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Newsletter

No. 215

August, 1976

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DEADLINE DATES: No. 216: 6 September 1976 No. 217: 4 October 1976
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All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
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 Texas A&M University
 College Station, TX 77843 U.S.A.

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Professor Bernard L. Shapiro
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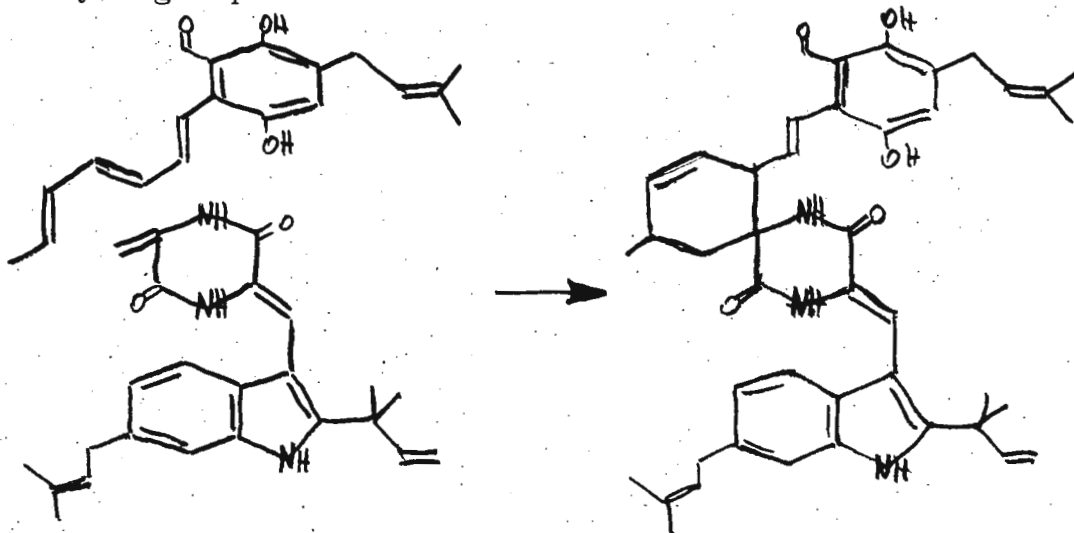
29.52.78 - 29.54.82 - 29.60.71

Structure of Cryptoechinuline B

Dear Prof. Shapiro,

Cryptoechinuline B (R. Cardillo, C. Fuganti, D. Ghiringhelli, *Chimica e Industria* 57, 687 (1975), an isoprenylated dehydrotryptophan derivative, isolated from the micelium of Aspergillus Amstelodami, has been studied in this laboratory by ^1H and ^{13}C techniques. The spectral evidence (J. Chem. Soc. Chem. Comm. in press) supports the assignment of the structure given in the figure.

Consideration of the type of molecular framework and of the substitution suggests that the extractive could be derived by regiospecific Diels-Alder condensation



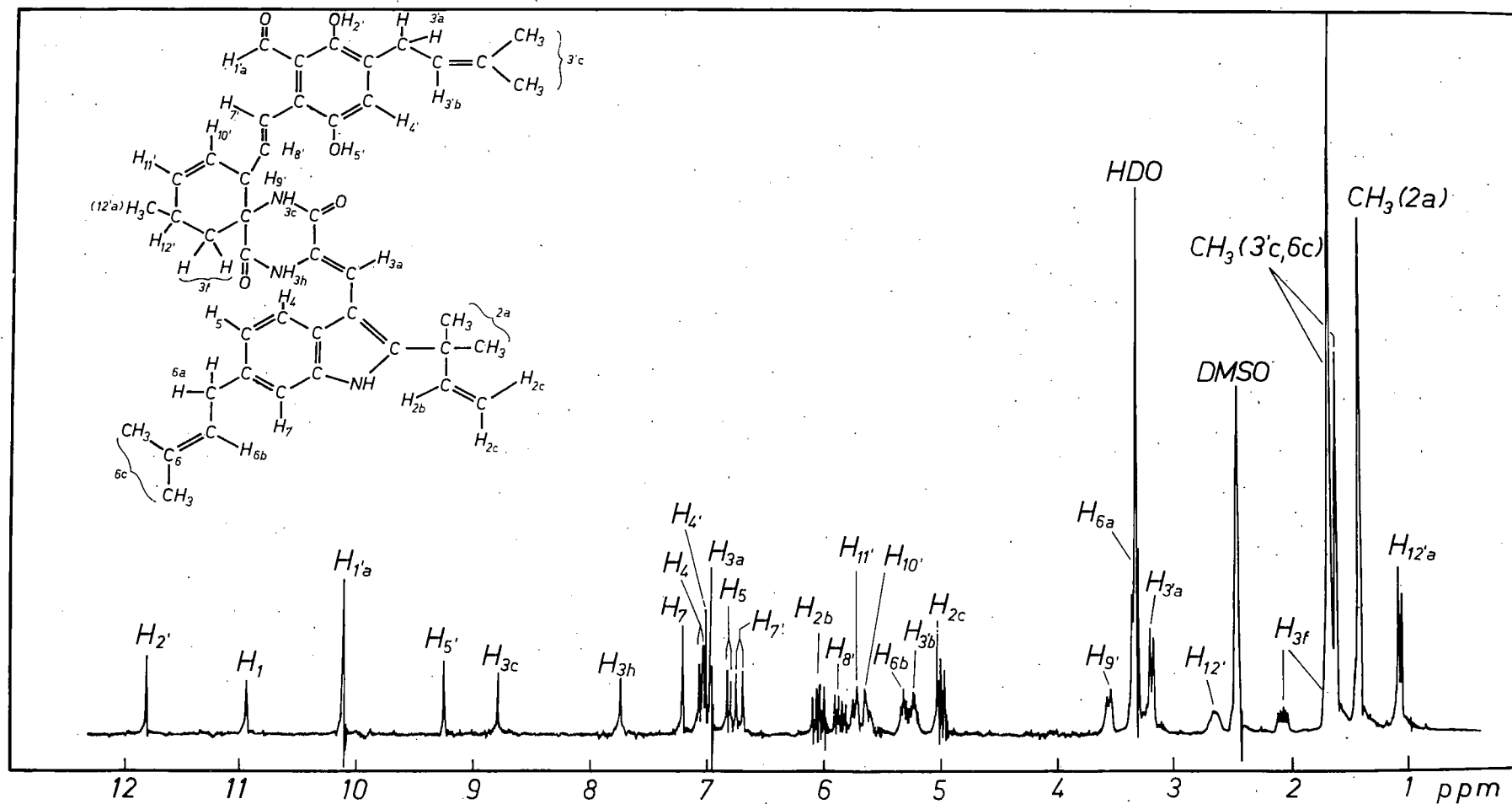
from auroglaucine and neoechinuline C, which are known metabolites of the fungus.

I hope this contribution will put me back on your mailing list. With many thanks and best regards.

Yours sincerely,

G. Gatti

(G. Gatti)



270 MHz-NMR Spectrum of Cryptochinuline B


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DATA 4/6/1976

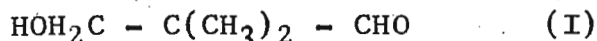
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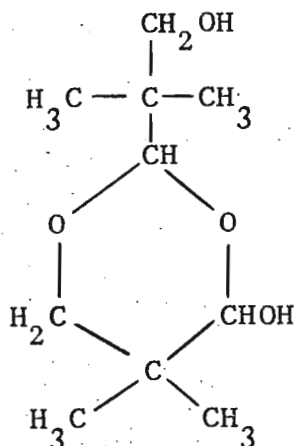
Title: 3-Hydroxy, 2,2-dimethyl propionic aldehyde: the structure of its dimer.

