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FORTHCOMING NMR MEETINGS (Additional listings are solicited)

1985 Eastern Analytical Symposium - November 19-22, 1985; Penta Hotel, New York; see Newsletter No. 321, pp. 17-18, and No. 324, pp. 46-47.

British Radiofrequency Spectroscopy Group - April 9-11, 1986; Oxford University, Oxford OX1 3QR England; see Newsletter No. 323, p. 23.

27th ENC - April 13-17, 1986; Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, NY 14642, 716-275-5541; see Newsletter No. 323, p. 31.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

1986 Eastern Analytical Symposium - October 6-10, 1986; Hilton Hotel, New York; see page 27.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed. Please make your wishes known.

All Newsletter Correspondence
 Should be Addressed to:

Professor Bernard L. Shapiro
 Department of Chemistry
 Texas A&M University
 College Station, Texas 77843 U.S.A.

DEADLINE DATES

No. 327 (December) --- 22 November 1985

No. 328 (January) ---- 27 December 1985

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Editor, TAMU NMR Newsletter
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DSS for H.-H. Match for ^{29}Si NMR

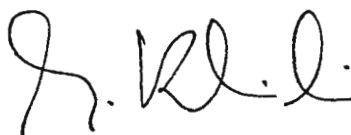
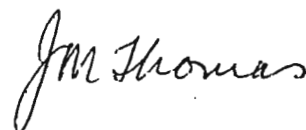
26 August 1985

Dear Professor Shapiro,

In March this year we took delivery of a Bruker MSL 400 multipurpose spectrometer which we shall use to continue our multinuclear NMR studies of solids. The instrument is not yet fully operational.

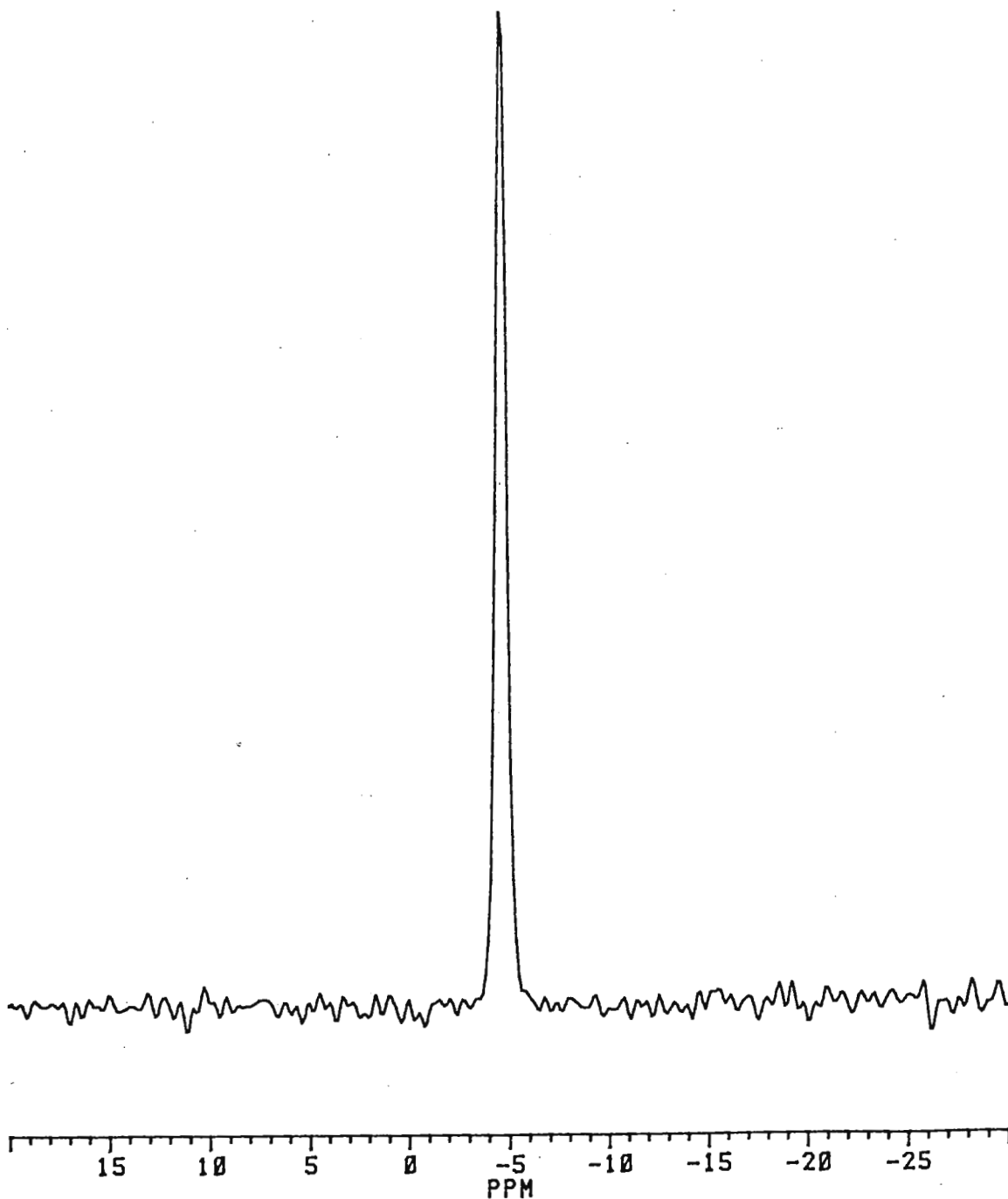
Continuing our interests in ^{29}Si solid-state NMR¹ we wish to use cross-polarisation to gain information on proton-silicon interactions. The compound originally suggested² for setting the Hartmann-Hahn match, which is known as Q_8M_8 , is difficult to prepare and therefore not readily obtained (Isocommerz, an East German company which is the only source we are aware of quotes \$350 per gram). Instead we have successfully used the sodium salt of 3-(trimethylsilyl)-1-propane sulphonic acid (DSS) (\$7 per gram from Aldrich, catalogue no. 17,833-7). The spectrum of DSS consists of a single line at about -4.6ppm from TMS with a linewidth of 40Hz for the powdered sample. The Hartmann-Hahn match is easily established on a single shot using a 5s recycle time and 5ms contact time. The accompanying spectrum indicates the signal to noise we can obtain from 8 scans using a Bruker magic-angle-spinning double-bearing probehead.

Yours sincerely,

T.A.CarpenterJ.KlinowskiJ.M.Thomas

References

1. C.A.Fyfe, J.M.Thomas, J.Klinowski and G.C.Gobbi,
Angew.Chem.Int.Ed.Engl., 22, 259 (1983); J.Klinowski, Prog.NMR Spectrosc.,
16, 237 (1984)
2. E.Lippmaa, M.Magi, A.Samoson, G.Engelhardt and A.-R.Grimmer,
J.Amer.Chem.Soc., 102, 4889 (1980)





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August 26, 1985

Professor Bernard L. Shapiro
Texas A & M University
Department of Chemistry
College Station, TEXAS
77843-3285

Dear Barry:

^{35}Cl NMR Transport Studies

We have recently been using ^{35}Cl NMR to study the transport of Cl^- in human erythrocytes. The quadrupolar ^{35}Cl nucleus is an excellent candidate for *in vitro* transport studies because it has a relatively short relaxation time. Figure 1A shows the time course of the efflux of Cl^- from human erythrocytes initially containing $\approx 140 \text{ mM}$ Cl^- inside, but washed free of Cl^- on the outside, after the addition of the counter ion H_2PO_4^- to the outside. Fifty sequential spectra are presented, requiring 1000 scans each.

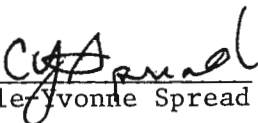
The puzzling feature of these experiments, done at a 50% hematocrit, is that we do not see the signal from the intracellular Cl^- under the conditions of the experiment. This is because it is too broad. If we increase the hematocrit to 80%, add the inhibitor DIDS to block transport, add 20 mM Co^{+2} to broaden and shift the extracellular Cl^- , and increase the sweep width we see the spectrum presented in Figure 1B. Underneath Figure 1B is the two line simulated spectrum (1C) with the following parameters:

	$\Delta\nu$	% area
intracellular	2700 Hz	85%
extracellular	280 Hz	15%

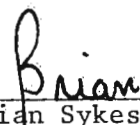
The extracellular resonance is normally 10-20 Hz wide in the absence of paramagnetics.

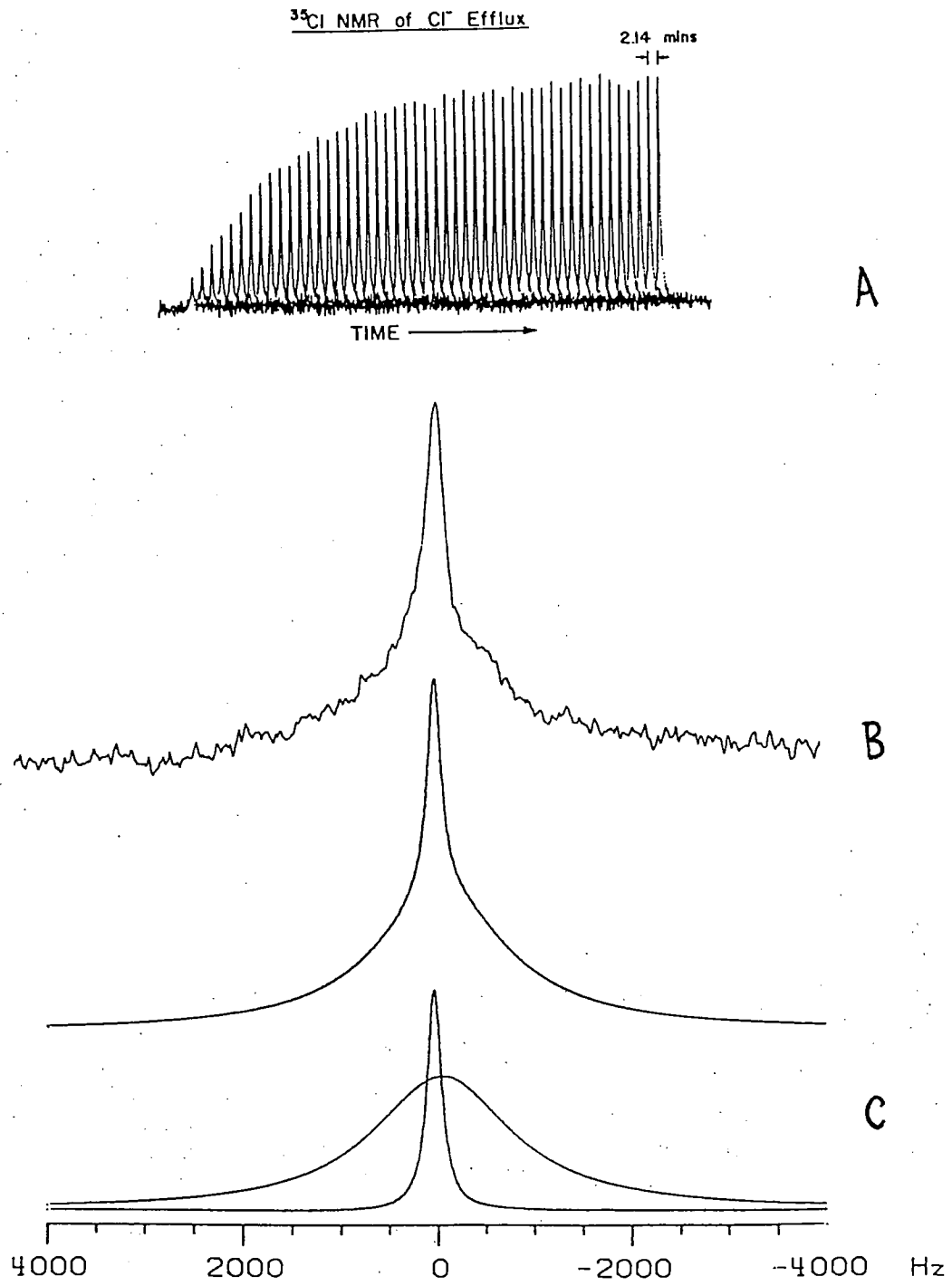
Apparently the intracellular Cl^- is broadened by interaction with the high concentration of hemoglobin within the cell.

