NMR vysokého rozlišení
(2D experimenty)*



2002



Kurt Wüthrich

*NMR metodika určování prostorové
struktury biomolekul*

2003



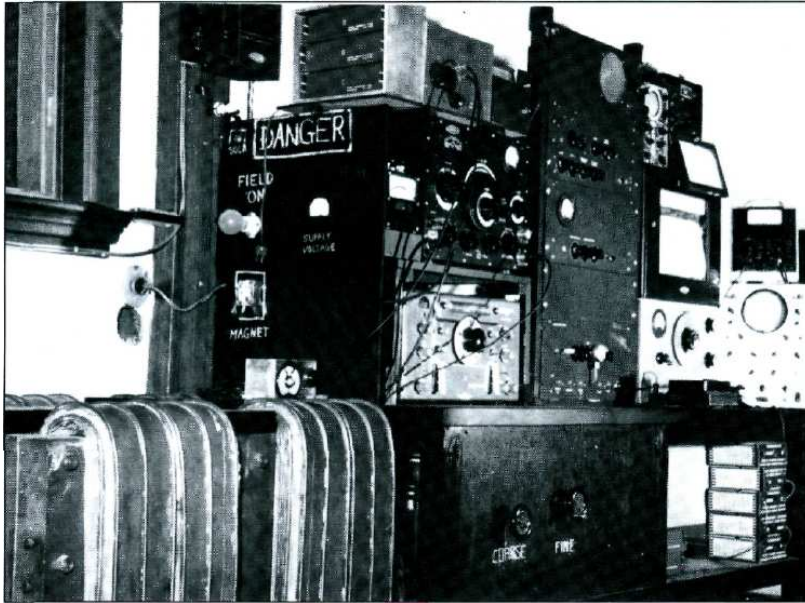
Peter Mansfield



Paul Lauterbur

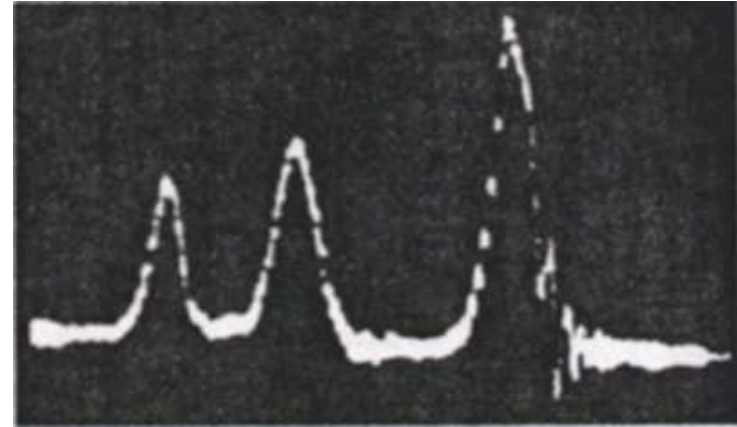
*zobrazování magnetickou rezonancí
(MRI)*

NMR

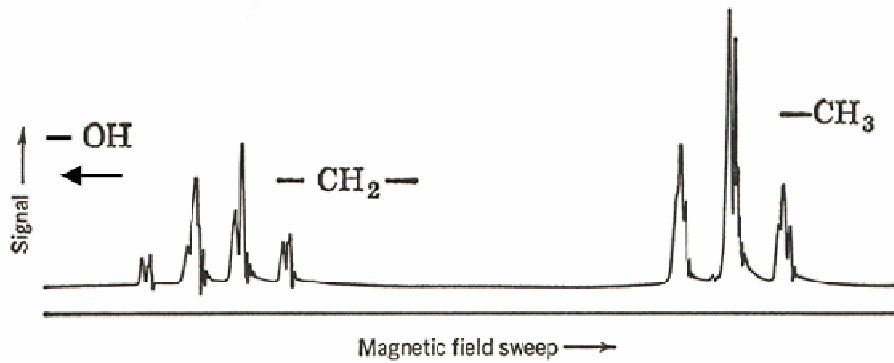


Early CW spectrometer built at Caltech in 1951 for the study of solids.

Purcell
1951



Varian 60 MHz spektrometr
1958



NMR



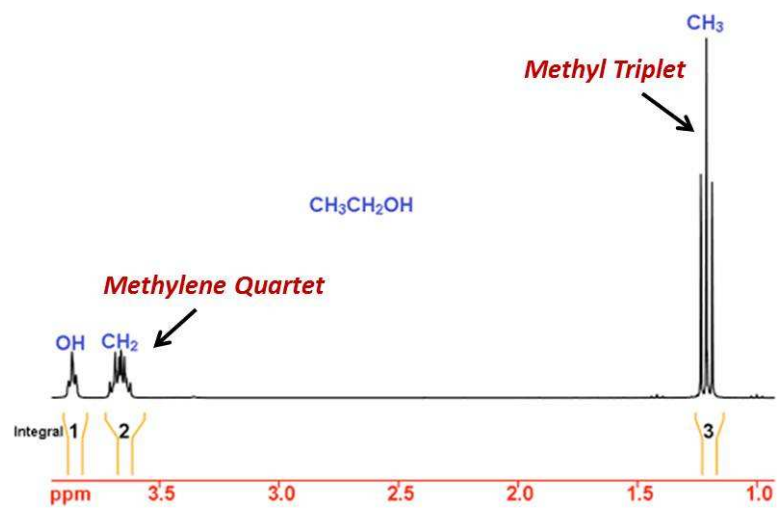
Bruker



Jeol



Varian / Agilent



^1H NMR Spectrum of *ethanol* at 700 MHz

Rozkvět NMR

První aplikace – měření magnetických momentů jader

Finding the magnetic moment of a nucleus was difficult because different electronic environments around each equivalent magnetic nuclei shifted the peak from its true value. Annoyed physicists dubbed the phenomenon the "**chemical shift**," not realizing the analytical potential of their discovery.