Dear Professor Shapiro:

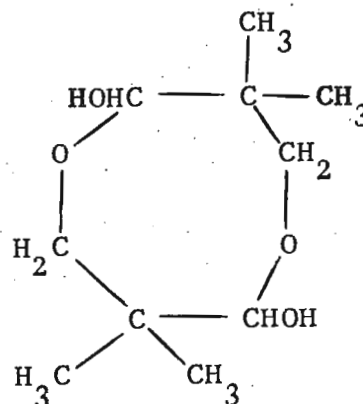
It is well known¹⁾ that 3-hydroxy, 2,2-dimethyl propionic aldehyde



exists in equilibrium with a dimeric form. The equilibrium depends on the physical state of the compound; for example (I) is usually separated from the reaction mixture (isobutyraldehyde and formaldehyde) as a crystalline solid which consists of a dimeric form. When the solid is melted only the monomeric form is present; after cooling it gives slowly the dimer. In solution the equilibrium position depends also on the solvent. This kind of behaviour is similar to that of other aldehydes²⁾. According to what is known for similar compounds one can suggest different linear and cyclic structures. On the basis of infrared and mass spectral data of the acetylated product, only the following two cyclic dimeric form are possible:



(II)

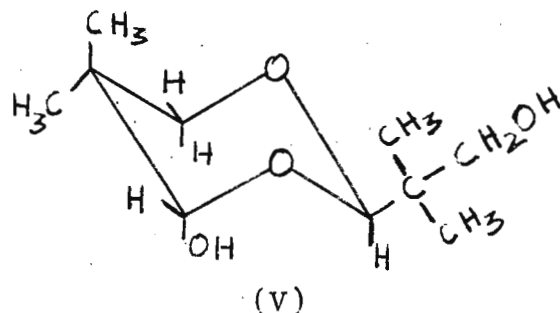
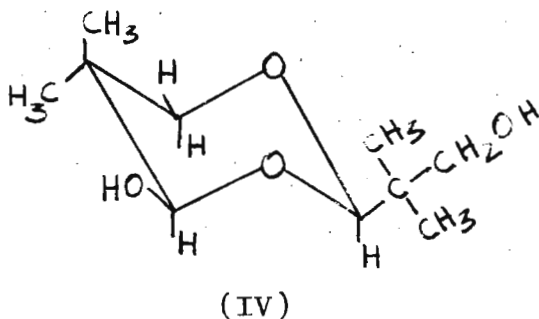


(III)



A solution of (I) just dissolved in CDCl_3 , in which the monomer is practically absent, gave an nmr spectrum which agrees with structure (II). Furthermore the nmr spectrum obtained in a solvent such as DMSO, where it is possible to evidence the OH group and its coupling with vicinal protons definitely shows the presence of the $-\text{CH}_2\text{OH}$, $-\text{CHOH}$ groups, ruling out the possibility of structure (III).

The nmr spectra present signals whose intensity increases with time. These signals must be attributed to an isomer, since the purity of product is very high. After some hours the two isomers presented peaks of comparable intensity and it was then possible to determine the spectral parameters of both. The data obtained let us conclude that the dimer of (I) is a mixture of the stereoisomers (IV) and (V), in agreement with what can be derived from a conformational analysis:



The more stable structure is the (IV) one which has the OH group equatorial.

Yours sincerely

E. Santoro

E. Santoro, M. Chiavarini

- 1) - E. Spath and I. Szilagyi
"Chem. Ber.", 76 B, 949 (1943)
- 2) - C.A. Armour et al.
"J.C.S.", 301 (1964)
- M. Vogel and D. Rhum
".O.C." 31 1775 (1966)



MONTEDISON

July 5, 1976

Prof. B.L. Shapiro,
Department of Chemistry
Texas A & M University,
COLLEGE STATION,
Texas 77843 - USA

DIPE/CER/PM
Stabilimento Petrolchimico
Via G. Motta
30175 Porto Marghera
(Venezia) ITALY

Dear Professor Shapiro,

I send you here attached a brief note on the structure of the lactam of the ϵ -amino-hexenoic acid as my contribution for the inscription to TAMU Newsletter for 1976.

Subject :

STRUCTURE OF THE LACTAM OF THE ϵ -AMINO-HEXENOIC ACID (I)

Among other impurities in the oxidation of the caprolactam, such as valeramide and adipimide, we have also found (I) and succeeded in chromatographically obtaining a sufficient amount of such compound to examine it by NMR.

A 20% solution w/v in CDCl_3 of (I) was prepared using TMS as a reference to evaluate the chemical shifts.

The proton spectrum of (I) is reported in Fig. 1. The structural formula obtained from NMR analysis is given hereafter; numbers from 1 to 6 indicate the different protons

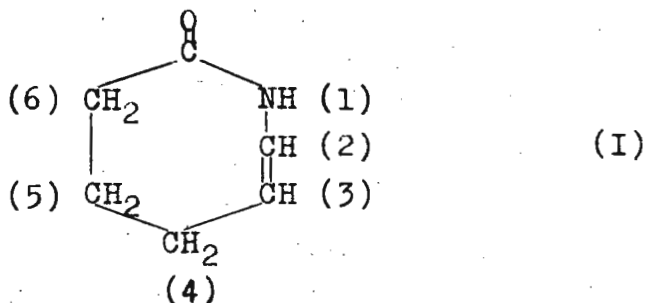


Table 1 indicates the chemical shifts in ppm and the coupling constants in Hz (the sign of the J was not determined).

TABLE no. 1

$\delta(4,5,6)$	=	1.5 + 3	$J(2 - 3)$	=	\pm 10
$\delta(3)$	=	5.02	$J(2 - 1)$	=	\pm 5.5
$\delta(2)$	=	5.8	$J(3 - 4)$	=	\pm 4.2
$\delta(1)$	=	8 + 8.4	$J(2 - 4)$	=	\pm 1.9

The bands included between 1.5 and 3 ppm refer to the methylenic groups indicated with numbers 4, 5 and 6.

The numbers of the protons related to the remaining three groups are confirmed by the integrals.

The olefinic proton (3) is related to a multiplet of apparently 5 lines, which is produced by the splitting with the olefinic proton (2) through $J(3, 2) = \pm 10$ Hz and with the methylenic protons (4) through $J(3, 4) = \pm 4.2$ Hz according to a first order spectrum interpretation.

The c.s. of (3) is located at 5.02 ppm.

The olefinic proton (2) is related to a multiplet of 12 lines. It is produced by the splitting with the olefinic proton (3) through $J(2, 3) = \pm 10$ Hz, with the proton (1) through $J(2, 1) = \pm 5.5$ Hz and with the methylenic protons (4) through $J(2, 4) = \pm 1.9$ Hz according to a first order spectrum interpretation.

The c.s. of (2) is located at 5.8 ppm.

The wide band (quadrupole moment) located between 8 and 8.4 ppm is related to the (1) proton. This one, bonded directly to the nitrogen atom, exchanges with D_2O and it is therefore possible to remove the coupling with the olefinic proton (2). This coupling must be a vicinal one since a long-range coupling through two or more saturated bonds is unlikely.

The 12 line multiplet of the olefinic proton (2) has converted into two triplets after deuteration.

A further reason for the presence of nucleus (2) in alpha position to the nitrogen atom, is the shift to a lower field because of its electrophilic character. After deuteration, the $>NH$ bond disappeared.

The $J(3, 4)$ coupling constant is of the same order of magnitude as found in the literature for similar compounds

$$J_{vic}(\underline{CH} - \underline{NH}) = 4.5 \text{ Hz}$$

Yours sincerely

Giorgio Gurato

(Giorgio Gurato)