Best regards,


Carole Yvonne Spread


Fred Brauer


Brian Sykes



Institut für Molekularbiologie und Biophysik

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Professor B. L. Shapiro

TAMUNMR Newsletter

Department of Chemistry

Texas A&M University

College Station, Texas 77843

1085

September 12, 1985

Complete Protein Fingerprints by DQ Spectroscopy

Dear Barry:

At pH values below ca. 6.0 the amide protons of a protein exchange sufficiently slowly with H₂O to be observed with water-suppression by continuous selective irradiation. However, some NH-C^αH-cross peaks in 2D correlated spectroscopy (COSY) may be "bleached out" due to saturation of C^αH-signals under the waterline (1), so that at any given temperature an incomplete "fingerprint" of the protein (2) is obtained. In contrast, these missing NH-C^αH-connectivities do show up in 2D double quantum spectra obtained with the same solvent saturation scheme as for COSY. This relies on the fact that double quantum coherence is excited starting both from C^αH and NH. In terms of product operators the evolution of initial NH-magnetization in the course of the DQ-experiment ($\pi/2 - \tau/2 - \pi - \tau/2 - \pi/2 - t_1 - \pi/2$ - acquisition) may be described as follows (3):

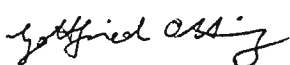
$$I_{Nz} \xrightarrow{(\pi/2)_x} -I_{Ny} \xrightarrow{H_{II}(\tau/2) - (\pi)_Y - H_{II}(\tau/2)} 2I_{Nx}I_{\alpha z} - [I_{Ny}]$$

$$\xrightarrow{(\pi/2)_x} -2I_{Nx}I_{\alpha y} \xrightarrow{(2Q)^{sel}} \xrightarrow{(\pi/2)_x} -I_{Nx}I_{\alpha z}$$

where the indices N and α denote the protons bound to N and C^α, respectively. The term in square brackets is eliminated by phase cycling. The operation (2Q)^{sel} stands for the selection of the DQ-coherence by phase cycling from the mixed zero- and double-quantum order represented by the operator $2I_{Nx}I_{\alpha y}$. Clearly, this pathway does not depend on initially available C^αH-magnetization. A second, analogous pathway can be outlined starting from C^αH-magnetization.

A paper has been submitted to J. Magn. Reson. which contains an experimental verification of the principles outlined here.

Best regards,



Gottfried Otting



Kurt Wüthrich

REFERENCES

1. A. Kumar, G. Wagner, R. R. Ernst, and K. Wüthrich, Biophys. Res. Commun. 96, 1156 (1980)
2. G. Wagner, and K. Wüthrich, J. Mol. Biol. 155, 347 (1982)

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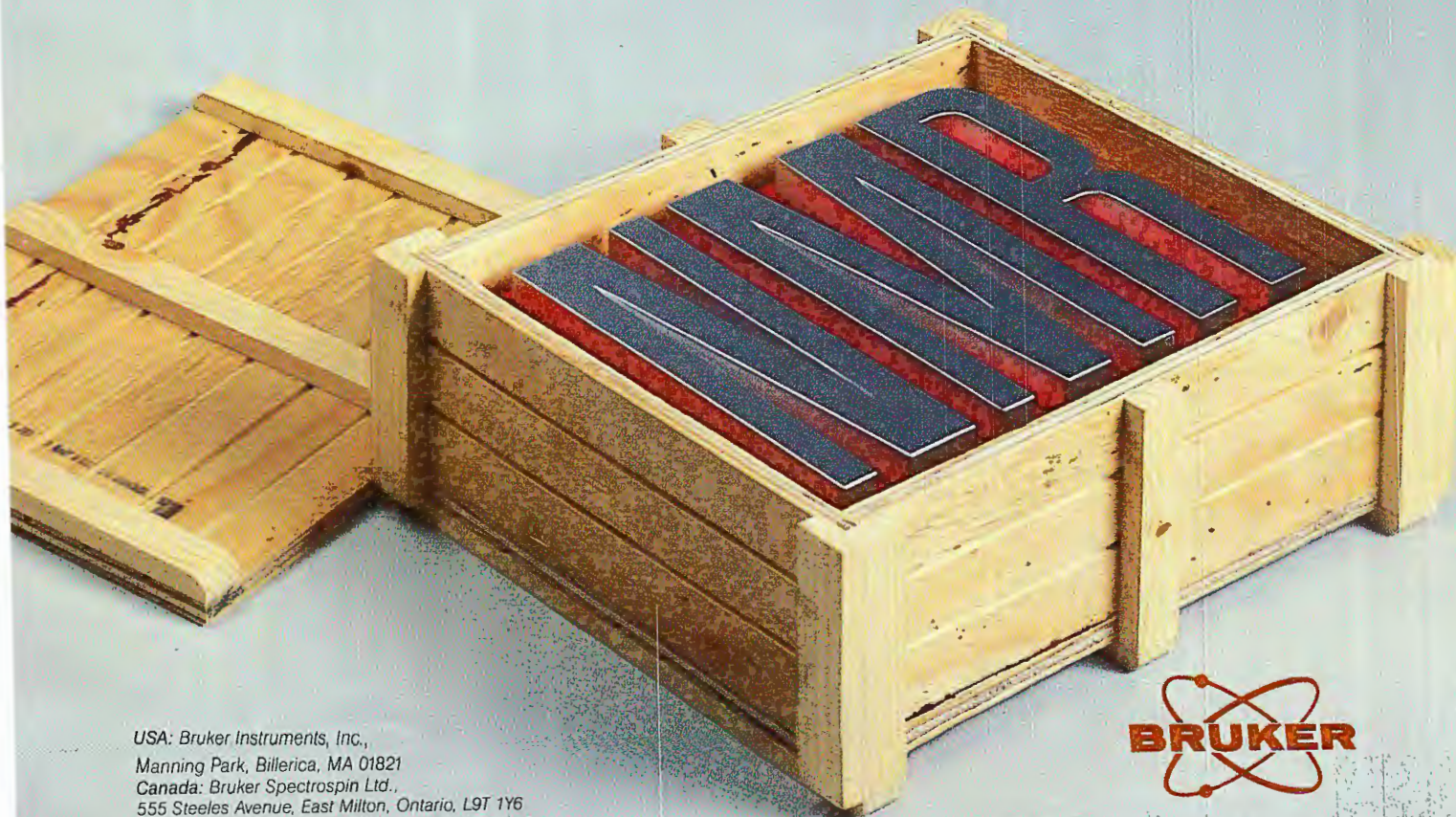
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Dear Barry

CALIBRATION OF A HOMONUCLEAR DECOUPLER

We have recently taken delivery of a new Bruker AM-400, and have been testing out the homonuclear decoupler in an effort to get optimum parameters for NOE experiments. Our first experiment (Fig. 1) was designed to test the bandwidth of the

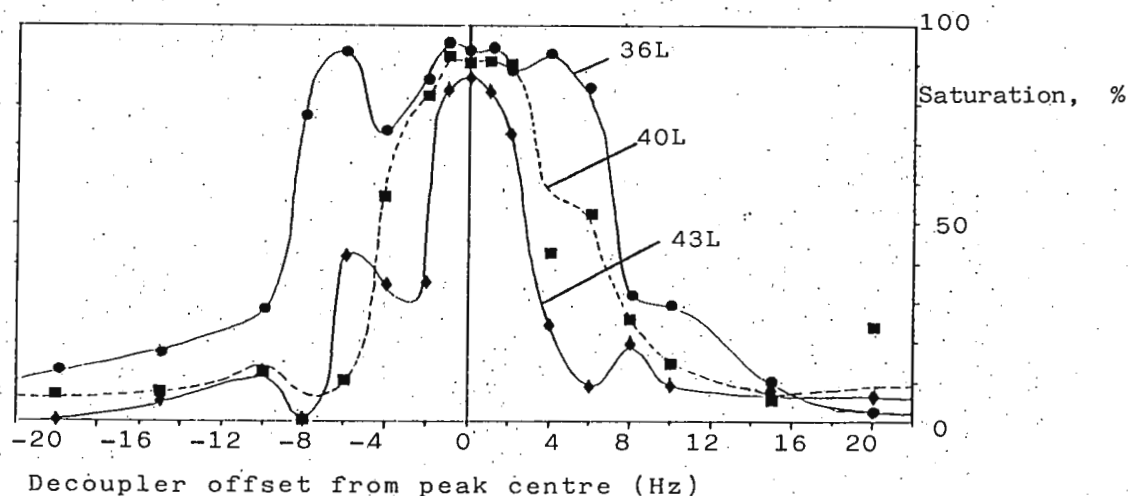


Figure 1

decoupler at various power levels, marked on Fig. 1 as attenuations (in dB) of the low-power decoupler. The spectrum consisted of a single sharp well-digitized peak; the decoupler position was moved off-resonance and the height of the resultant peak was plotted as a function of decoupler offset. Four scans were acquired at each frequency. The results of this rather crude experiment are a little disconcerting, for two reasons. Firstly, as we have observed on other spectrometers, the bandshape is not symmetrical, so it makes a difference on which side of a peak the decoupler is placed. Secondly, and more significantly, the bandshape has 'wings', most noticeably at ± 7 Hz at 43L and ± 4.5 Hz at 36L. This has particular implications for low-power irradiations in crowded

spectra. To take the worst example, if you wish to saturate selectively the high-field signal of a pair of signals 6 Hz apart, the selectivity will in fact be about four times worse at 43L than at 40L. Finally the inverse relationship of bandwidth to pulse length is only approximate: 180° pulse lengths were measured as 0.23s for 43L, 0.11s for 40L, and 0.037s for 36L.

Our second experiment (Fig. 2) is described on the Figure.

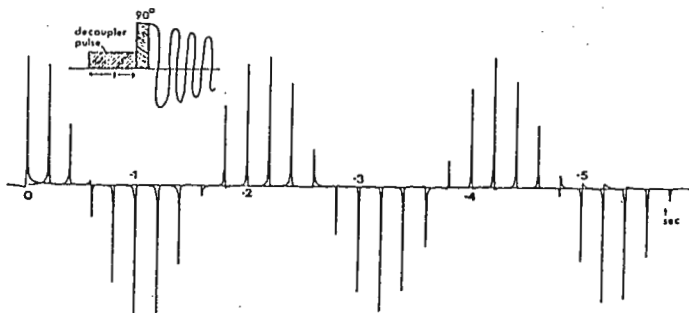


Figure 2

A power of 40L was used. This gives an accurate measure of the decoupler pulse width, and also shows that the decoupler has a remarkably low inhomogeneity (at least, we found it remarkable).

As a result of these experiments, we use 40L for most of our 1D NOE experiments, and pre-irradiation times of $\geq 0.08s$.

Please credit this to Tony Thomas's account.

Yours sincerely

M.P.W.

Dr M P Williamson



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September 19, 1985

Professor Bernard Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

 ^{13}C Solid-State NMR of Stratum Corneum

Dear Professor Shapiro:

We have been using ^{13}C solid-state NMR to study the molecular properties of pig stratum corneum (s.c.), the outer layer of the epidermis. The s.c. consists of a corneocyte membrane, with keratin and extended domains of lipid bilayer in the intracellular space, and contains 79% protein and 21% lipid by weight.

With a variety of pulse sequences (CP with several contact times, Dipolar Dephasing, ^{13}C T_1 discrimination) and MASS, we can take advantage of the heterogeneity of this system, to observe both the protein and lipid components. To date, we have identified two types of lipid signals--a highly fluid (liquid-crystalline ?) and an immobile (gel ?) type.