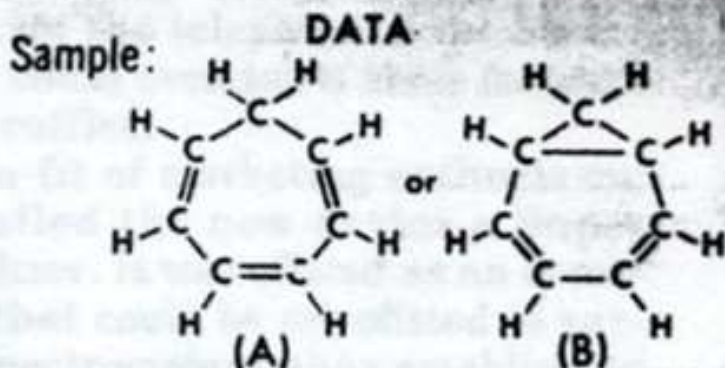
Rychle převzato chemiky

... the "annoying" features of an NMR spectrum, from a physicist's point of view, gave an ideal combination of "enough information to be useful and not so much to be an embarrassment of riches"

http://www3.wooster.edu/chemistry/is/brubaker/nmr/nmr_landmark.html

Rozkvět NMR

20 USE OF INTEGRATED INTENSITIES IN STRUCTURE ANALYSIS (Number 20 of a series)



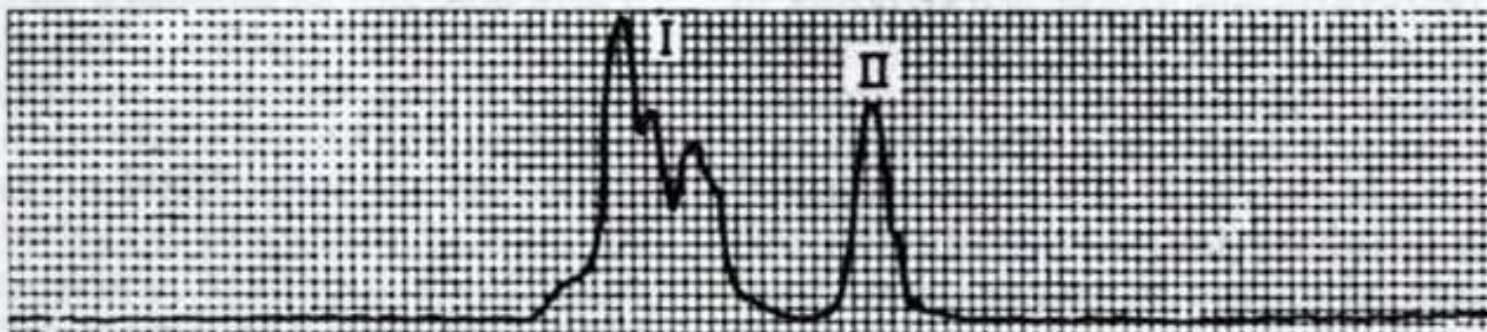
Volume: 0.01 cc.
Signals Observed: H^1
Frequency: 30 mc.
Field: 7050 gauss

INTERPRETATION

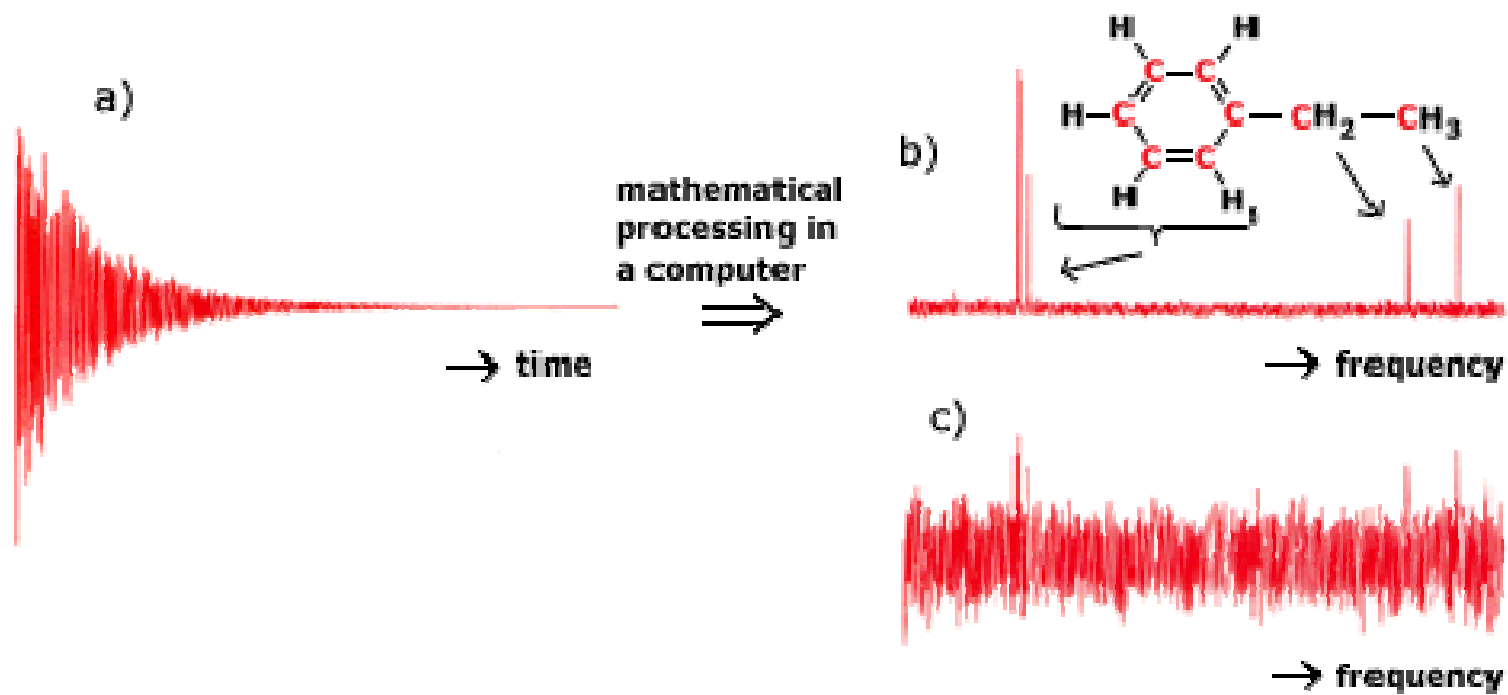
In solving the problem of whether structure A or B correctly represents the sample submitted for analysis, it becomes necessary to measure the areas under the nuclear resonance peaks. Region I contains peaks corresponding to the protons attached to doubly bonded carbon atoms, while region II corresponds to protons attached to carbon atoms forming only single bonds. The ratio of areas (I:II) should be 3:1 for compound A and 1:1 for compound B. The measured value of 2.9:1 leaves no doubt of the identity of the sample with structure A.