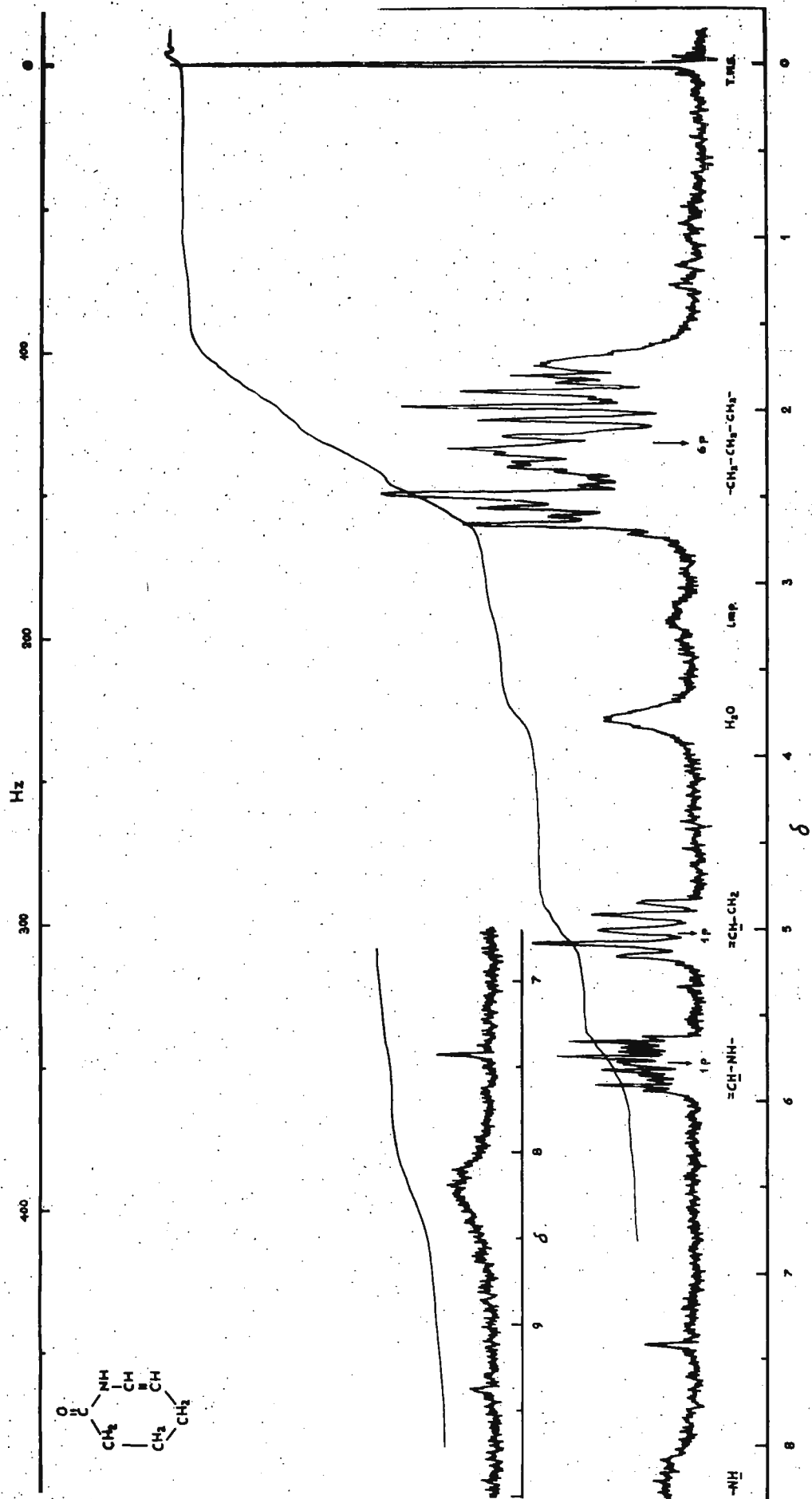


Fig. 1

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July 8, 1976

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

Cr(dpm)₃ ; A PARR Soluable in Nonpolar Solvents.

Dear Barry,

The use of paramagnetic relaxation reagents (PARR's) to quantify ¹³C FT NMR spectra is steadily increasing. However, the most commonly used reagent, Cr(acac)₃, is not as inert to physical interaction with organic substrate molecules as previously thought and besides, the solubility in hydrocarbon solvents is too limited for general ¹³C NMR purposes. A more bulky reagent, trisdipivaloylmethanatochromium(III), turned out to be superior to "chromacac" in this sence, thus making it possible to achieve the desirable leveling of T₁ / NOE. Since this reagent is not commercially available I will give a short and convenient recipe:

3 g. of chromium(III)chloride hexahydrate, 20 g of urea and 5 g of dipivaloylmethane are mixed in EtOH / H₂O (3:1). The mixture is refluxed during 24 hrs. and 100 ml of H₂O is added to the deep purple cooled solution. A sloppy graduate student should get about 60% yield. Sublimation. m.p. 229° C.

The use of reagents of this type (Gd or Cr) would probably be a valuable substitute to the more timeconsuming pulse-modulated technique.

Thanks for the blue reminder.

Very best regards

Ulf

/ Ulf Edlund/

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF ALBERTA
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July 7, 1976

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station
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TITLE: Problems with V-2708 Power Supply

Dear Barry:

I would like to initiate my subscription to the TAMUNMR Newsletter with this letter describing briefly two problems that we had with our V-2708 power supply. Perhaps some of your readers would be interested in our solutions.

The first problem concerns the loss of lock of our flux stabilizer when we have a power flicker in our building. This causes both the stabilizer and the commutator of the power supply to oscillate resulting in damage to the carbon brushes. This happened once on an overnight experiment and left the transformer badly pitted. Our electronics shop built an interlock which opens the feedback loop between the power supply and the stabilizer as soon as it senses an oscillation. This circuit is available upon request.

The second problem concerns the pitted transformer. Basically we followed the procedure used by Nunnally and Hollis¹ to smooth the winding surfaces, with one modification: we reversed the direction of the commutator stepping motor (and limit switches) and connected the power input to the transformer to the top of the transformer instead of its original position on the bottom. (The commutator now rests on a "fresh" surface at the bottom third of the transformer instead of the top third.) This was accomplished by carefully chiseling away the casing on the top of the transformer to expose the top

Prof. B.L. Shapiro

July 7, 1976

copper winding. We then cut the copper winding, unwound about 2-3 inches and drilled holes to accommodate a suitable wire clamp for the power input. We then manually checked for mechanical clearance of the commutator and adjusted the limit switch activators accordingly. Carefully inspect for loose copper shavings.

Since the two modifications we have had no further problems with our power supply. Two or three days of down time is well worth saving \$12,000.00 for a new power supply.

Sincerely,

Tom Nakashima

Tom Nakashima

TN/lis

References

1. R. Nunnally and D.P. Hollis, TAMU NMR News Letters, 206, 16 (1975).

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Chemical Shift Study on specific interactions between α -Lecithin and some naturally occurring Amino-Acids.

Dear Professor Shapiro,

Recent ^{13}C -, ^1H -nmr, CD and IR studies aimed at the detection of electrostatic interactions between Amino Acid (AA) side-chain residues in charged poly-peptides and the polar head groups of lipid Phosphatidyl-Choline (PC) (1,2,3,4). These studies showed contradictory results concerning this kind of interaction and also the possibility that geometrical requirements are to be fulfilled to explain some anomalies(5).

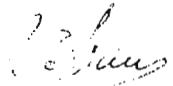
In an attempt to detect this kind of interaction in a quantitative but simpler way, we undertook a preliminary ^{13}C -, ^1H -nmr Chemical Shift study of some naturally occurring AA differing in shape, charge density and polarity which were dissolved in H_2O and in PC/ H_2O dispersions.

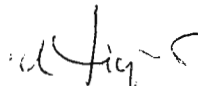
The chosen AA were: Gly, L-Ala, L-Phe, L-Pro, L-Asp, L-Glu and L-Lys. The spectra of the 1M solutions and of the AA+PC/ H_2O dispersions (three values of AA/PC molar fraction were analysed: 1, 2, 5) were taken at two different temperatures, 32° and 45°C, which are lower and higher with respect to the transition phase temperature of PC lipids. The pH value was 7, the optimal one for this type of investigation(6). Unsonicated PC dispersions were used since it is known that they provide a better approach to the membrane structure than phospholipid vesicles obtained by sonication(7). $^{13}\text{C}\{^1\text{H}\}$ spectra were obtained with a 90MHz-Bruker-FT, external lock C_6F_6 and TMS as external reference. ^1H -nmr spectra were obtained with a 270MHz-Bruker-FT, internal lock D_2O and internal reference DSS. Five independent runs were undertaken to minimize the statistical error, the reproducibility better than ± 0.2 ppm and ± 0.01 ppm for C -13- and H -NMR, respectively.

We find that, within experimental error, there are no chemical shift changes in going from AA solutions to the different AA+PC/H₂O dispersions. This invariance of Chem.Sh. values, in particular for the ¹³COO⁻ and H_α groups, indicates that there are no detectable changes in aggregation of AA and their mean environment over this 5-fold concentration range. We may, therefore, conclude that the AA are more or less distributed in the aqueous solution channels of the PC liposomes. The dominant interaction in these systems is the one of AA with H₂O (and H₂O with PC polar heads). Polar PC heads and AA are not easily accessible one another when dissolved in water. The invariance of the ¹³C_α, ¹³C_β, ¹³C_γ, ¹H_β, ¹H_γ, etc., Chem.Sh. further indicates that changes in hydrophobic interactions have to be ruled out. We would like to thank our friend A. Giannotti of the BRUKER SPECTROSPIN for his assistance and help, and the ALEXANDER VON HUMBOLDT-STIFTUNG for a fellowship.

Please credit this contribution to the account of Prof. Lippert of this Institute. We sincerely hope that this contribution arrives in time in order to keep us on the TAMU-NMR-L mailing list.

Yours sincerely


L. Pogliani


D. Ziessow

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TELEPHONES
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Department of Chemistry
Texas A&M University
College Station, TX 77843

July 26, 1976

Sir:

Mild and Simple Recovery of Substrates from Doped NMR Samples.

Additives to nmr sample solutions have become popular, which by electron-nuclear relaxation¹ achieve intensity decontrasting² or just removal of NOE effect³, ("shiftless relaxation agents"⁴), in hard-pulsed FT nmr.

To restore nmr as a nondestructive technique in such cases, we have investigated suitable sample recoveries, and the most satisfactory procedure is exemplified below on Fe³ acetylacetonate. The metal is precipitated as sulfide, and the ligand is pumped away from the substrate.

Rinse the nmr solution over into a vial (e.g. with CHCl₃). Add a mixture of 0.4 ml of methanol and 0.1 ml of water (in case of a 5-mm sample size). Allow H₂S to bubble in for 10-20 sec. Black iron sulfide should precipitate. Allow to stand stoppered for 1/2 hr. Filter through a small, tight plug of cotton in a disposable pipet and rinse. Concentrate, and pump at high vacuum at room temp.