We have used the following experiments (see attached figure) to study different components of the s.c. Our observations are summarized below:

- A. CP (1 ms contact time) - typical protein spectrum, sharp resonance at 33 ppm due to a rigid lipid $[(\text{CH}_2)_n]$ (*)
- B. CP (15 ms contact time) - attenuated protein signals, narrow resonances for fluid lipid $[(\text{CH}_2)_n]$ at 30 ppm (↓)
- C. Dipolar Dephasing (40 μsec) - protein carbonyl, nonprotonated aromatic, mobile CH_2/CH_3

Please credit this letter to Fouad Ezra's subscription.

Sincerely,

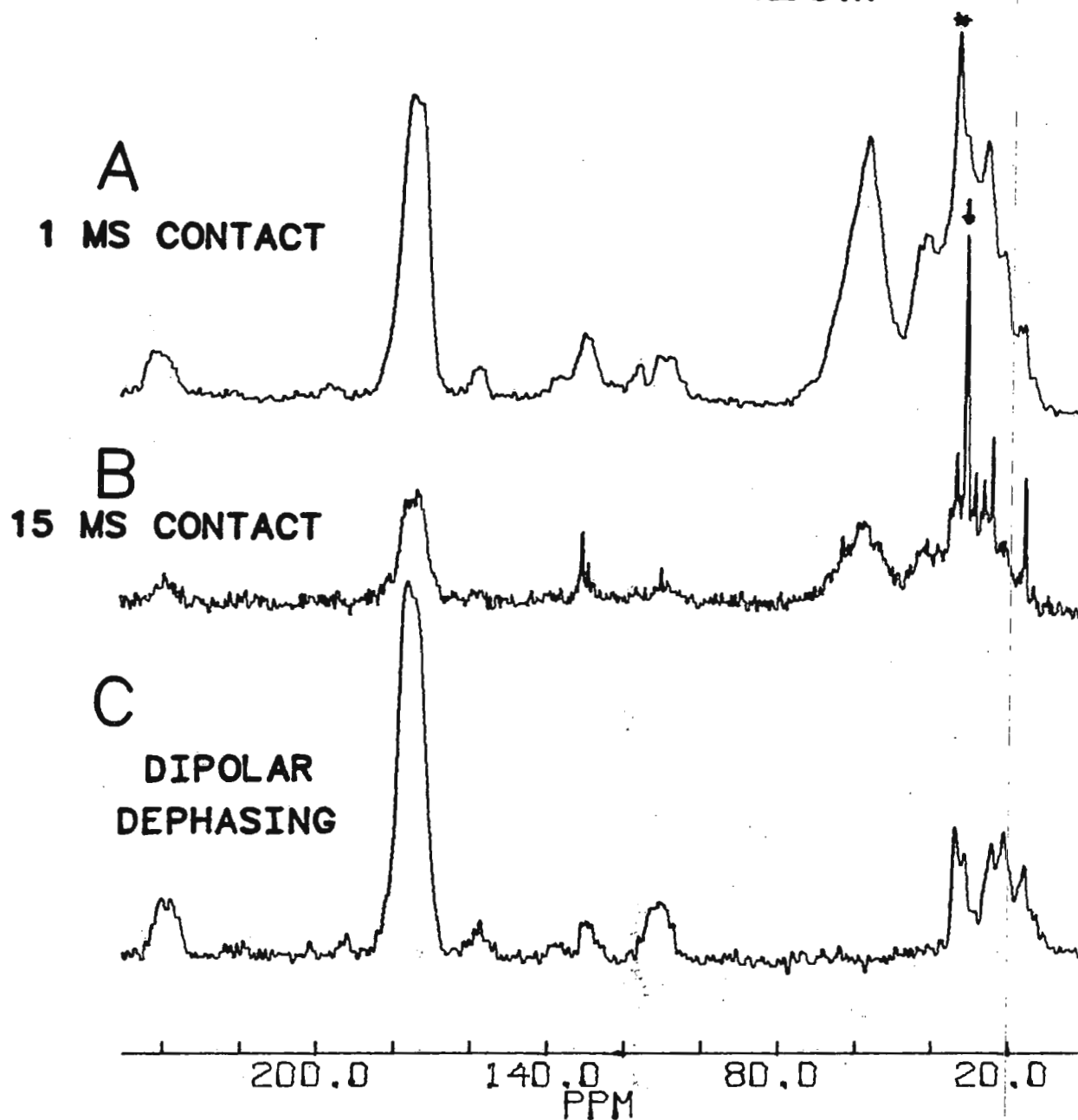
The Procter and Gamble Company
Research and Development Department

Robert A. Kinsey

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C-13 CP-MASS PIG STRATUM CORNEUM



75.46 MHz ^{13}C NMR spectra of pig stratum corneum with modifications of the CP pulse sequence, on a Bruker CXP-300 with a Doty Probe, MASS ~4.9 kHz, using a 4.5 μsec 90° ^1H pulse, 4 sec recycle, 20 Hz exponential multiplication. A) CP, 1 ms contact time, 500 scans. B) CP, 15 ms contact time, 3000 scans. C) Dipolar Dephasing, 1 ms contact time, 40 μsec delay, 500 scans.



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27 August 1985

Professor B.L. Shapiro
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Texas A&M University
College Station, Texas 77843
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Antimony-Fluorine Spin Coupling

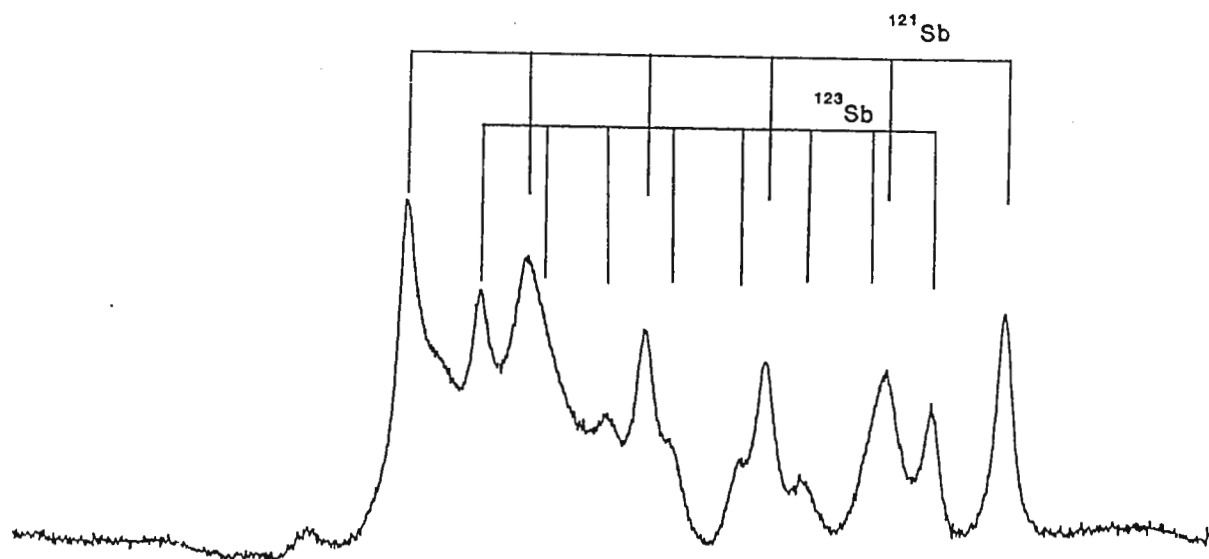
Dear Barry,

It has not been possible to measure the antimony-fluorine spin coupling of SbF_6^- from the fluorine resonance spectrum of the ion due to rapid quadrupolar relaxation. An estimate of $J^{19\text{F}-121\text{Sb}}$ of 1840 Hz for aqueous KSbF_6 was found from the ^{121}Sb spectrum (1). In the diagram there is the fluorine resonance spectrum of a complex of $\text{NO}^+\text{SbF}_6^-$ and hexamethylbenzene dissolved in sulfur dioxide. Both the $^{19\text{F}}-^{121}\text{Sb}$ and $^{19\text{F}}-^{123}\text{Sb}$ spin couplings are clearly visible. Presumably complexing of NO^+ with hexamethylbenzene gives a large cation with a diffuse positive charge and little interaction with the SbF_6^- anion (2). This gives a very small electric field gradient at antimony and reduces the rate of quadrupole relaxation sufficiently to observe $J^{19\text{F}-121\text{Sb}}$ of 1.95 ± 0.002 KHz and $J^{19\text{F}-123\text{Sb}}$ of 1.05 KHz. The ratio of J values (1.86) agrees closely with that of the gyromagnetic ratios (1.85). The spectral pattern is characteristic of coupling to a quadrupolar nucleus with the outer lines narrower and more intense (3). There is a broad impurity peak under the low field part of the pattern.

Yours truly,

S. Brownstein

- (1) E.L. Muettertriss and W.D. Phillips. JACS 81, 1084 (1959).
- (2) S. Brownstein, E. Gabe, F. Lee and L. Tan. J. Chem. Soc. Chem. Commun. 1566 (1984).
- (3) D.W. Aksnes, S.M. Hutchison and K.J. Packer. Mol. Physics 14, 301 (1968).



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NE-L5 Yellow	505-PS	60MHz: Routine analysis, quality control. Not compatible with vortex plugs and coaxial inner cells.	178	2.40	2.30	2.20
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NE-M5 Green	507-PP	90-100 MHz: General research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	3.85	3.75	3.65
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			203	7.15	7.05	6.95

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				1-24	25-49	50-up
NE-L10	513-1PP	60MHz: Routine analysis, quality control. Compatible with vortex plugs. Not recommended for use with coaxial inner cells.	178	\$7.50	\$7.25	\$3.75
			203	8.25	8.00	7.50
NE-M10	513-5PP	90-100 MHz: General research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	12.25	11.75	11.00
			203	13.00	12.50	11.75
NE-H10	513-7PP	100 MHz and up: Research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	14.25	13.75	13.00
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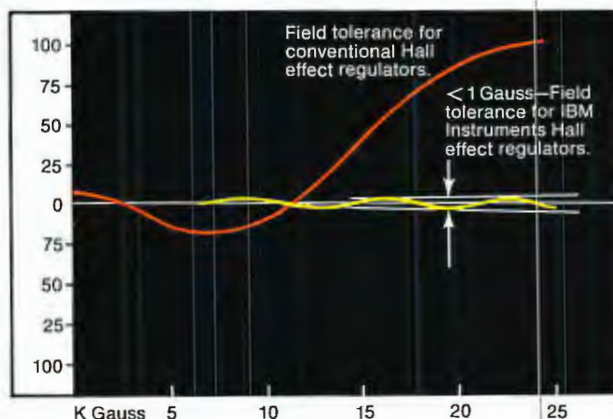
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September 4, 1985

Tin COSY Experiments

Dear Barry:

In response to the "pink sheet" delivered to one of us recently, we'd like to make two announcements (A,B), one request (C), and one technical contribution (D). These are as follows:

- A) Ruth Stark can now be found in the Department of Chemistry, College of Staten Island.
- B) TAMU is famous (did you know that already?) -- there is even a restaurant named after it in the Soho area of New York City. We've enclosed a book of matches for you and reproduced the logo here for TAMU readers.

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- C) Please call this account the C.U.N.Y NMR account rather than the Ruth E. Stark account.
- D) Organotin compounds are notoriously messy; they form strange equilibrium mixtures, cyclize, exchange rapidly among themselves, and the like. In trying to identify at least some of the

compounds/complexes in what we hoped was a rather straightforward organotin thioester but which turned out to have a very complex $^{119}\text{-Sn}$ spectrum, we thought it might be helpful to run some 2D spectra. Rather than test things out on the complex thioester we tested the experiments on a sample of $(\text{Bu}_3\text{Sn})_2\text{S}$. This latter might be expected to have a single peak in its 1D spectrum, but this turns out not to be the case. The COSY spectrum (proton decoupled) contains a minor component of something which shows a classic AX pattern in the cross-peaks. We've checked for all of the obvious tin impurities which we might expect to find due to the synthetic process, and they resonate several ppm away from our AX peaks. A $^1\text{H} - ^{119}\text{-Sn}$ 2D correlated spectrum only shows tin-proton connectivities to our main peak, and the proton spectrum looks "butyl-ish". It's a fun puzzle and an intriguing break from the other messy spectra which we're used to dealing with, like 2D spectra of biological polymers.