The sample was furnished through the courtesy of
Professor E. J. Corey, Chemistry Department, University of Illinois.

INCREASING MAGNETIC FIELD \longrightarrow

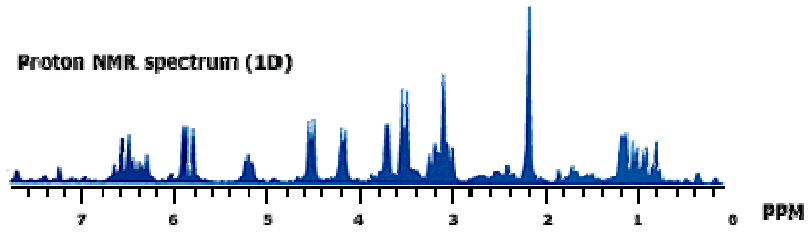
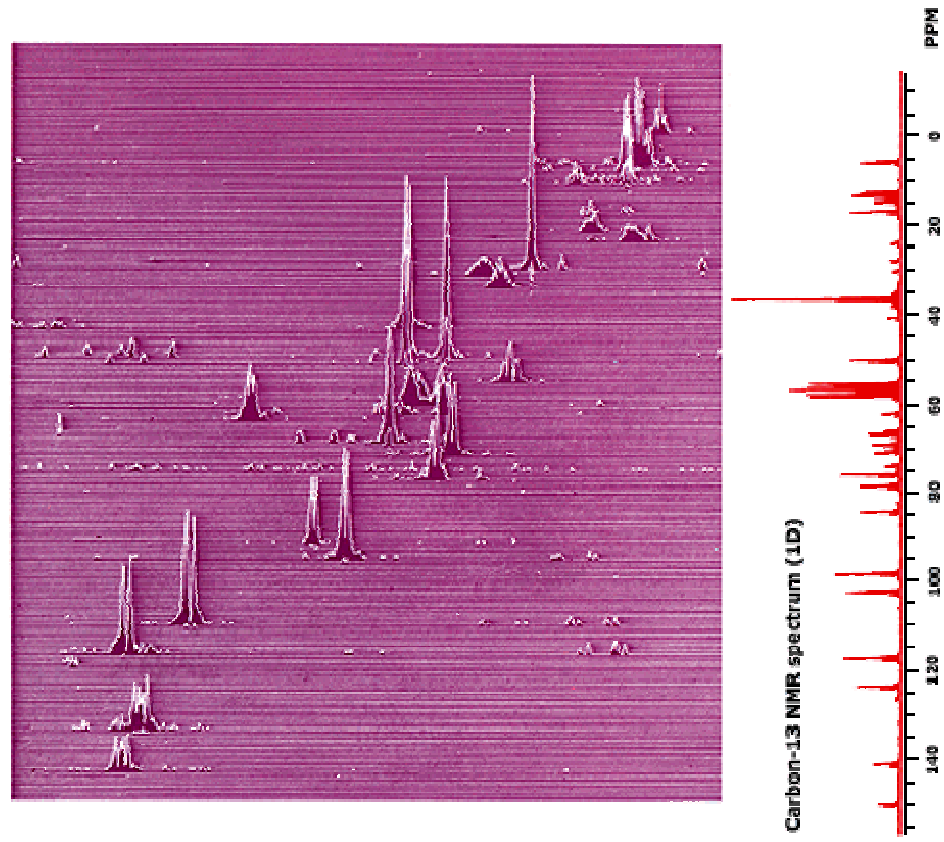
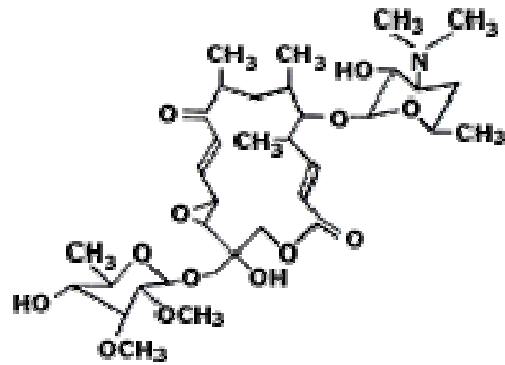