Cordially,


Sandor Barcza

SB:rck

References

1. J. R. Lyster Jr. and G. C. Levy, Topics in Carbon-13 NMR Spectroscopy, Vol. I, G. C. Levy, ed., Wiley & Sons, New York, 1974, pp 79-148, esp. see pp 121-7.
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4. O. A. Gansow, A. R. Burke, W. D. Vernon, *ibid.*, 94, 2550

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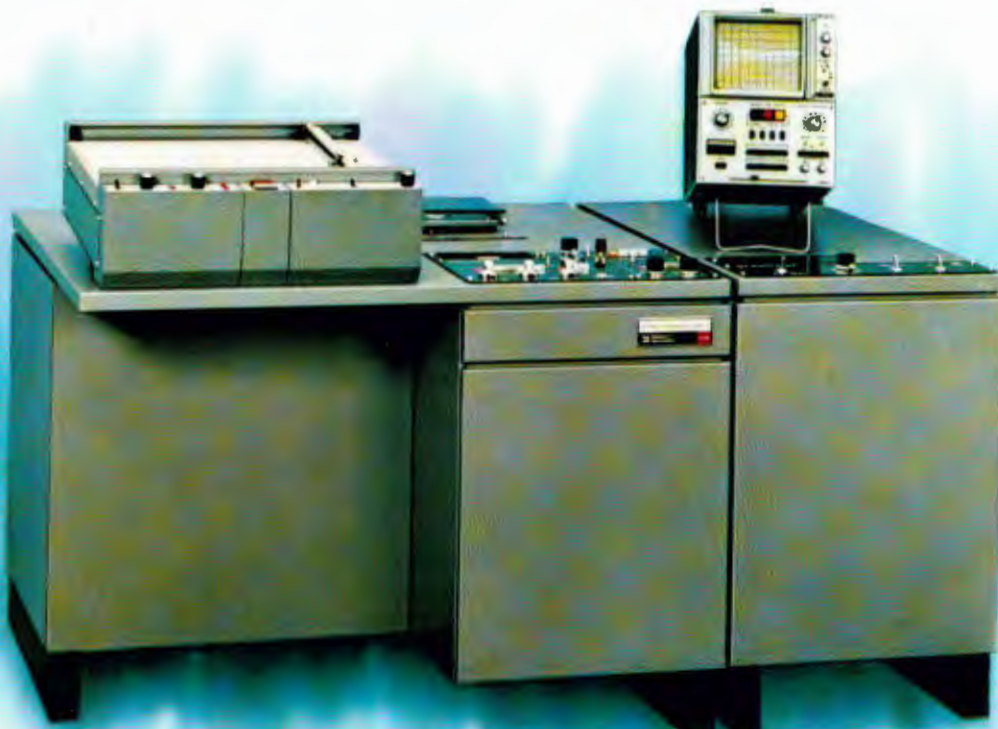
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July 19, 1976.

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

Assignment of carbon signals in a natural product with the aid of gated decoupling

Dear Professor Shapiro:

After solving an almost infinite number of problems we are happy owners of a beautifully working XL-100.

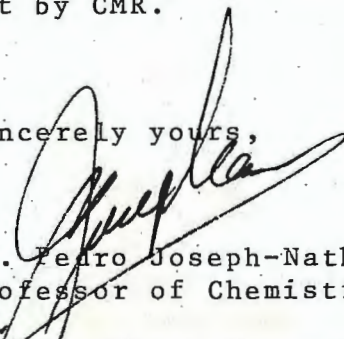
Following previous PMR studies of helenalin¹, we describe now the CMR. Figure 1 shows the PND spectra of the natural product and the derived acetate, while Figure 2 compares the PN and gated decoupled spectra of helenalin (note the plot expansion).

Gated decoupling is an alternate method to off-resonance decoupling for distinction of C, CH, CH₂ and CH₃ signals, having the extra benefit of long range coupling information. Although it is more time consuming, it can be performed routinely on overnight experiments since no specific decoupling frequency has to be selected and no measurements of residual couplings are done for specific assignments.

Using chemical shifts, multiplicities and long range couplings the spectra on the figures allow assignment of helenalin carbons as: C-1, 51.42; C-2, 163.70; C-3, 129.74; C-4, 211.91; C-5, 57.86; C-6, 74.10; C-7, 50.95; C-8, 78.24; C-9, 39.51; C-10, 26.21; C-11, 137.95; C-12, 169.60; C-13, 122.76; C-14, 20.13; C-15, 18.71 ppm from internal TMS in CDCl₃ solution.

This data should be useful for future structure elucidation of sesquiterpene lactones, since only very few related natural products^{2,3} have been studied yet by CMR.

Sincerely yours,


Dr. Pedro Joseph-Nathan
Professor of Chemistry

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PJN/psp

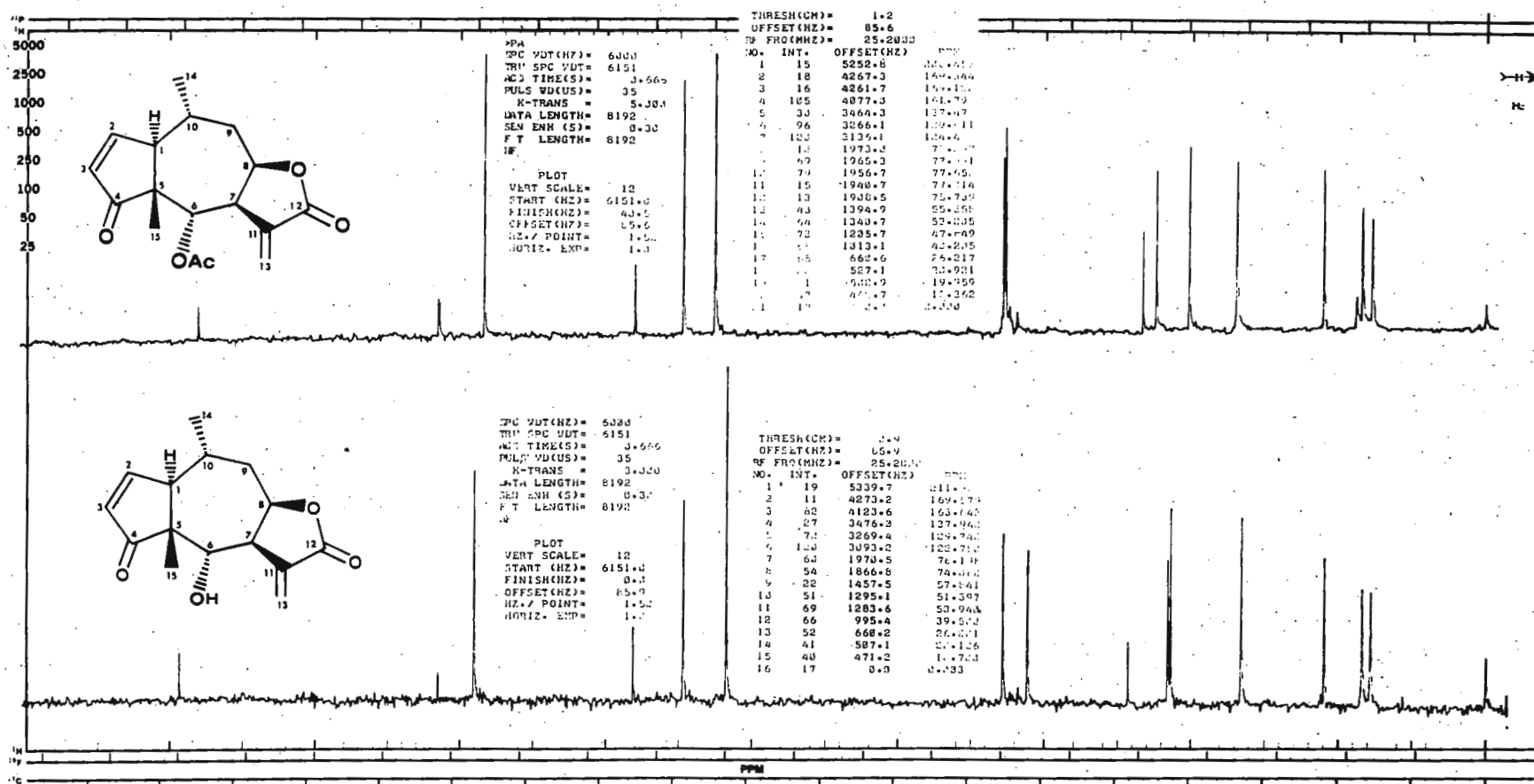


Figure 1.- PND ^{13}C FT (8K) spectra of helenalin (~300 mg, 3 K transients) and helenalin acetate (~250 mg, 5K transients) at 25.2 MHz in CDCl_3 (~4 ml) 12 mm tube.