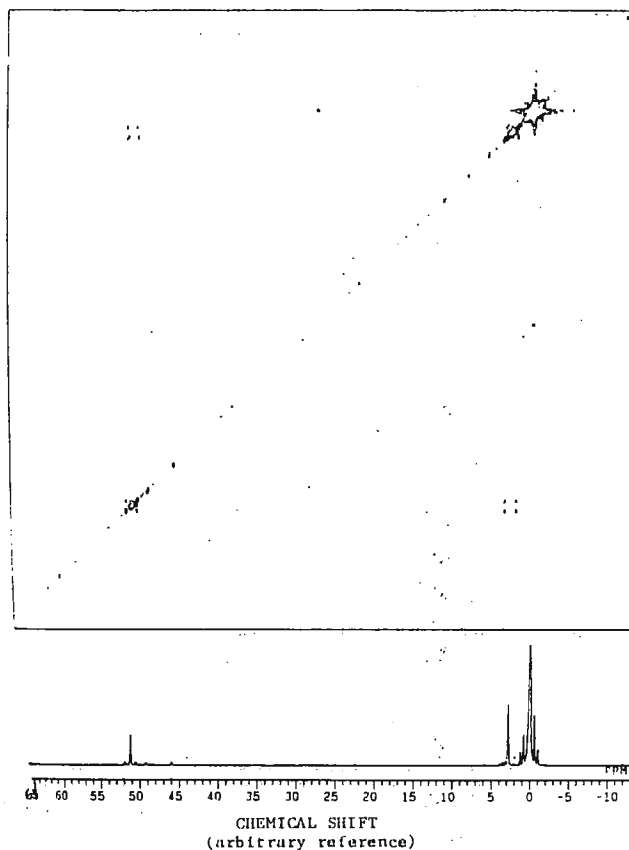
Ruth

Ruth E. Stark
College of Staten Island

Michelle

Michelle S. Broido
Hunter College

RES:mg





DEPARTMENT OF HEALTH & HUMAN SERVICES

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NIH Bldg. 29, Rm. 432

Food and Drug Administration
Bethesda, MD 20205

10 September 1985

Professor B. L. Shapiro
Dept. of Chemistry
Texas A & M University
College Station, TX 77843

Dear Prof. Shapiro;

INSTRUMENTAL HYBRIDIZATION

Since my last contribution, there have been several instrumental developments in the laboratory, and the one which I would like to describe involves hybridization of our JEOL GX-400 with a GE-1280 data system. Our interests cover both solid-state powder pattern spectroscopy and high-resolution two-dimensional spectroscopy. As reported previously (TAMU 313-31), an interim approach for ^2H spectroscopy was achieved on our GX-400; however, there were still spectral width limitations. In addition, the two-dimensional portion of our research was restricted in regards to processing phase-sensitive data due to software limitations, to be corrected in future releases we are told. Nevertheless, we sought a common solution to two rather disparate problems.

By "borrowing" the 1280-based digital half of my home-made spectrometer, and performing some minor GX surgery, with helpful comments from Dan Evans (JEOL) and Joe DiVerdi (SKF), the hybridization was achieved. The GX-400 spectrometer controls the RF and timing of an experiment; however, the analog quadrature FID signals are routed out of the GX system and into the 1280 where they are digitized, signal averaged, and processed by standard NMC-type software. The surgery required installing a toggle switch (+5V or ground) to manually instruct the GX to route the data to the (non-existing) 16-bit digitizer, thus providing the analog FID's at convenient connectors, and tapping out the ADC trigger. These signals are connected to the ADC inputs and trigger of the 1280. Coherent operator performance is required to write pulse sequences (phase cycling, etc.) which are complementary in each system and tell each system to perform the experiment, taking care to start them in the proper order. Although somewhat inelegant, the system works very well and will suffice for another month or so until our microVAX II arrives to handle at least the data processing part of the problem.

As an example of the performance, figure 1 illustrates an absorption-phase 2DNOE experiment on an 11-base oligodeoxyribonucleotide. The sensitivity and resolution of the GX-400 coupled with the versatility of the hybridization yield excellent results for these types of studies. Figure 2 illustrates the bandwidth (> 500 kHz) which may be achieved with the GX receiver, when the audio filters are bypassed (software) and an Explorer digital oscilloscope (interfaced to the 1280) is used as a digitizer.

Best regards,

A handwritten signature in cursive script, reading "Andy", is written over the typed name.

R. Andrew Byrd

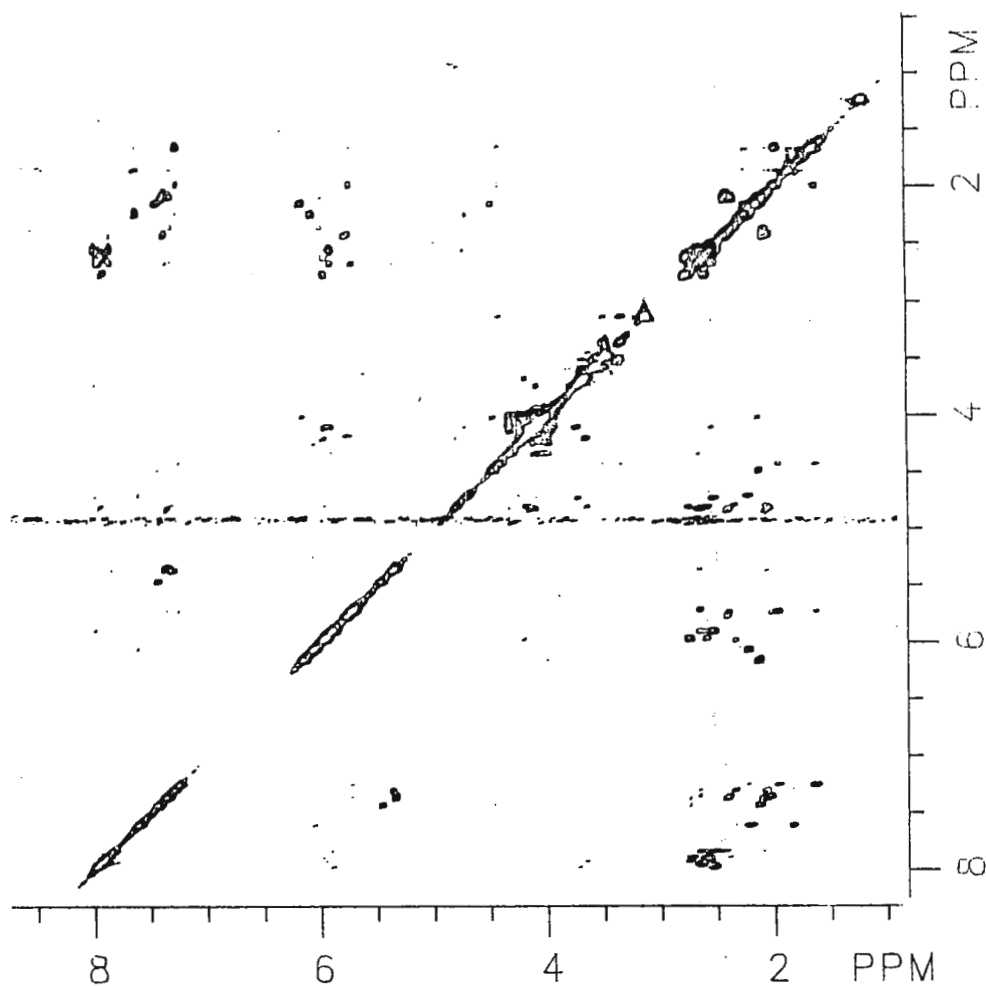


Fig. 1. Absorption-phase ^1H 2DNOE spectrum obtained at 400 MHz, 5°C , with a 400 msec mixing time, final data matrix = 512×1024

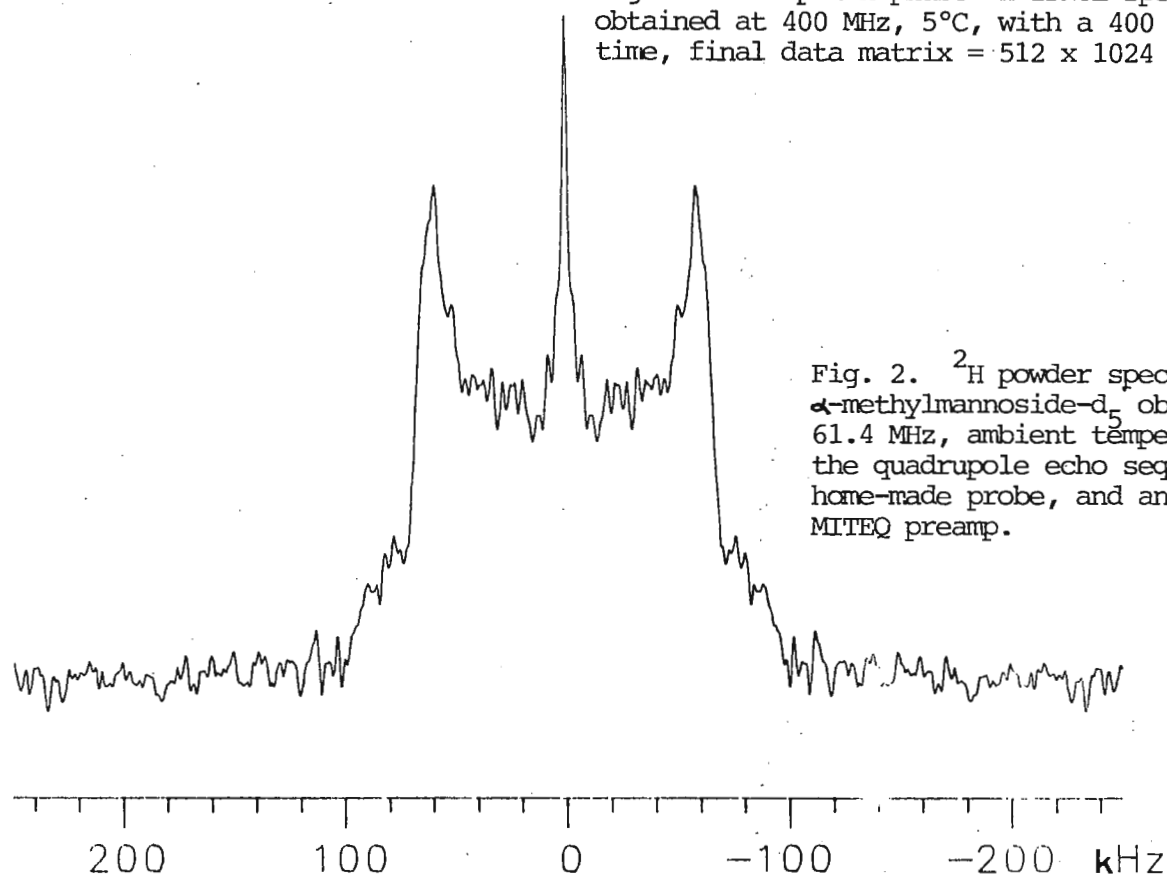


Fig. 2. ^2H powder spectrum of α -methylmannoside- d_5 obtained at 61.4 MHz, ambient temperature, using the quadrupole echo sequence, a home-made probe, and an external MITEQ preamp.