Pulsní metoda měření



R. Ernst, Nobel Prize poster

Vícerozměrná spektra

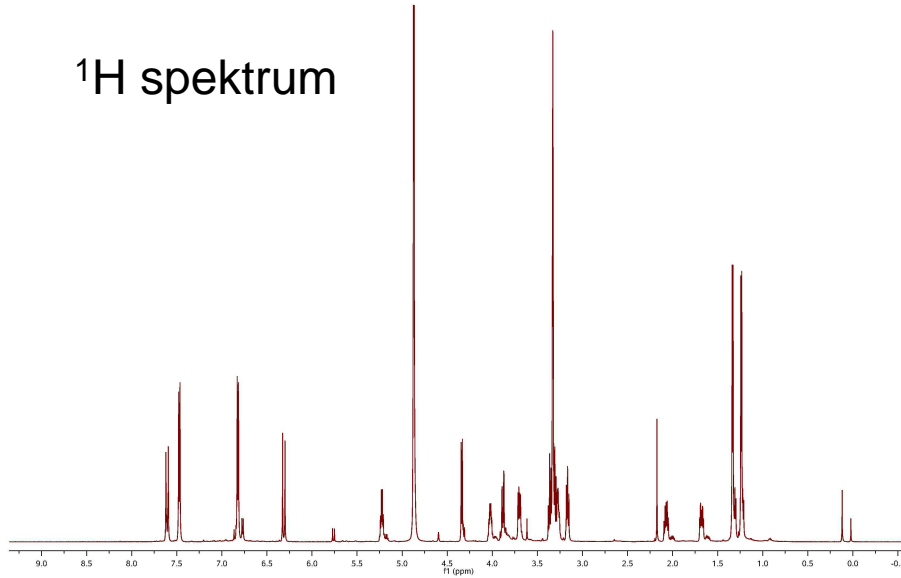


Ralph U. Hurd, General Electric

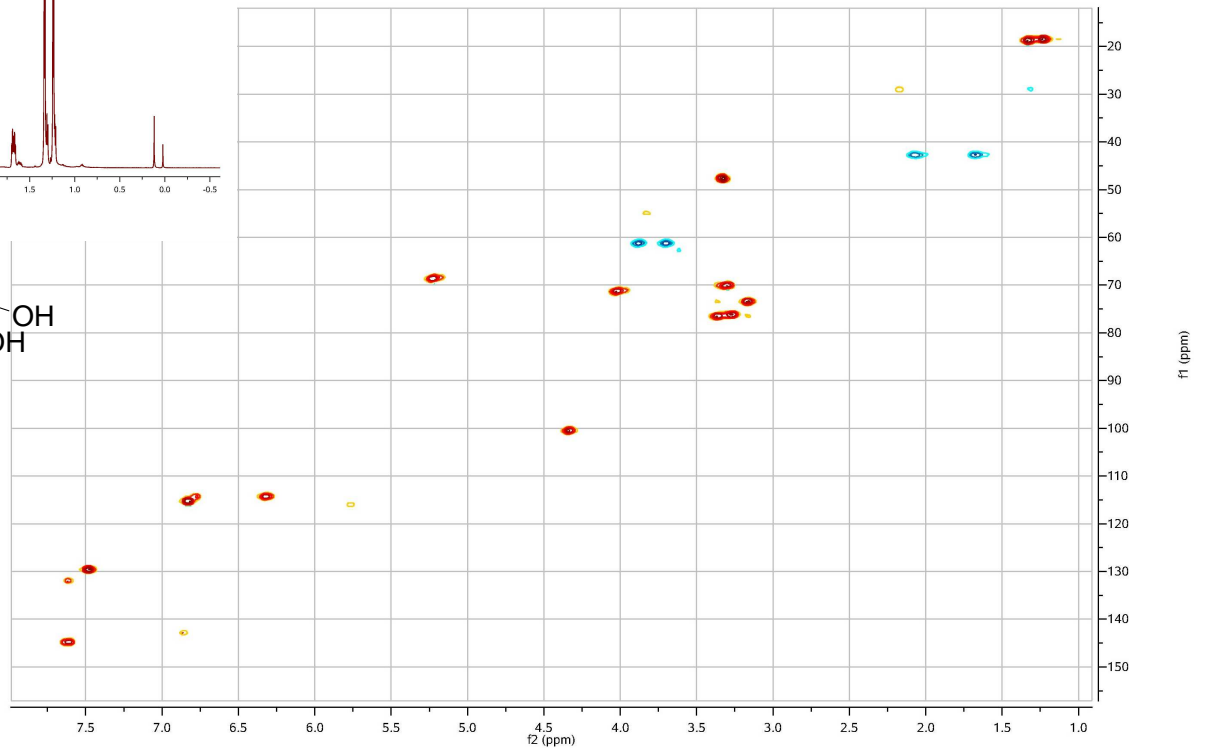
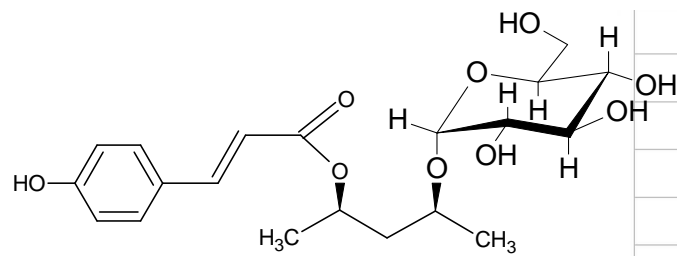
R. Ernst, Nobel Prize poster