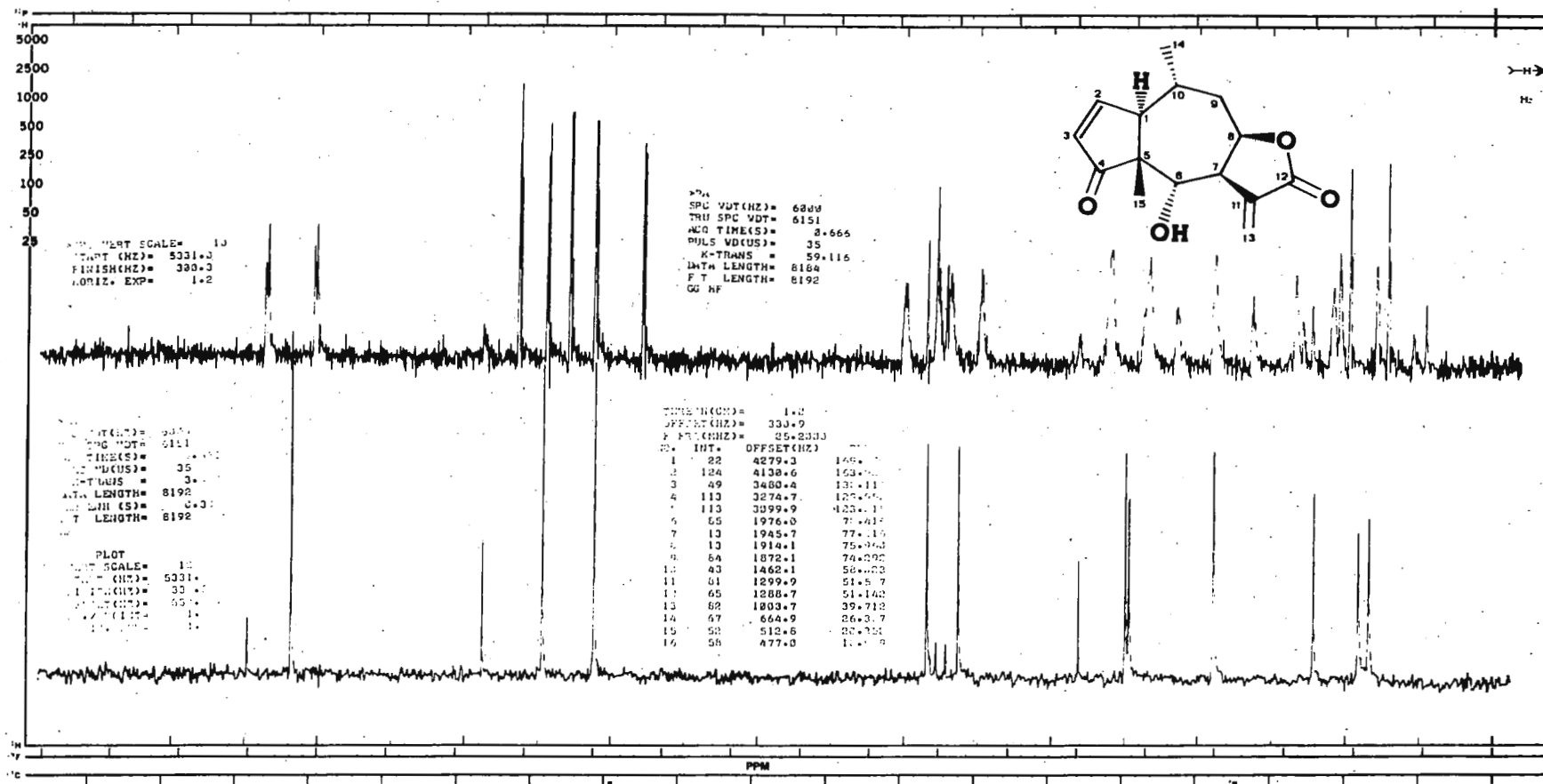


Figure 2.- PN (3 K transients) and Gated (59 K transients) decoupled spectra of ~300 mg of helenalin in ~4 ml CDCl₃ at 25.2 MHz in 12 mm tube.

July 19, 1976

Dr. B. L. Shapiro
TAMUNMR Newsletter
Department of Chemistry
Texas A & M University
College Station, Texas 77843

"Solution to Baseline Artifacts in High Dynamic Range Spectra"

Dear Barry:

I have been in communication with Jim Prestegard of Yale regarding his findings on baseline glitches caused as apparent harmonics of large peaks. He reported in last month's letter that these glitches appeared in spectra whenever the large peak was not an integral number of cycles from the carrier. Further, he observed this phenomenon on an IBM 1800 and on a Nicolet-Bruker BNC-12.

We talked about this problem and I did a few experiments and discovered that the problem appears to be principally related to the sine look-up interpolation routine in the FFT routine. I carried out integer Fourier transforms of simulated free-induction decays with no interpolation between points in the 1025-point sine look-up table and with appropriate linear interpolation. The results are as shown in the accompanying figure. The upper trace is part of an 8192 point Fourier transform with a simulated 20-bit word length without interpolation and the lower trace transform of the same data with interpolation. The lower trace is shown at a higher amplification to demonstrate that the glitches really have disappeared.

It appears that there are a number of Fourier transforms from various sources which do not interpolate during the sine look-up routine. I knew of this feature in the Nicolet and Bruker software and have informed the companies of the problem. I have been assured that it has now been corrected. I am using this letter to inform others who might be using IBM 1800 systems of the problem.

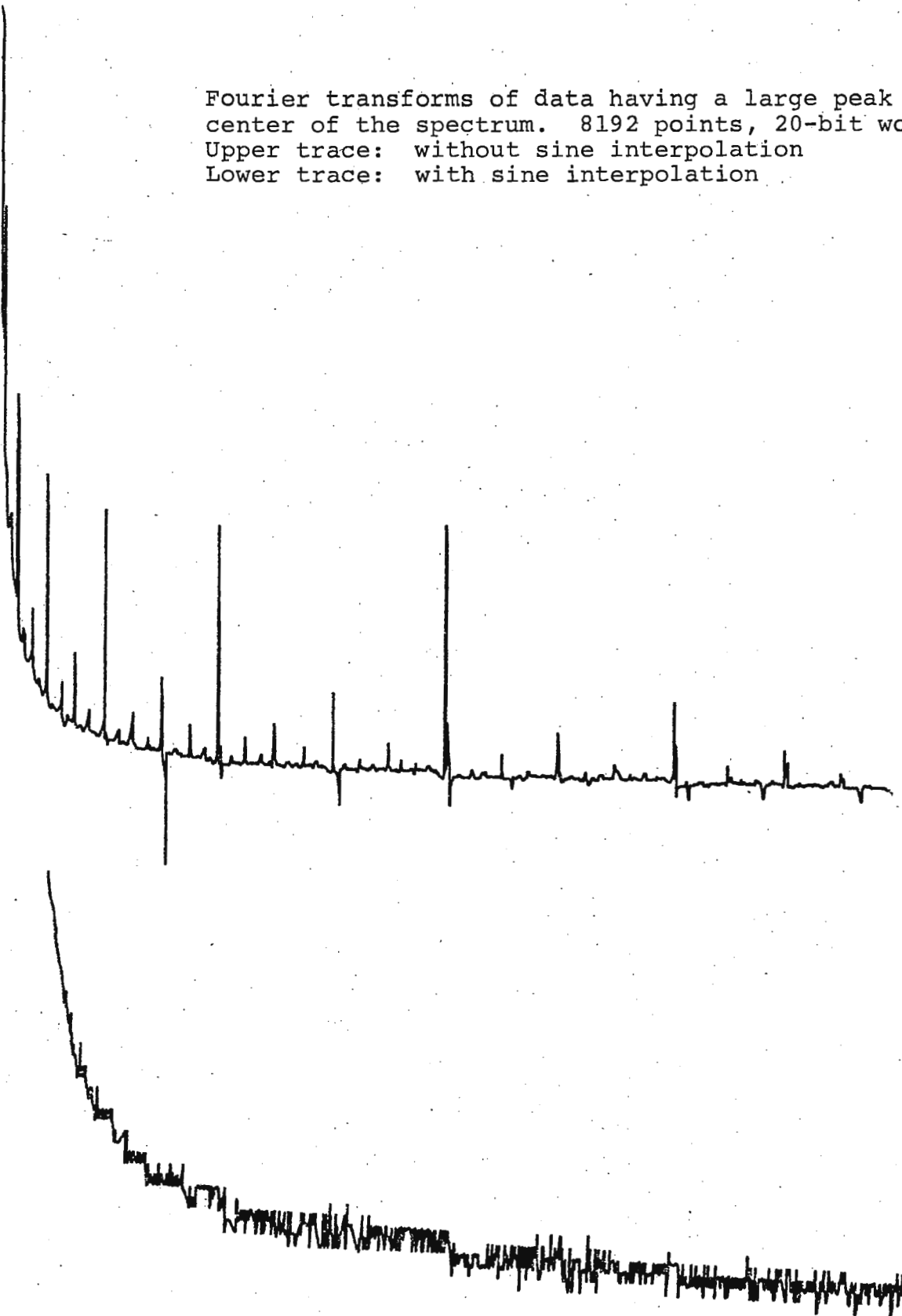
The program that we used to carry out these simulations was written for the 36-bit word PDP-10 and we have been simulating a number of computer configurations to discover optimum methods of handling FT data. We found that the interpolation glitches also appear in 16-bit word machines, of course, but that they are less apparent since the overall signal-to-noise is lower after the 16-bit transform. We will be reporting shortly on a method of increasing the available post-transform dynamic range to 200,000:1 in single precision.