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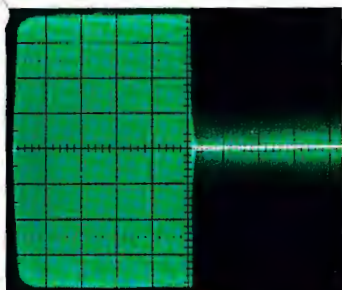
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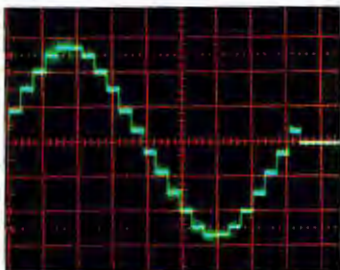
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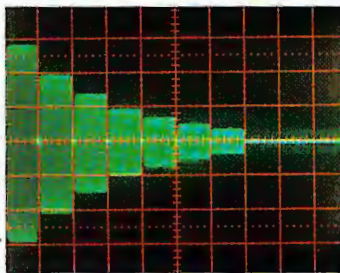
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Villeurbanne, le 16 Septembre 1985

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College Station, TEXAS 77843.3255

Spectres R.M.N. de Microorganismes

Cher Docteur SHAPIRO,

Nous avons eu à effectuer des mesures RMN (spectres - temps de relaxation) sur des végétaux. Ceci nous a conduits à mettre au point une micro-bobine de réception ($\phi = 0,2$ mm) permettant d'observer le spectre ^1H de grains de pollen (courgette (100 μ), maïs (50 μ)) et présentant tout à la fois :

- . un bon coefficient de remplissage
- . un bon coefficient de surtension
- . un bon accord et une bonne adaptation avec l'électronique du spectromètre XL 100 Varian utilisé.

Les premiers résultats sont prometteurs puisque, malgré la largeur naturelle importante du pic de l'eau, on observe 2 pics : l'un provient de l'eau du pollen, l'autre des lipides (essentiellement membranaires (fig. 1)).

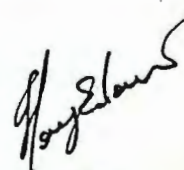
Nous réalisons actuellement un système de gradients adapté à cette micro-bobine de réception pour la coupler à un dispositif d'imagerie.



J. DELMAU



J.C. DUPLAN



E. HOUG

Pollen de courgette frais

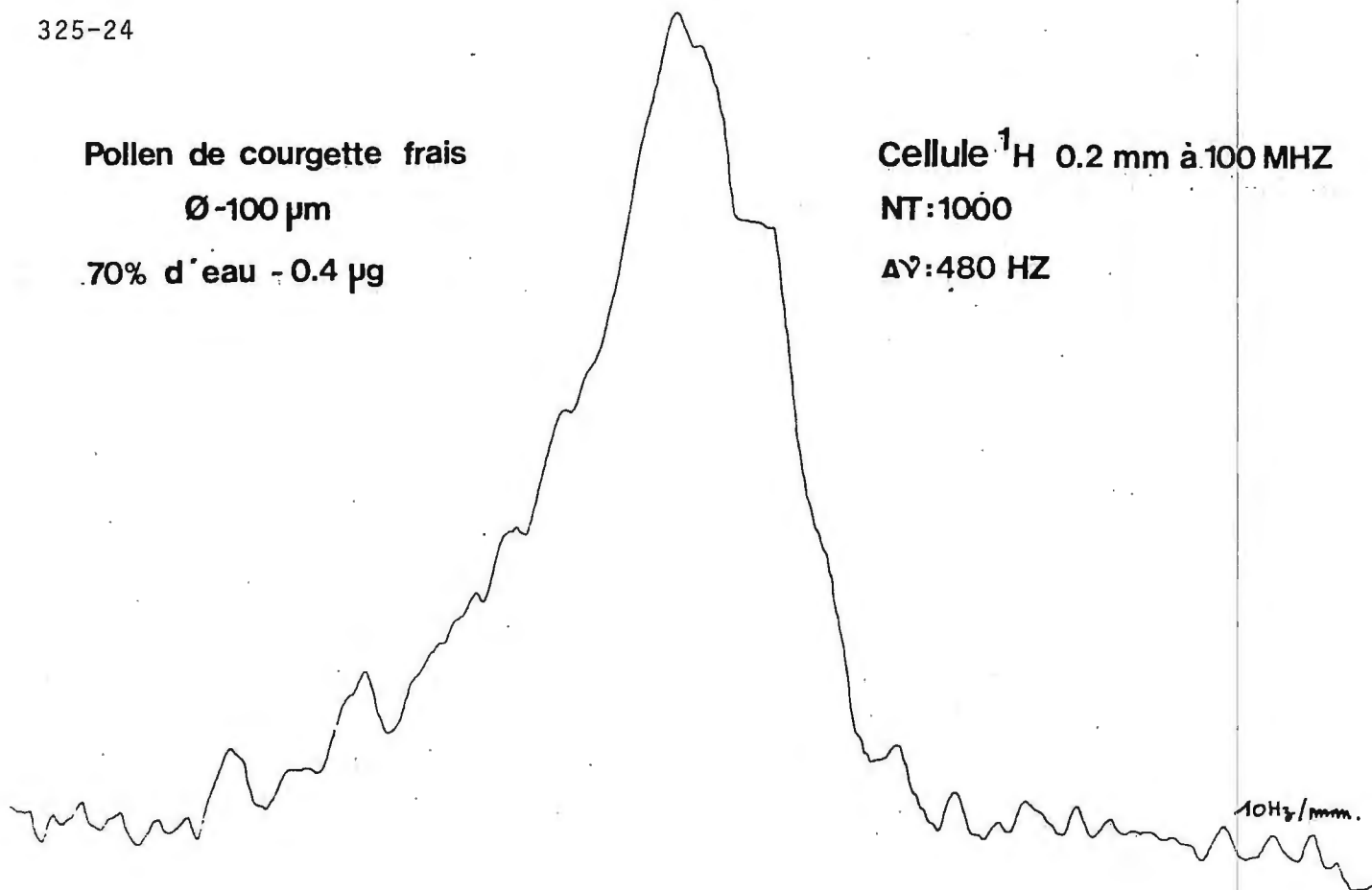
Ø-100 µm

70% d'eau - 0.4 µg

Cellule ^1H 0.2 mm à 100 MHz

NT: 1000

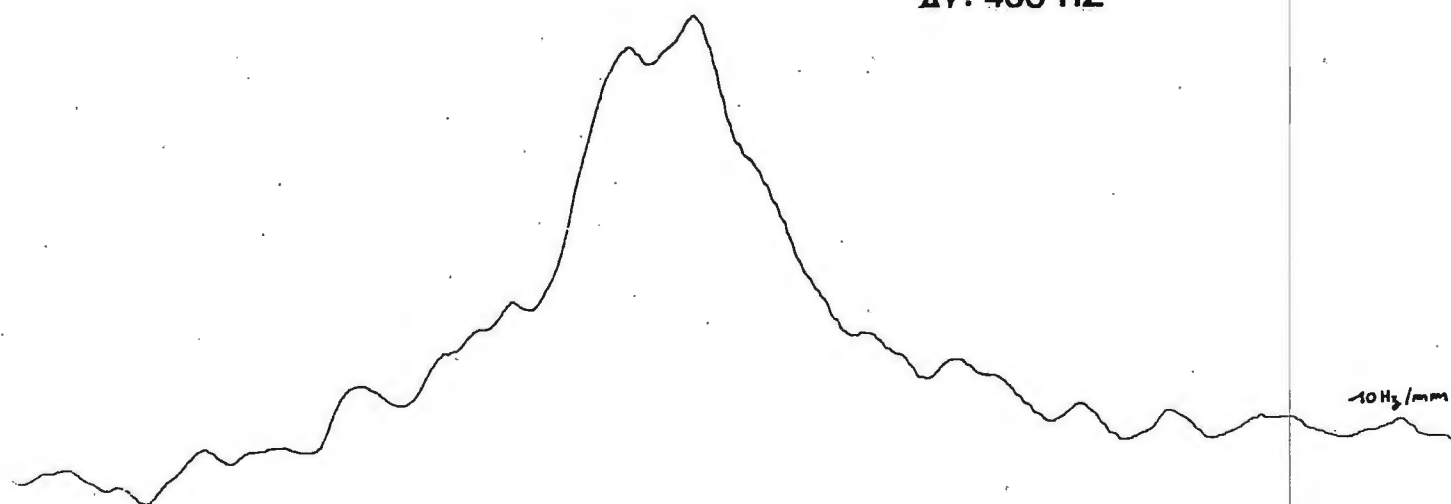
$\Delta\gamma$: 480 HZ



Pollen de courgette déshydraté

NT: 1000

$\Delta\gamma$: 430 HZ



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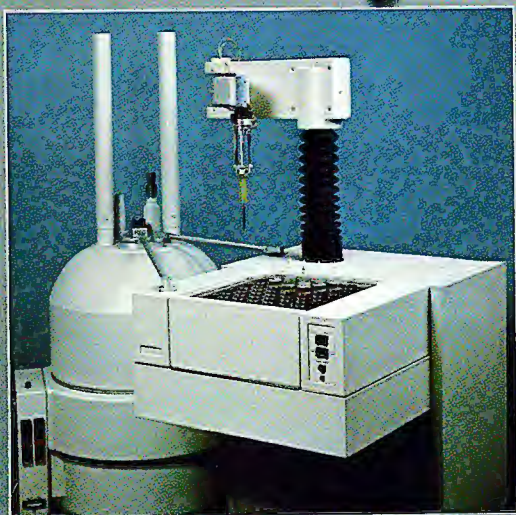


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International, P.O. Box 671, New Brunswick, NJ 08903. (201)524-5633. **Care should be exercised in considering the title and authors of the proposed presentation; if the presentation is accepted, both title and authors will be considered final and not subject to change.** Authors of accepted presentations will receive forms for submission of a 200 to 300 word abstract which will appear in the final program. The Silver Jubilee EAS will be moving to a new home at the New York Hilton Hotel, the finest convention site in the New York City area.

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Professor B.L. Shapiro,
Department of Chemistry,
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^{13}C COSY 2D spectra of labeled antibiotics