Vícerozměrná spektra

^1H spektrum



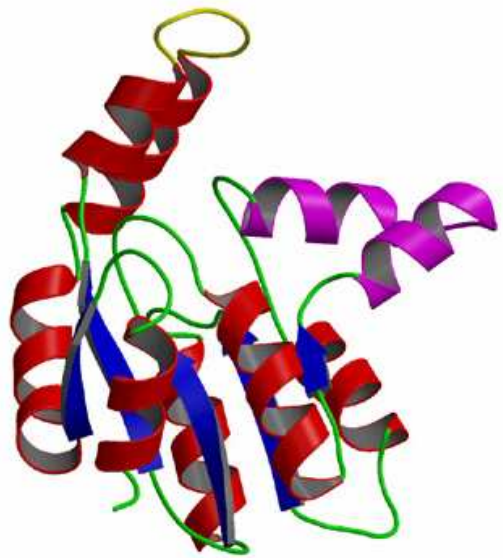
2D HSQC korelační spektrum



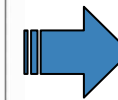
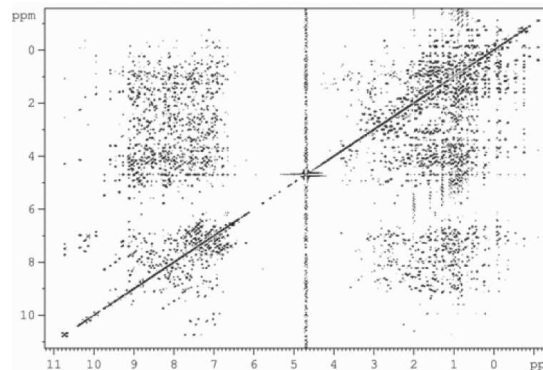
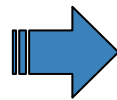
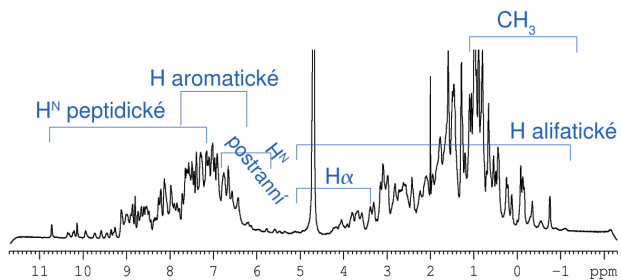
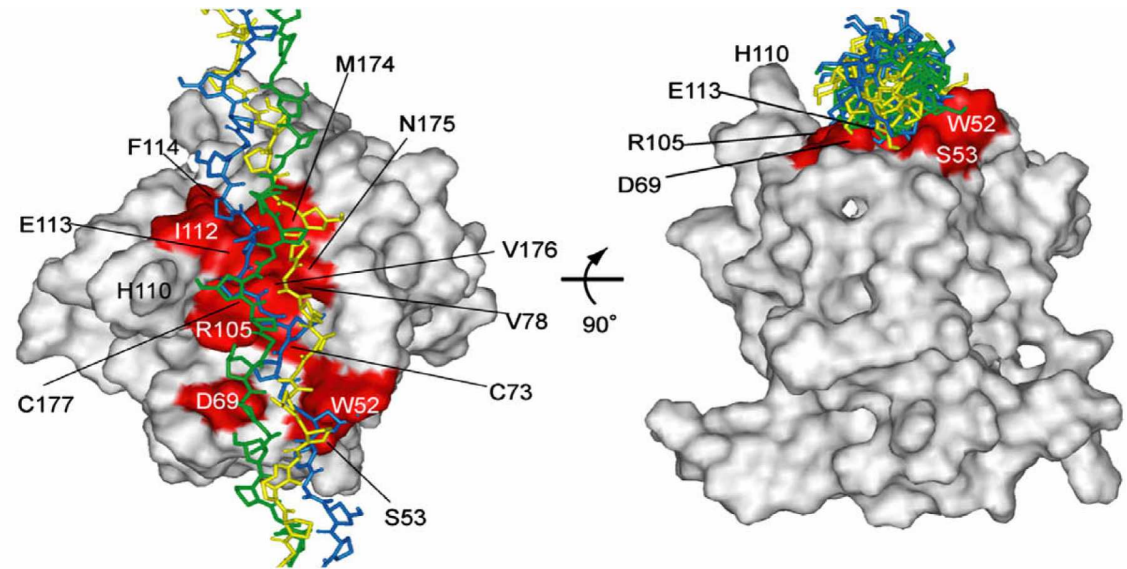
NMR biomolekul