Sincerely,



James W. Cooper
Associate Professor

Fourier transforms of data having a large peak near the
center of the spectrum. 8192 points, 20-bit word.
Upper trace: without sine interpolation
Lower trace: with sine interpolation



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July 19, 1976

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

Interactions of TMS Salts with Proteins; Postdoctoral
Position Available

Dear Barry:

We read with interest two recent TAM NMR Newsletters (Thomas, No. 212, p. 48, and De Marco, No. 213, p. 24) detailing problems with using various sodium salts of TMS as aqueous references. Those problems concerned shift changes of the reference with solution conditions.

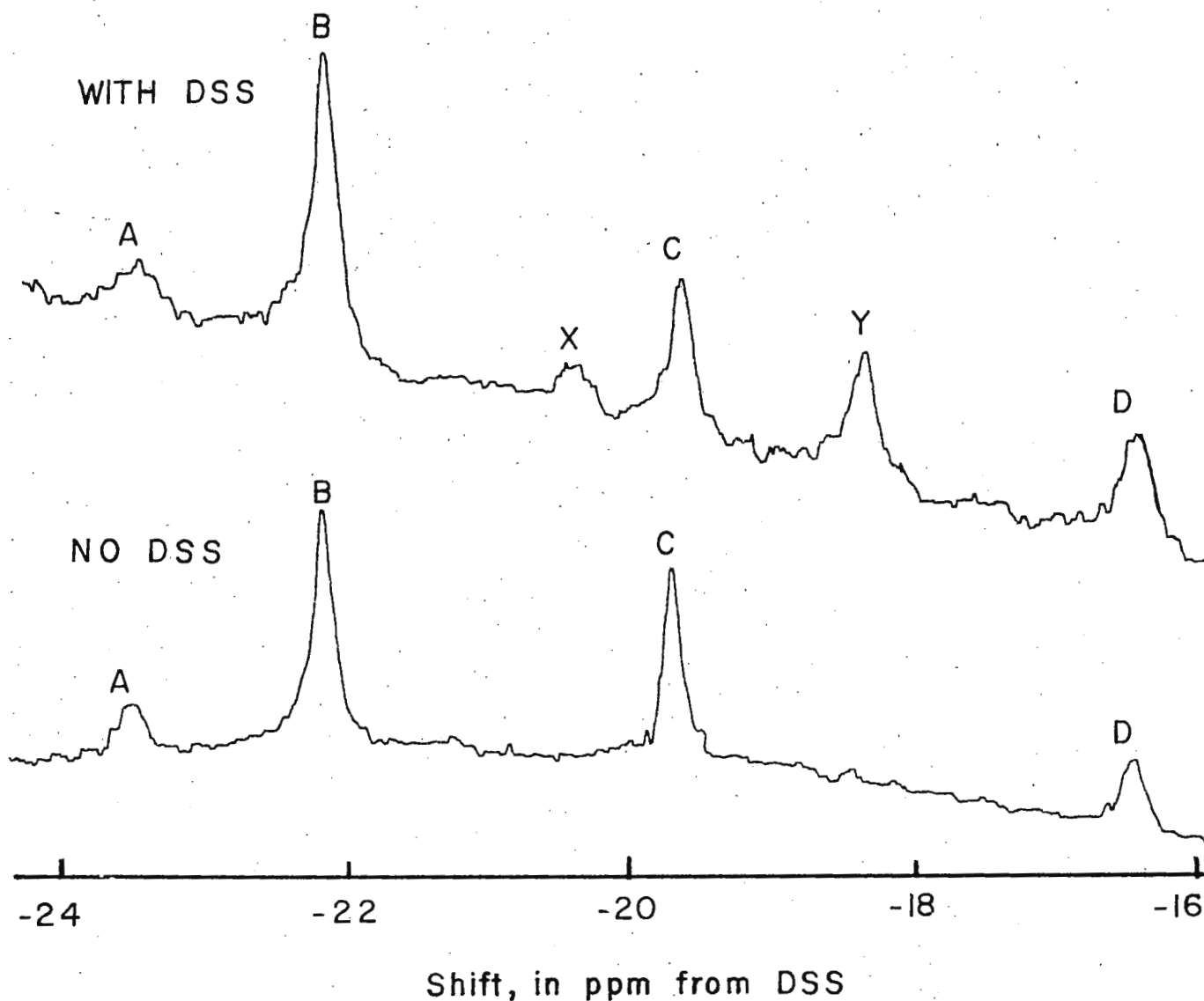
Our recent experiences with proton nmr of some hemoglobins indicate that even more serious problems can occur than just reference position changes, namely, specific interactions with the protein. In the figure we exhibit a portion of the downfield proton trace of the low-spin cyano-met form of a hemoglobin monomer (5mM protein, pH = 6.0 I = 0.2 NaCl, 25°) before (lower trace) and after (upper trace) adding DSS to the D₂O solution. The peaks labelled A-D arise from the native protein: peaks X and Y arise from a form of the protein which interacts with DSS in or very near the heme cavity. Additional DSS increases peaks X and Y at the expense of peaks A-D. The interaction of DSS with the protein is pH-dependent, occurring only in the acidic range.

In our case, the problem of interaction with DSS was easily recognizable by virtue of the paramagnetic shifts which amplify the inequivalence of the native and "intercalated" proteins. It is not obvious that this interaction is as easily detected in diamagnetic proteins. We solved our problem by using t-butanol which we confirmed did not affect the nmr spectrum at all. Our experience suggests that it is worthwhile to compare spectra in the presence and absence of sodium salts of TMS before using them as reference.

Sincerely,

Gerd N. La Mar
Professor of Chemistry

GNL:jkg



Postdoctoral Position

Two postdoctoral positions will be open next year, starting in January and sometime in the summer. Stipends run \$8,500-9,000, depending on experience. Research involves investigation of structure-function relationships in hemoproteins, particularly in their high-spin ferrous and ferric states using multinuclear FTNMR. Interested persons should submit a C.V. and two letters to me at Davis.

G. N. La Mar

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GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

July 23, 1976

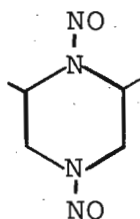
Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
USA

Multiple Rate Processes by DNMR

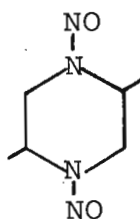
Dear Barry:

For some time Dieter Höfner in my group has been trying to apply DNMR techniques to cases where several intramolecular rate processes are operative concurrently. Although the theoretical treatment of the bandshapes is straightforward in principle, the practical analysis of the experimental spectra proved to be trickier than we had anticipated. Other TAMU readers contemplating similar studies may perhaps profit from our experience with this kind of work.

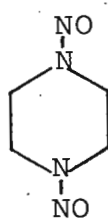
In the nitroso compounds shown below (some of which have repeatedly been looked at by other workers, but never quantitatively) the processes of interest are the hindered rotations about the N-N bonds; ring reversal is completely averaged out at all temperatures investigated.