Dear Professor Shapiro,

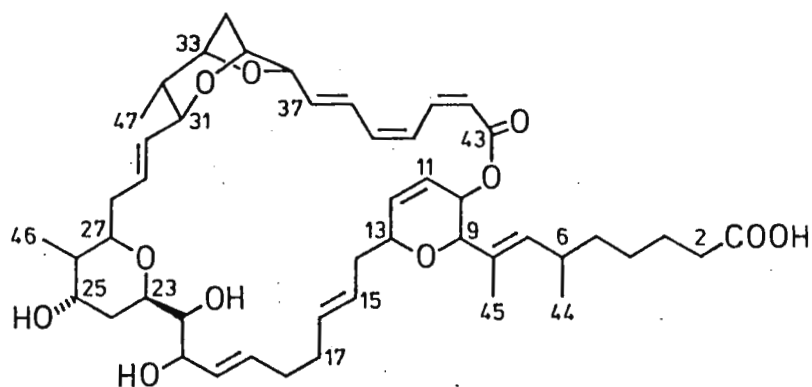
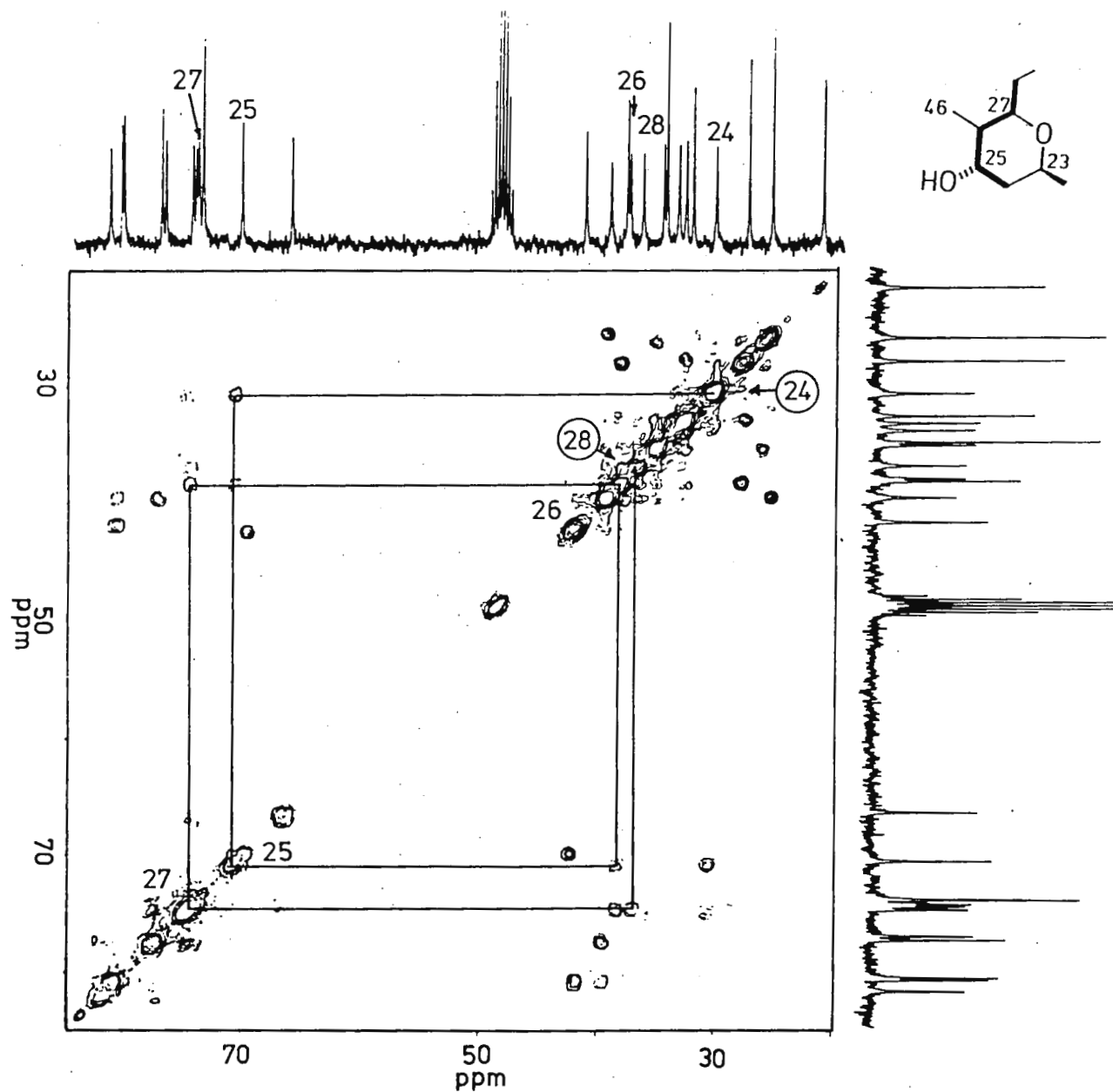
Much of our work is concerned with the structural elucidation and biosynthesis of new antibiotics isolated from gliding bacteria. The introduction of the two dimensional techniques has greatly facilitated this work, in particular ^1H COSY and heteronuclear shift-correlated 2D spectra are regularly used with great effect. Recently during an investigation of the biosynthesis of the new antibiotic sorangicin A with doubly labeled ^{13}C acetate we were surprised to find that the ^{13}C spectrum of the labeled material was overtly complex. We soon realised that this arose from the multiple incorporation of acetate into the antibiotic and that our feeding procedure required modifying. Although the product gave limited biosynthetic information we were able to demonstrate the usefulness of ^{13}C COSY 2D spectra for structural work. These gave direct confirmation of the molecular backbone. In particular the connections C26 to C27 (see figure) and C32 to C33, which had been previously inferred from nOe's and long-range ^{13}C - ^1H shift correlations, were observed directly. A preliminary communication of the structural elucidation is to be published shortly.

Yours sincerely,

V. Wray
Victor Wray

R. Jansen
Rolf Jansen

High-field region of the ^{13}C homonuclear shift-correlated 2D spectrum of labeled sorangicin A. Inset ^{13}C spectra are of unlabeled product.



Sorangicin A

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DEPARTMENT OF CHEMISTRY

Havemeyer Hall

No Problem with the Subway !

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843-3255

September 26 1985

Dear Barry:

I was interested by a recent contribution (TAMU 322-48) about the effects of subways on High Resolution NMR. Those of your readers who have visited the Chemistry Department here at Columbia will probably recall that the Broadway Local (IRT) subway line runs right outside the Chandler Laboratory, which is actually on Broadway. The nearest subway station is at 116th street and Broadway, a distance approximately equal to the length of a Subway train. Thus, the trains are probably accelerating when they pass our building.

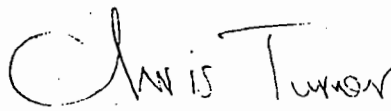
One of our spectrometers is less than 150 ft. the other three are between 200-300 ft, away from the subway tracks. However, we have never suffered from any problem which can be traced to the Subway, despite the fact that magnetic field changes of ± 20 milligauss can be observed with a Gaussmeter. All of our machines exceed the signal/noise and resolution specifications guaranteed by their various manufacturers, though I should note that we have been able to install all our magnets in rooms that do not suffer from vibration.

The probable reason why the measured magnetic field changes, which correspond to $\pm 85\text{Hz}$ for proton NMR, do not produce noticable effects on the resolution or stability of our spectrometers, is that superconducting magnets act as highly efficient first-order magnetic flux stabilizers. Other people probably understand this better than I, but I believe the explanation runs something like this:- If you change the magnetic field experienced by a coil of wire, this produces an emf (the basic principle of an electrical generator) but a superconducting coil cannot support an emf. Since the resistance is zero, because of $V = I \times R$, then the voltage must be zero, as

long as the coil remains superconducting. The net result of this is that the current flowing in the superconducting coil instantaneously changes to compensate the external applied magnetic field. Now of course, this is only a first-order compensation, so the distribution of the current may change to cause changes in homogeneity, but our experience shows that large ferromagnetic objects such as gas cylinders etc. cause far greater problems than the Subway.

One might expect the Subway to contribute to the size of T_1 noise in 2-D experiments, however we have never been prevented from using any 2-D experiment because of T_1 noise. In common with many other chemists, we routinely measure NOE difference spectra and can reduce the size of the cancellation artifacts to about 1% if we try hard enough.

I appreciate that this was a very simplistic explanation of the effects of external applied magnetic fields on high resolution NMR spectrometers, and I would be grateful to any of your readers who can make a better job of this than I, but the take-home message is that we have no problem with the subway.


C. J. Turner



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0430

Prof. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station
Texas 77843 U S A

E. COSY

Dear Barry,

The resolution attained nowadays in phase-sensitive 2D correlation spectra is sufficiently high to permit the simultaneous determination of numerous coupling constants from a single COSY spectrum. There are however two inherent limitations which render the actual measurement difficult: (1) Peaks belonging to the same multiplet are likely to overlap for complex coupling networks, (2) Small coupling constants may be buried underneath the experimental linewidth.

A modified experiment "exclusive correlation spectroscopy" or briefly the E. COSY technique, presents an efficient remedy to remove the mentioned obstacles. E. COSY restricts, for weakly-coupled spin systems, coherence transfer to take place exclusively between connected transitions in the energy level diagram. The basic pulse sequence is identical to the one for multiple-quantum-filtered COSY:

$$\left(\frac{\pi}{2}\right)_{\beta} - t_1 - \left(\frac{\pi}{2}\right)_{\beta} - \left(\frac{\pi}{2}\right)_{-x} - t_2 ,$$

and the experiment may be understood as a combination of MQ-filtered COSY spectra of different orders. The highest order to be used in the combination depends on the coupling networks. A pQ-filtered spectrum must be included only if a pair of coupled spins is expected with at least p-2 common coupling partners. In practice, it is normally sufficient to combine pQ-filtered spectra for p=2,3, and 4 with the relative weights 1:2:4. In terms of the individual experiments $s(\beta)$ with the phase shift β , the following linear combination leads to the suppression of cross-peak multiplet components which correspond to correlations between non-connected transitions:

$$s(\text{E. COSY}) = 5 \cdot s(\beta=0^\circ) - 3.41 \cdot s(45^\circ) + s(90^\circ) - 0.59 \cdot s(135^\circ) \\ + s(180^\circ) - 0.59 \cdot s(225^\circ) + s(270^\circ) - 3.41 \cdot s(315^\circ),$$

whereby the coefficients are effected either by a variable scan number or by numerical weighting.

Fig.1 illustrates a procedure for constructing E. COSY cross-peak multiplet patterns by means of the I_1 - I_2 cross-peak in a four spin system $I_1 I_2 I_3 I_4$. The active coupling (here J_{12}) leads to the basic square pattern which occurs 2^n times where n is the number of coupling partners common to I_1 and I_2 . The figure assumes that $J_{13} \times J_{23} > 0$ and $J_{14} \times J_{24} < 0$.

Fig.2 shows an excerpt from a 300 MHz E. COSY spectrum of the cyclic decapeptide antamanide. The H_{β_1} - H_α cross-peak shown originates from the Pro⁸ residue. This is a particularly clear case where all four square patterns are well separated. The four framed regions were projected onto the horizontal axis, and the resulting traces are shown on right of the figure. The ${}^3J_{\alpha\beta_2}$ coupling constant can be determined as the relative displacement of the traces 1 and 3, or 2 and 4. In analogy, ${}^4J_{\alpha\gamma_2}$ is determined by comparison of the traces 1 and 2, or 3 and 4. The corresponding coupling constants involving H_{β_1} (i.e. ${}^2J_{\beta_1\beta_2}$ and ${}^3J_{\beta_1\gamma_2}$) are also contained in the figure, but because of the higher digital resolution in the ω_2 dimension they should be extracted for maximum accuracy from the cross-peak multiplet in symmetrical position with respect to the diagonal. The assignment of the two passive coupling constants ${}^3J_{\alpha\beta_2}$ and ${}^4J_{\alpha\gamma_2}$ is not evident from the H_{β_1} - H_α cross-peaks alone but can be determined by analysis of additional cross-peak multiplets of the Pro⁸ spin system.

A preliminary communication describing E. COSY will appear soon in the Journal of the American Chemical Society, and a more detailed account is in preparation.

Best regards.