Prostorová struktura molekul

Pohyblivost a lokální flexibilita struktury



Vzájemné interakce biomolekul



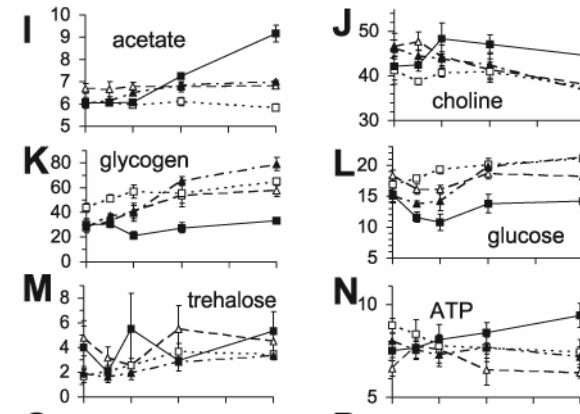
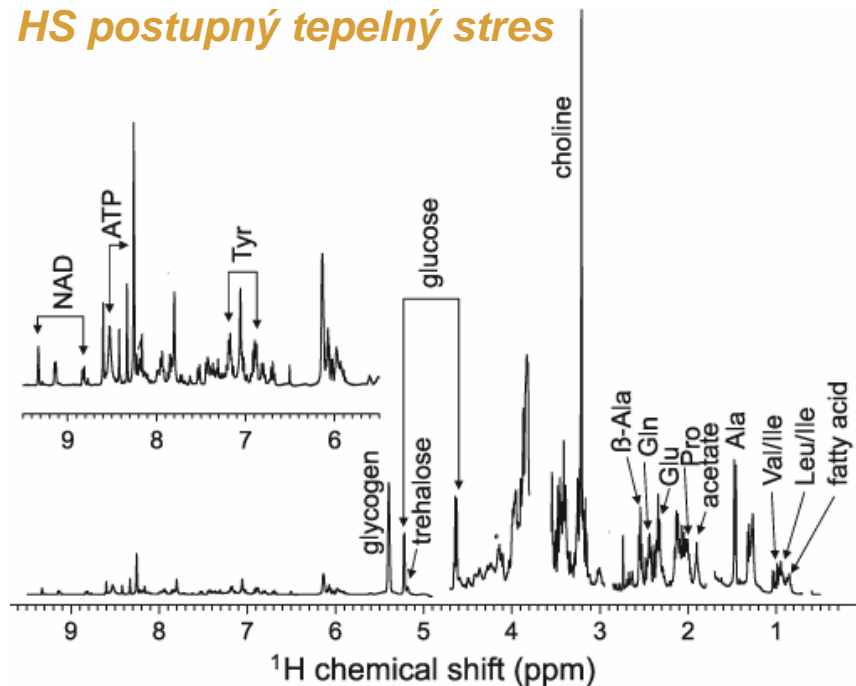
3D **4D**

zředění informace

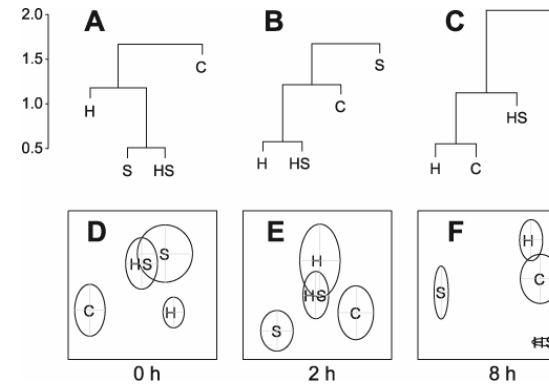
Metabolomika

analýza změn složení metabolitů v reakci na tepelný stres *Drosophila melanogaster*

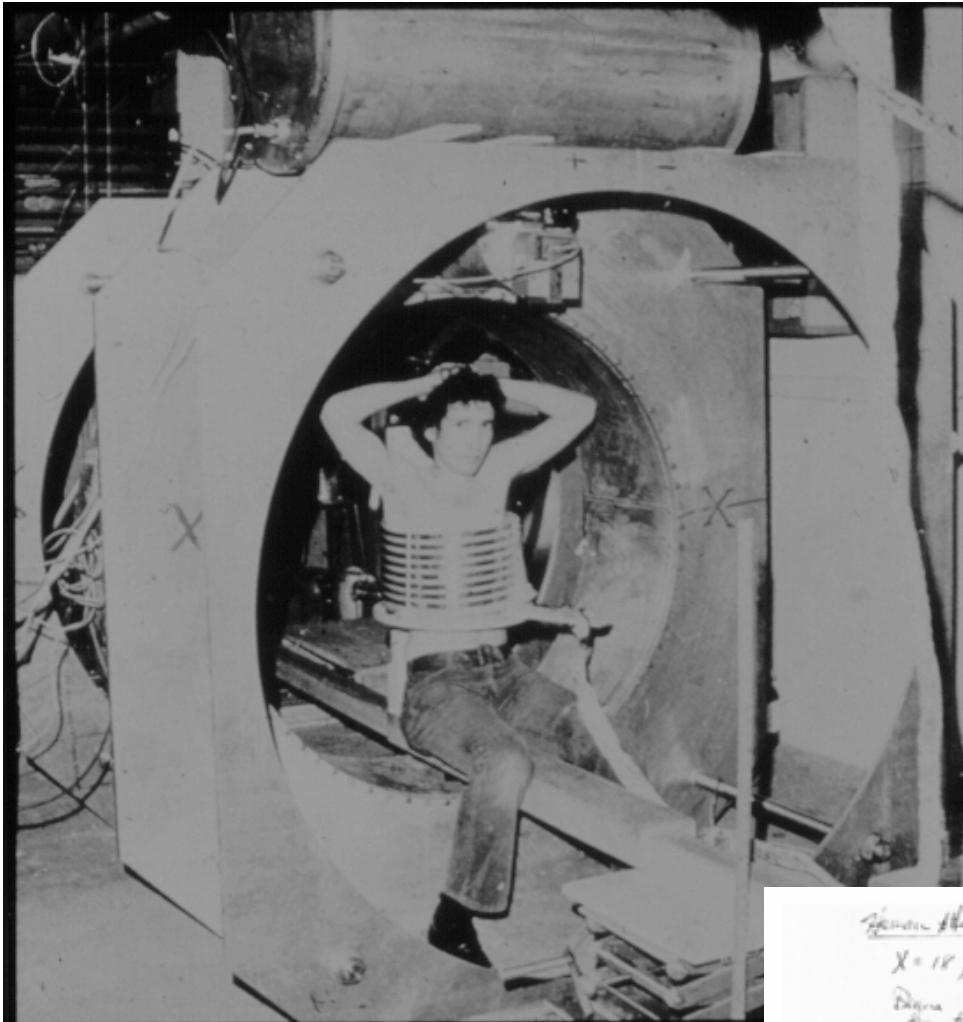
C kontrola
H malý tepelný stres
S velký tepelný stres (20% mortalita)
HS postupný tepelný stres