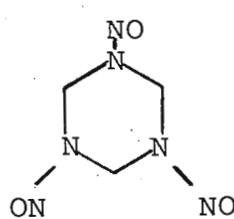
I



II



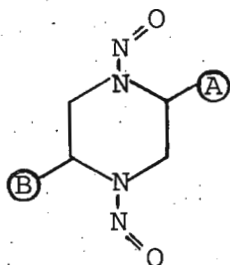
III



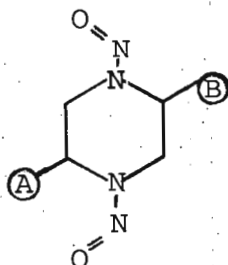
IV

(*cis*-2,6-dimethyl) (*trans*-2,5-dimethyl)

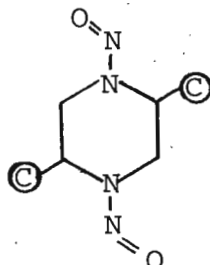
From elementary symmetry considerations one deduces that there should be 2 conformers for I, III and IV and 3 for II. All of them were found to be significantly populated and could be unambiguously identified from the spectra. As sensor nuclei for the dynamics we employed the methyl groups for I and II (showing up as doublets, sometimes further split by small long-range couplings) and the ring protons for III and IV (giving rise to an AA'BB' system plus 2 singlets for III and to 4 singlets for IV). The kinetic scheme for compound II, for example, then looks as follows:



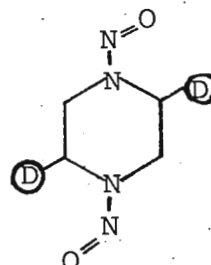
IIa



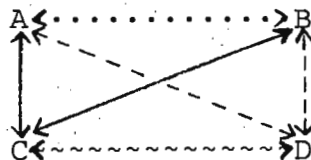
IIa'



IIb



IIc



Taking into account the constraints of the detailed balancing conditions, the system is characterized by 4 independent rate parameters, of which 2 (symbolized by the solid and dashed double arrows) correspond to single rotations and 2 (shown as dotted and wavy double arrows) to concerted double rotations. A similar analysis can be performed for the other cases.

This is not the place to report and discuss the final results; I only wish to make a few remarks concerning some technical aspects of the analysis. In the case of II, where the situation is still comparatively simple, a few trial simulations convinced us that a minimum of 2 rate parameters is needed. More systematic simulations yielded the rate constants [s^{-1}] and their estimated standard deviations shown on the left in the Table.

	Simulation				Iteration				
T[°C]	k_1	σ_1	k_2	σ_2	k_1	σ_1	k_2	σ_2	ρ
108.9	2.5	0.5	0.3	0.5	2.86	0.09	0.20	0.03	0.003
114.2	5.0	0.5	0.6	0.5	4.89	0.12	0.21	0.03	0.039
119.3	5.5	0.5	0.8	0.5	6.03	0.15	0.44	0.03	0.237
126.2	16.0	1.5	1.5	0.5	11.56	0.28	0.96	0.03	0.095
139.5	25	25	4.5	0.5	27.2	0.5	3.49	0.16	0.367
151.3	65	5	15.0	1.5	78.5	0.5	8.58	0.11	0.946
164.4	115	15	35	5.0	158.0	4.1	20.1	1.1	0.981
174.7	240	25	110	15	301.2	10.9	52.8	4.7	0.991
185.2	380	40	290	30	477	50	142.1	35.5	0.991

The bandshape fit seemed quite satisfactory at all temperatures when judged on the basis of our experience with single rate processes. The simulation approach could also be applied to I, but proved unfeasible for III and IV. At about this time Dr. David Stephenson, who has been working on the development of a general automatic spectrum analyzer, had a preliminary version of his program running, which, when applied to II, produced the results shown on the right in the Table. The discrepancies give sober men pause. Later we found that even an iterative analysis may sometimes not be reliable enough. An indication of this being the case can be gleaned from the correlation coefficients listed in the last column, which are seen to undergo a quantum jump at about 150°C. Another source of difficulty emerged in the iterative analysis of III, where the computations seemed to show evidence of a spurious rate process, which only vanished when we also treated the static parameters as free variables.

To summarize: the analysis of multiple rate processes by DNMR seems to be a tricky business indeed. Visual comparison of simulated and experimental bandshapes is clearly no longer adequate and even the results of an iterative analysis should be interpreted with a good deal of discretion.

Sincerely yours,

Gerhard

Gerhard Binsch

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Instrumentation Scientifique

Appareils Electroniques

Electronique Médicale

Recherche Océanographique

Professor Barry L. SHAPIRO

Department of Chemistry

Texas A & M University

COLLEGE STATION Texas 77843 USA

N/Réf. 76 06 545 CB/MCH

Wissembourg, le 29. 6. 1976

V/Réf.

¹⁹F FT Homodecoupling

Dear Professor Shapiro,

Besides some very promising results we got in our applications lab in Wissembourg about exotic nuclei, there is actually a number of classical NMR problems we are dealing with, having in mind the great potentiality of the FT methods. For example ¹⁹F FT homodecoupling.

One of the advantages of this technique is the huge decoupling range you get, because you do not lose too much decoupling power in side band modulation; we found it is possible to decouple without any problems $\pm 30\ 000$ Hz from CFC1₃ !

Then you obtain the entire ¹⁹F decoupled spectrum at once without tedious expansion adjustments. And last, but not least, the computer, gently locates immediately your decoupling offset, being kind enough to record, if you want two, three... ten selectively decoupled spectra. Then you just have to think about the structure of the compound you are studying.

The spectra shown are self-speaking.

Figure 1 represents the non decoupled spectrum.

Figure 2 shows the result of perfluormethyl decoupling.

A full study on the detailed spectrum analysis, including proton broadband decoupling and simultaneous ¹⁹F homodecoupling will be published soon.

Sincerely,

C. BREVARD

J. Y. FRAVAL

J. M. MATHIEU



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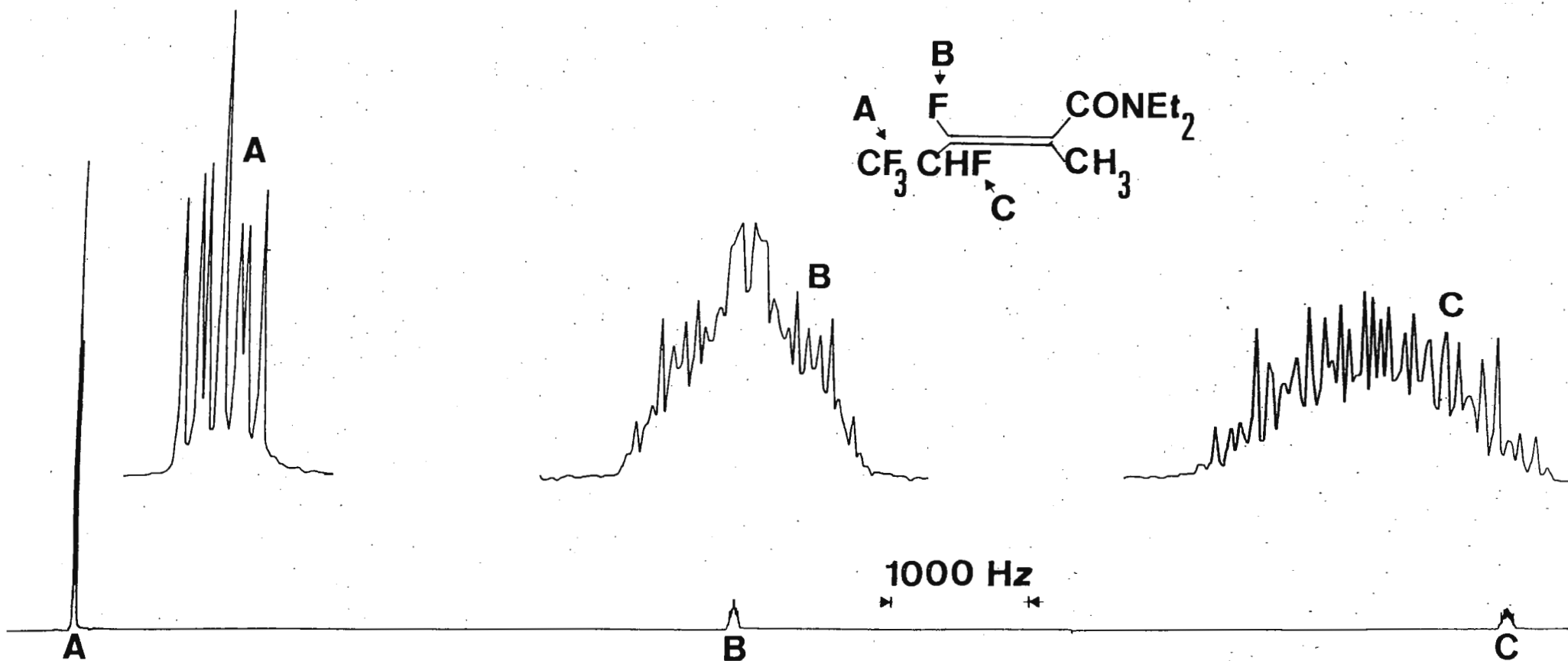