Sincerely yours,

Ole W. Sørensen
O.W. Sørensen

C. Griesinger

Michael
R.R. Ernst

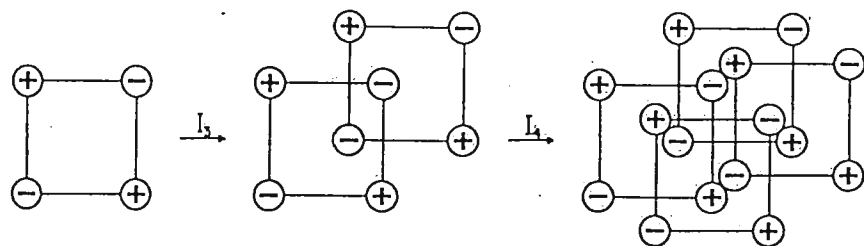


Fig. 1

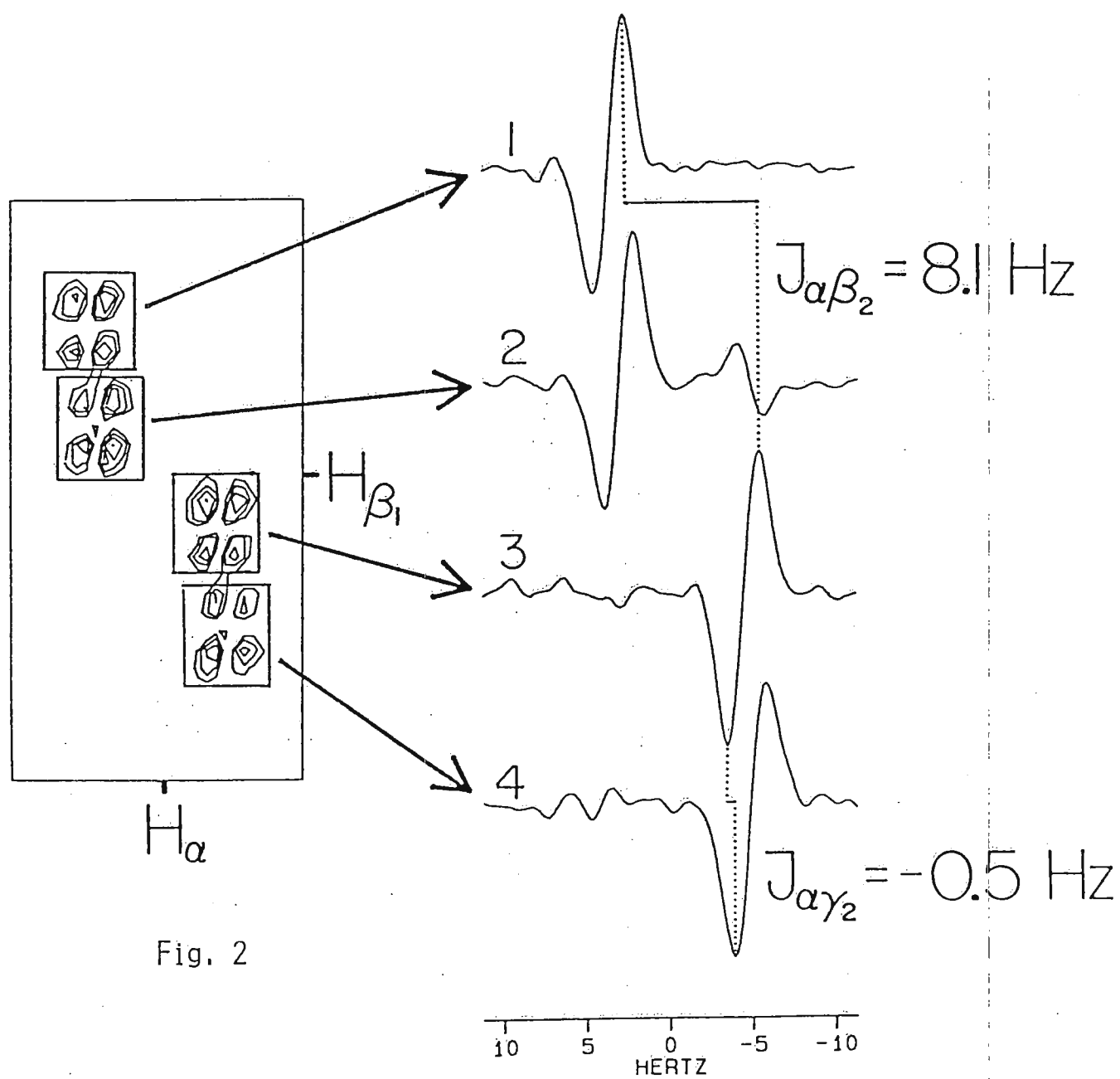
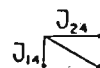
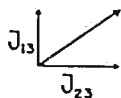


Fig. 2

CENTRO DE INVESTIGACION DEL IPN

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September 20, 1985

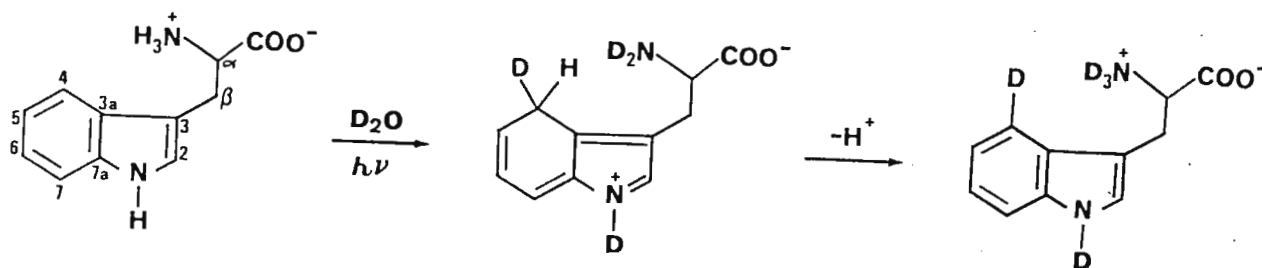
Professor Bernard L. Shapiro
 Department of Chemistry
 Texas A and M University
 College Station, Texas
 U. S. A. 77843

A ^{13}C nmr study of tryptophan

Dear Professor Shapiro:

Careful evaluation (see table) of ^{13}C nmr data for tryptophan¹ reveals controversial assignments of C-4, C-5 and C-6. Initial data of this biologically important molecule were assigned² based on the study of the parent indole and their monomethyl derivatives³. A further assignment of tryptophan methylester⁴ was extrapolated from 5-deuteroindole⁵. More recently, data derived for 3- ^{13}C -enriched tryptophan⁶ and INDO calculations⁷ were published.

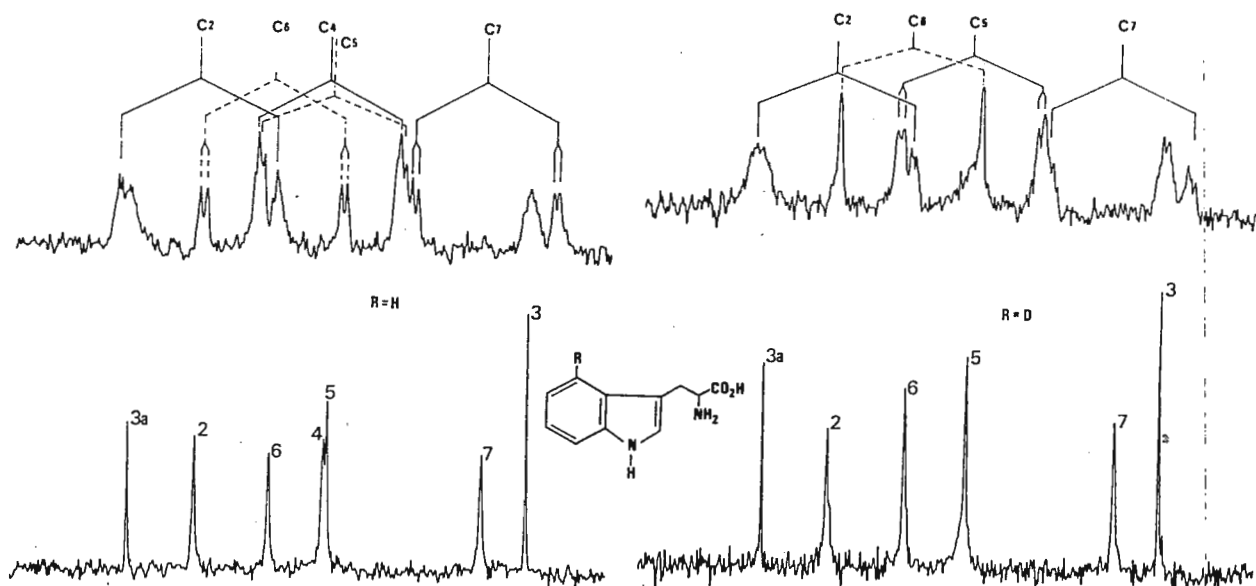
We now report an independent assignment of these three carbon resonances to settle down the controversy using 4-deuteriotryptophan. Such isotope incorporation was achieved⁸ by external photodeuteration with Pyrex-filtered UV light from a 400-W high pressure Hg lamp. In our hands, immersion irradiation using a low-pressure 110-W Hg lamp provided the desired compound.



Comparison of the spectra of the normal compound with those of the 4-deutero analogue is depicted in the figure. The C-4 resonance is assigned in the PND spectra from the disappearance of the signal at 118.4 ppm. C-6 is evident from the gated-decoupling experiment, since the original double doublet ($^1J = 158.4$ Hz; $^3J = 7.1$ Hz) at 120.6 ppm loses the long-range coupling constant upon deuteration at C-4. The remaining of the three signals under controversy is C-5, which appears at 118.2 ppm in the spectrum of the non-deuterated molecule. It underwent the typical two-bonds upfield shift to 118.0 ppm in the deuterated sample.

Atom	from ¹ (a)	from ² (a)	from ⁴ (b)	from ⁶ (c)	from ⁶ (d)	from ⁷ (e)	from ⁸ (f)	our(f)
C-2	127.6	124.8	123.5	124.3	126.2	127.1	124.2	124.2
C-3	nr	107.2	109.9	109.5	108.6	107.9	109.6	109.4
C-3a	121.8	126.3	127.4	127.3	127.7	128.3	127.3	127.3
C-4	124.5	118.7	118.5	118.3	119.5	119.9	118.3	118.4
C-5	120.5	121.7	119.1	118.3	120.5	121.3	120.8	118.2
C-6	128.9	119.1	121.6	120.9	123.1	123.9	118.2	120.6
C-7	114.3	111.6	111.5	111.4	113.0	113.8	114.4	111.4
C-7a	138.6	135.1	136.4	136.3	137.4	138.0	136.5	136.3

(a) in D₂O; (b) in CDCl₃ for tryptophan methylester; (c) in DMSO-d₆ for 3-¹³C-labelled; (d) in D₂O for 3-¹³C-labelled; (e) in H₂O; (f) in DMSO-d₆ for 4-deuteriotryptophan; nr; not reported.



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M.S. Morales-Ríos

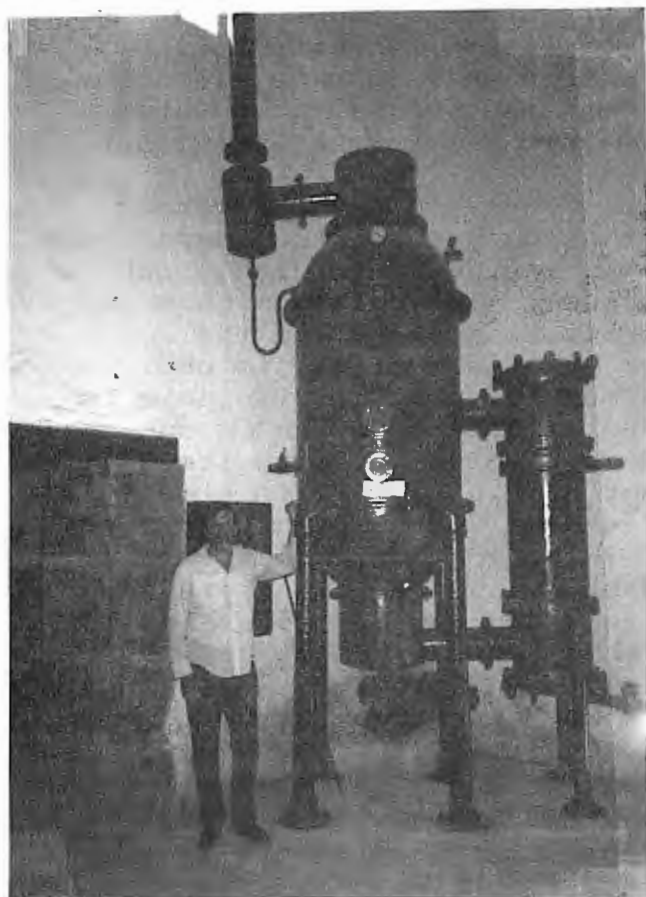
M.S. Morales-Ríos

Sincerely yours,

Pedro Joseph-Nathan
Pedro Joseph-Nathan

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Here is a photo of the dewar for our new magnet (the magnet itself is still on the drawing board). Special features include: 1. Varian look-alike dewar. 2. Auxiliary 270 MHz magnet on the side so that organic chemists can say they ran spectra on a 1000 without actually wasting its time. User friendly software simulates 1000 MHz spectra from 270 MHz spectra. 3. Special large capacity tube at the top that accepts money directly, avoiding messy conversion steps, from money to liquid helium.