multikomponentní statistická analýza



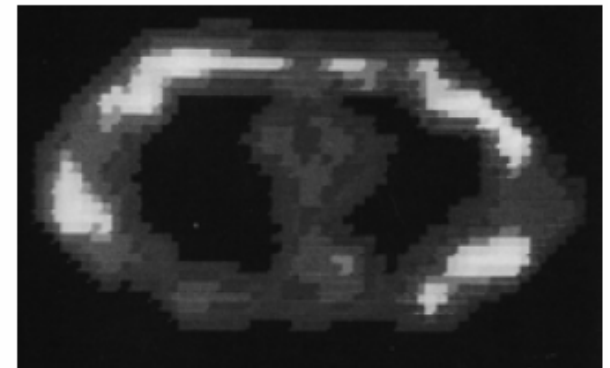
MRI



First successful NMR scan, July 1977
in Damadian's machine, patient Dr. Minkoff

Human Image 11:03 PM 7/17
X=18, Y=2, Z=6%
Done at 3% from bottom up of
scan to right Power supply

FANTASTIC SUCCESS!
4:45 AM First Human Image
Complete in Amazing Detail
Showing Heart
Lungs
Arteries
Musculature



MRI

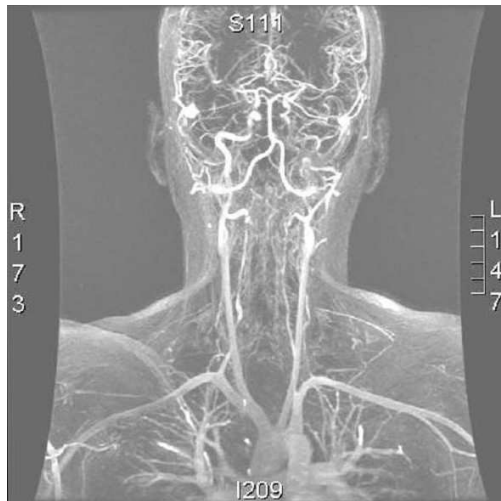


denes

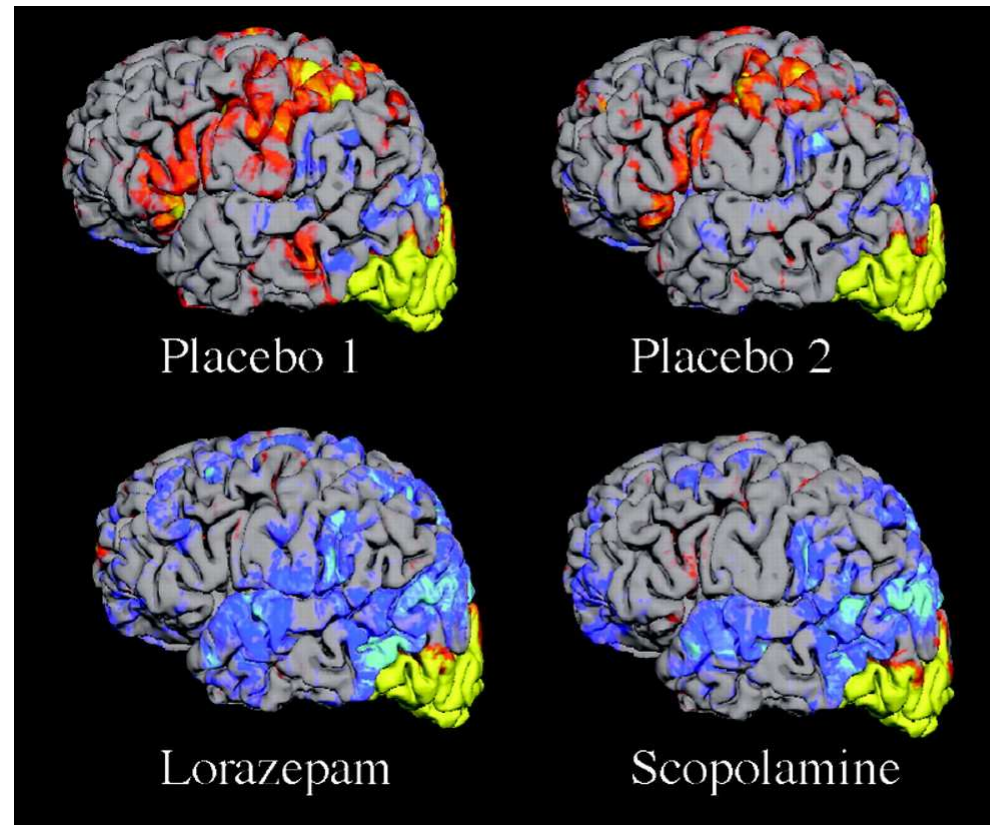


MRI

Angiografie

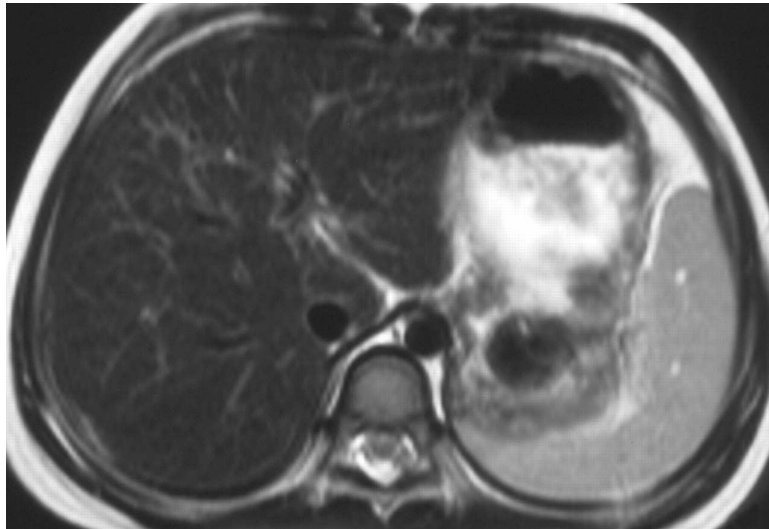
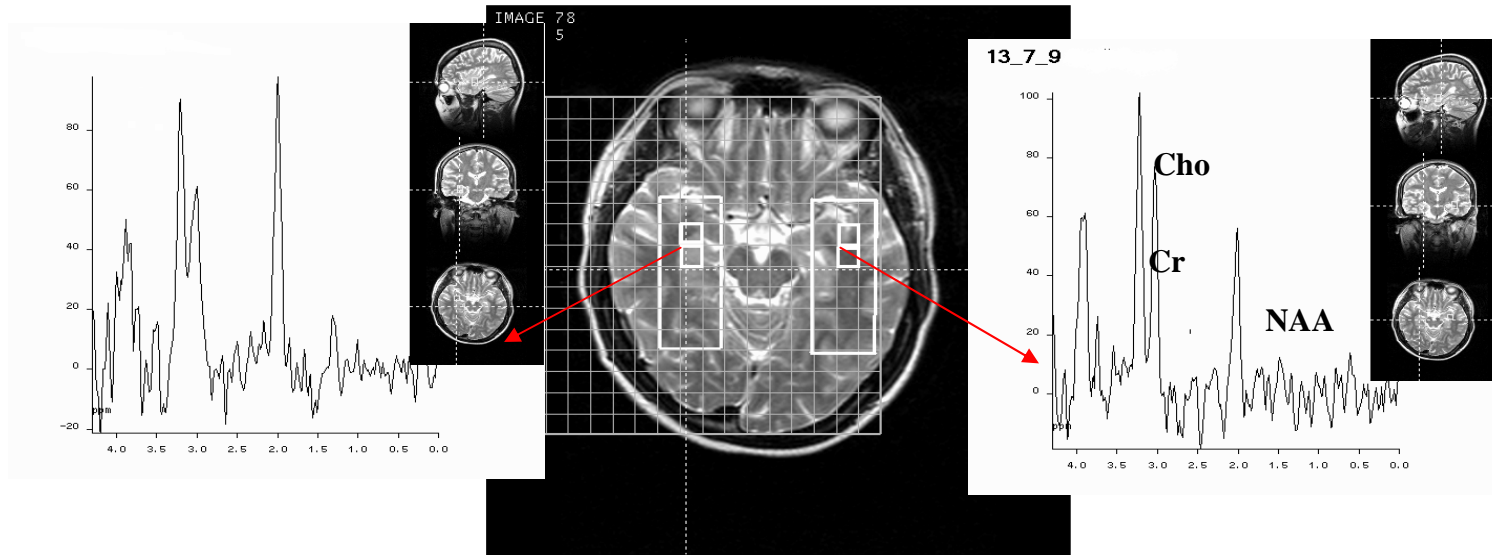


Funkční MRI

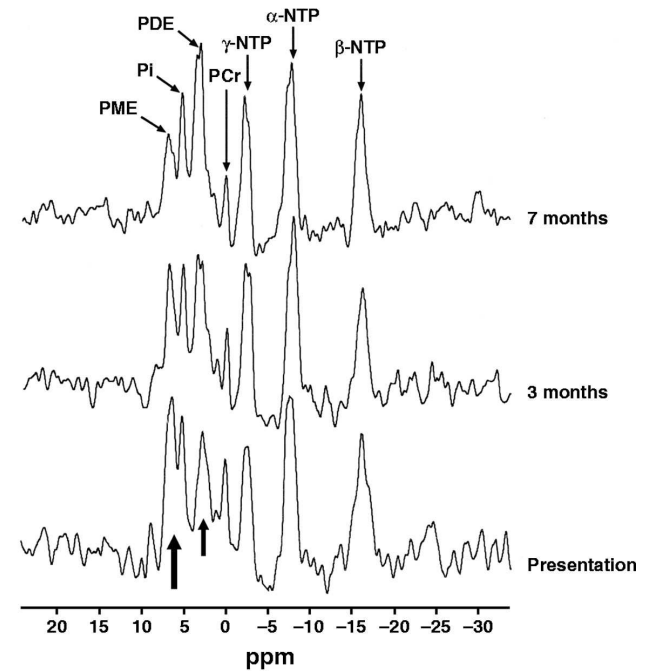


aktivace různých částí mozku při použití „drog pravdy“

in vivo MR spektroskopie



Wilson's disease



Cvičení z NMR biomolekul

domácí slivovice