We will gladly accept dealer inquiries and development grants. (Actually this is some kind of wine making device which I discovered in a wine museum near Selinunte, Sicily.)

SUBWAYS, OR GARBAGE OUT - GARBAGE IN -- THE BRANDEIS EXPERIENCE

This is an addendum to a recent Newsletter item by Chacko and Mildvan on the bad influence of subways on NMR instruments. Waltham does not have, or contemplate, a subway system, but I inadvertently accepted a lab for our instruments that is next to a driveway to our main science receiving room. We did have some trouble with our homemade 500 MHz instrument's lock system (which I fixed by fiddling with the gain ratio and integrator time constant) and I then had occasion to look into field fluctuations near the magnet. I borrowed a fancy gaussmeter with analog output and a recorder, and tied the probe of the gaussmeter to a heavy support oriented to pick up the vertical component of field. I moved this assembly around on the floor to the point (at the magic angle) where the 500's vertical component is small enough so that I could turn the gain way up on the gaussmeter. (In retrospect, a fancy gaussmeter is not really needed.) I regret that I did not keep a record of my observations but my recollections follow:

The elevator, about 15 meters (M) away, and small cars, about 10 M away, give a fluctuation of the order of a milligauss. Obviously bigger trucks give bigger fluctuations. Occasionally there was recorded a huge fluctuation, many milligauss, which is also easy to see by looking at, or recording, the offset signal going from the lock system back to the field offset. This fluctuation was mysterious, and I'm still not sure, but I think it was due to a giant garbage compactor that is about 4 M from the magnet, on the floor below; I did establish that a steel door to said compactor produces such a fluctuation, but this door generally stays open.

Our small-bore 500 never falls out of lock due to these fluctuations though I have to say that we don't do 2D runs on small molecules which might be more sensitive to fluctuations than the H₂O solvent work that we specialize in. A new Varian XL300 that is about 8 M from the compactor and is used for all kinds of runs has never shown problems that we have attributed to field fluctuations. Therefore I am skeptical that they represent an insuperable problem, and suggest that variations in experiences may be due to variations in spectrometers. Researchers with problems might look at the way their lock system works.

I am hardly an expert in commercial NMR systems, or feedback systems, but can suggest the following: Aside from obvious parameters such as signal/noise and offset or offset instability in the lock detector, there are several things to check. The relative gain of the lock signal that you look at (absorption) compared to the (dispersion) signal that is fed back to the field offset is one. These should be reasonably well in quadrature. Another variable is the roll-off characteristic of the output amplifier which in our case is an op-amp integrator with a resistance R in series with its feedback resistance C with time constant $RC = .4$ sec. This time constant should probably be optimized for the lock solvent and be of the order of its relaxation times(?). There are whole books written on feedback systems and one could probably do better than this. Our system generally is used with 10% D₂O in water but can go as low as 5%; it uses Cryomagnet Systems probes in which the proton coil is double tuned for lock.

Stabilizing a system with feedback against slow fluctuations ought to be easy. Maybe the subway-induced fields fluctuate more rapidly than those we have, but the magnet eddy currents should slow them down to a large extent. If the problem really can't be solved at the spectrometer there are other possibilities. A gaussmeter such as I described could be connected to a DC amplifier and a coil around the magnet in such a way as to buck the fluctuations. A physicist colleague who has these subway problems (near Paris) in connection with high resolution electron scattering believes they can only be explained as due to distributed ground currents due to finite track resistance. This suggests obvious modification of the subway, but a high level of understanding of the source of the problem ought to exist before proposing expensive modifications. An even better approach would be for the instrument makers to eliminate the lock entirely, which ought to be possible; an array processor ought even to be able to analyze each FID for dynamic as well as static field variation, and correct for it. Until such time, if you are shopping for a new NMR and have fluctuations, consider ways to simulate these during the demo, by doing calisthenics with a big hand held magnet, for example. Or bring a DC power supply and a big coil.

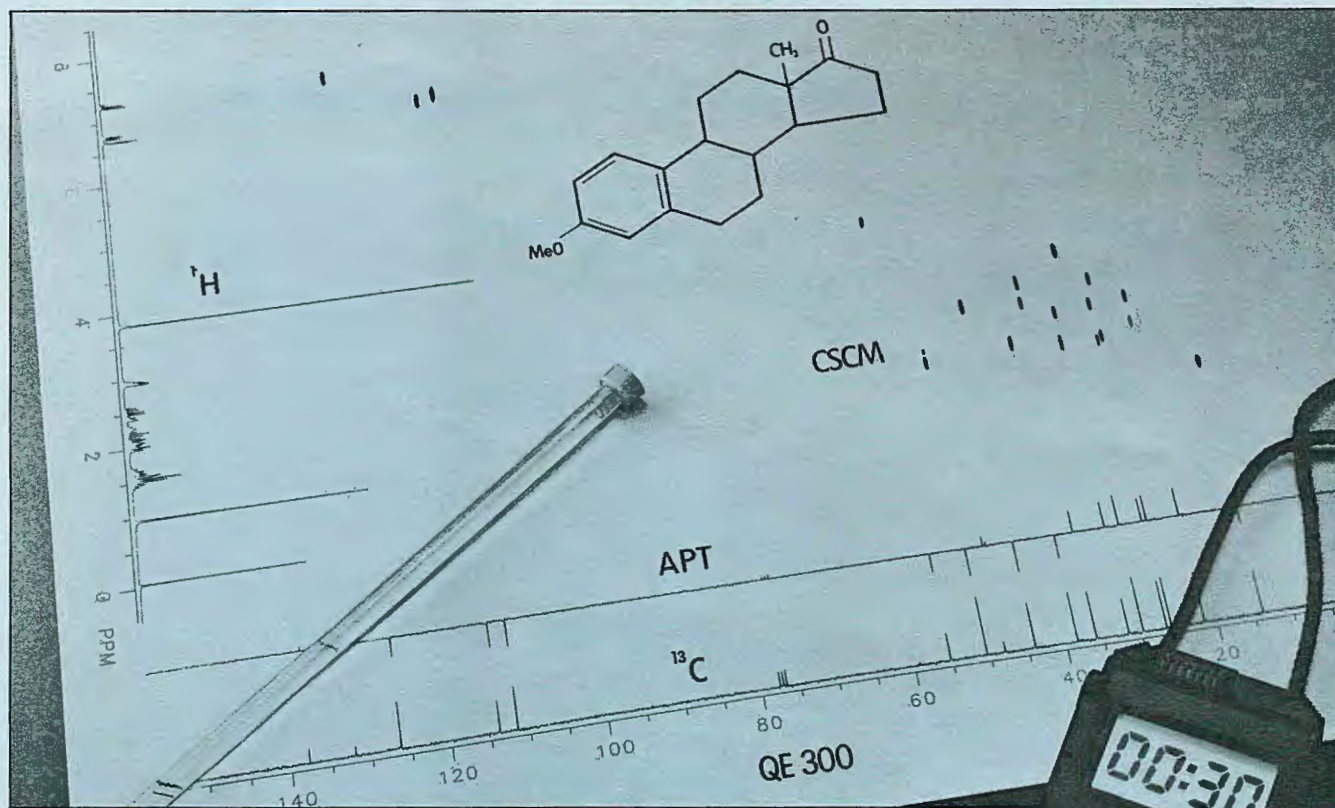
We also have no known problems with either instrument due to vibrations even though we can feel the floor shake; we beat on the magnet and even transfer nitrogen without much noise. Maybe it's because the 500 has excellent rf gating; poor phase stability, perhaps originating in the probe, combined with poor gating, could give noise.

Sincerely,

Al Redfield
Alfred Redfield

Sept. 23, 1985

Biochemistry, Brandeis University, Waltham MA 02254 USA



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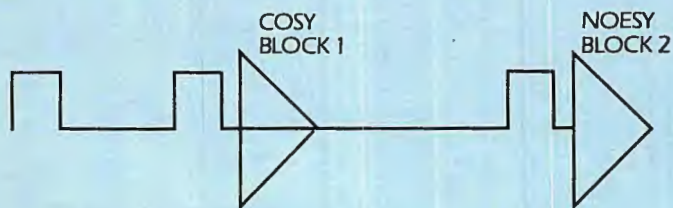
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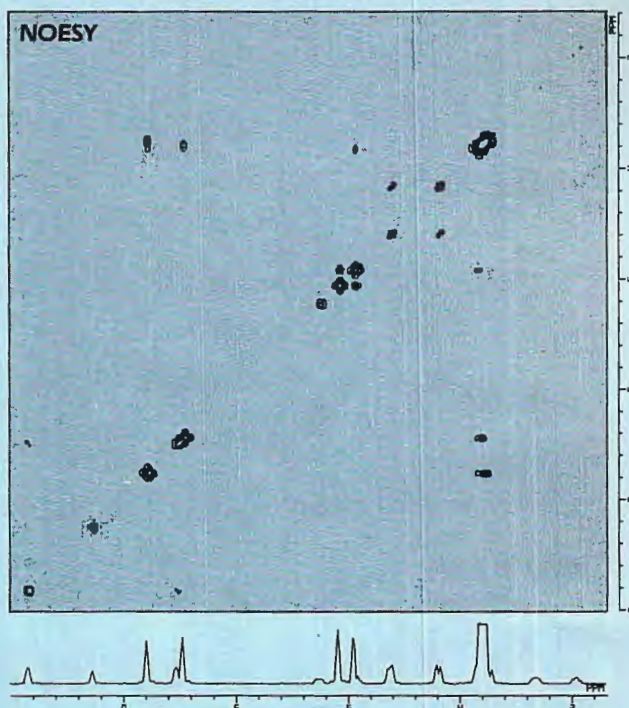
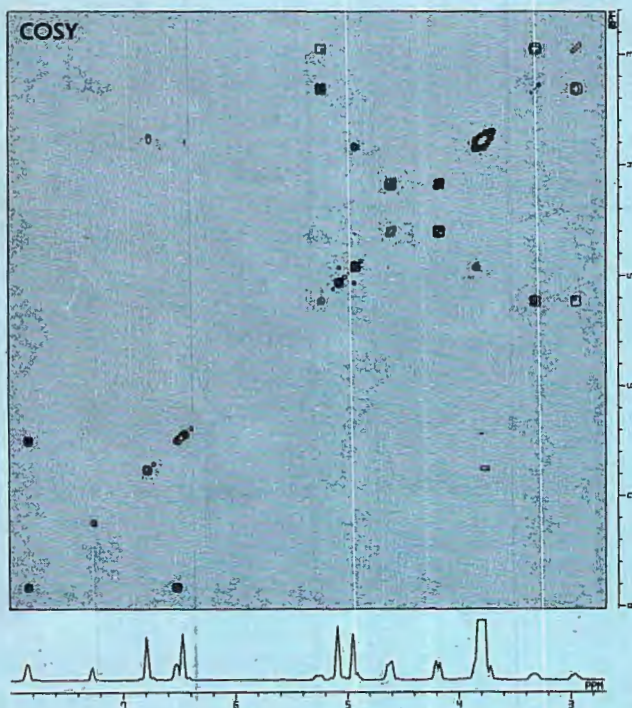
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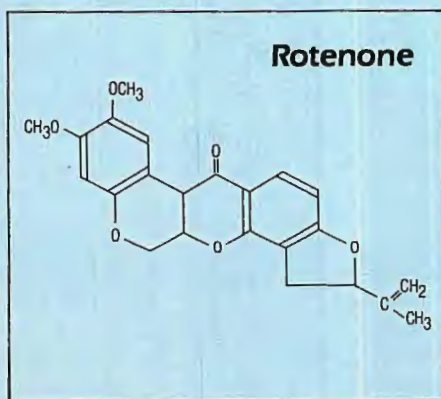


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