Fig. 1

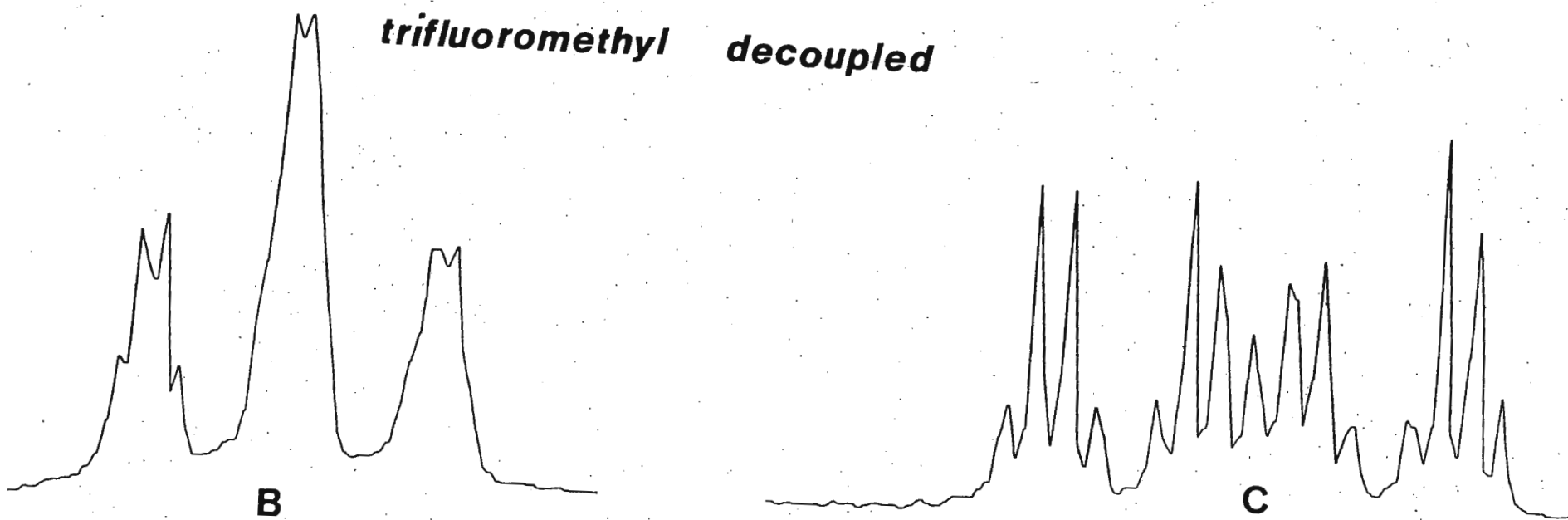


Fig. 2

UNIVERSITY OF MARYLAND
COLLEGE PARK, MARYLAND 20742

DEPARTMENT OF CHEMISTRY

July 29, 1976

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

Resolution Enhancement on an XL-100

Dear Barry:

We have recently completed modifications of Varian software which enable us conveniently to do convolution difference resolution enhancement ("CDRE") of FT spectra on our XL-100, in a manner analogous to that described by the Oxford Enzyme Group.¹ Instead of computing difference spectra, however, we simply use the function $(1 - Ke^{-t/\tau_1})e^{-t/\tau_2}$ as our weighting function for the FID. K is the scaling factor which determines the relative magnitude of the e^{-t/τ_1} convoluted FID which would be subtracted from the unweighted FID, and τ_1 and τ_2 are the (positive) time constants. The function in parentheses provides the resolution enhancement, and the final convolution (with e^{-t/τ_2}) serves to regain some of the lost signal/noise. We seem to obtain the best combinations of enhanced resolution and sensitivity when the final weighting is started not at $t=0$, but at $t=t_g$. By looking at the oscilloscope display of the resolution-enhanced FID, one can determine at what time point the displayed data have become essentially all noise, and set t_g accordingly. This "delayed" sensitivity enhancement ("DSE") feature may also be useful when one finds after accumulating his data that he grossly overestimated T_2^* , and has obtained a short, say, 0.5 sec FID, and, say, 1.5 sec of just noise. Using DSE, the noise appearing late in the time-domain data may be eliminated without at all attenuating the signal appearing early, and without broadening the lines in the spectrum.²

The accompanying 100.1 MHz ^1H spectra of myelin basic protein, all computed from the same FID, illustrate our implementation of CDRE. The FID was accumulated with an acquisition time of 2 sec as part of


Professor B. L. Shapiro
July 29, 1976

a WEFT³ sequence. Spectrum A is the FT of the unweighted FID. The glitch at $\delta=4.85$ arises from incompletely eliminated HDO. In spectrum B, a DSE was used with $\tau=0.2$ sec and $t_s=0.625$ sec. There was an improvement in the signal/noise, and without any line broadening, but it is not obvious in this presentation. In spectrum C, a "mild" CDRE including DSE was performed with the values $\tau_1=0.05$ sec, $K=0.82$, $\tau_2=0.2$ sec, and $t_s=0.625$ sec.

All the parameters (the time constants τ_i , the scale factor K , and t_s , the starting time point for DSE) may be entered from the teletype keyboard, just as any other parameters. We have installed these modifications both on the Varian disk FT and in-core FT programs for the 620 L/100 computer. The patches are too long to reproduce here, but a copy and instructions for use may be obtained by writing to R. Rowan.

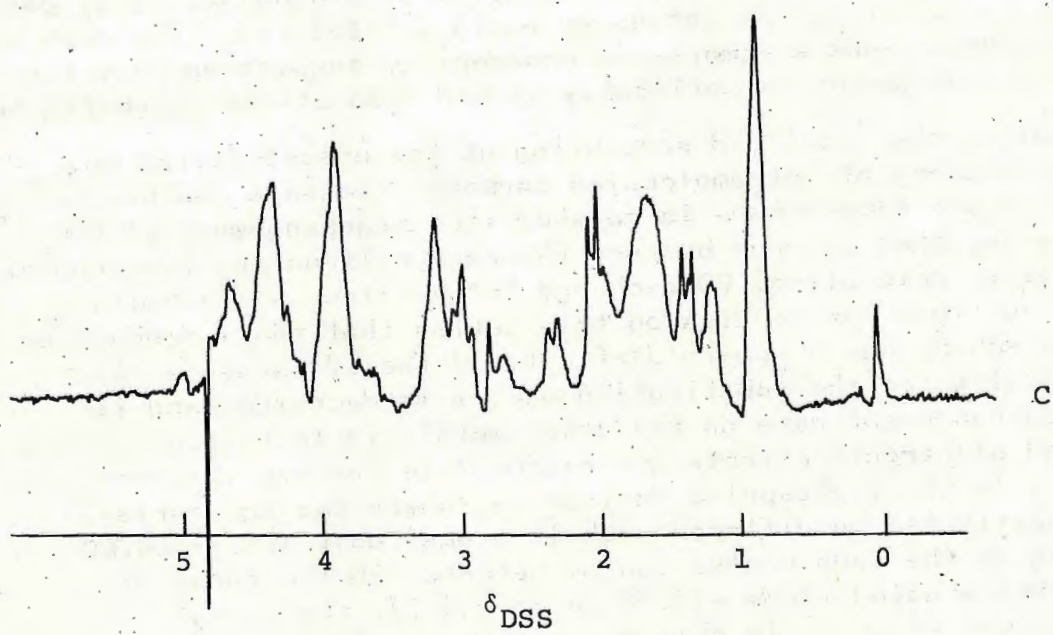
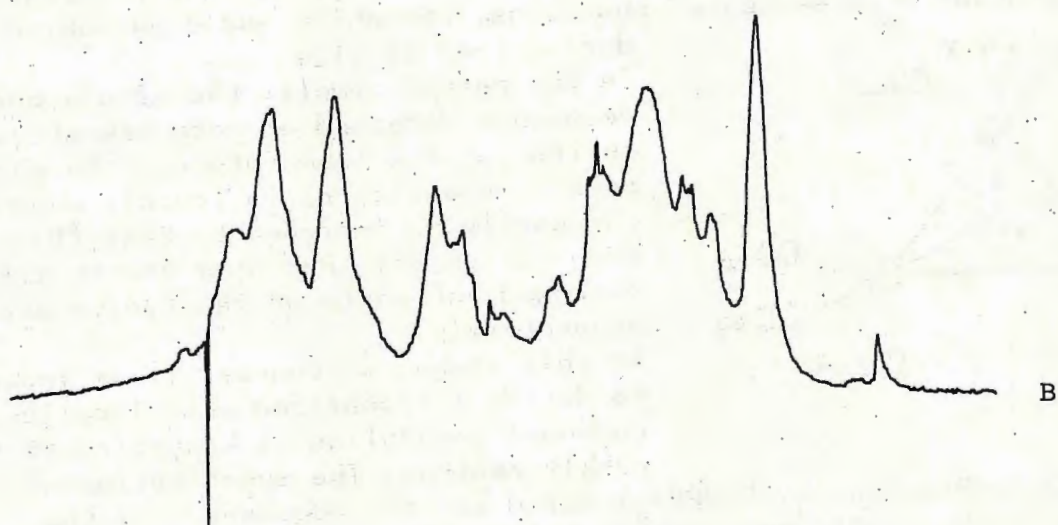
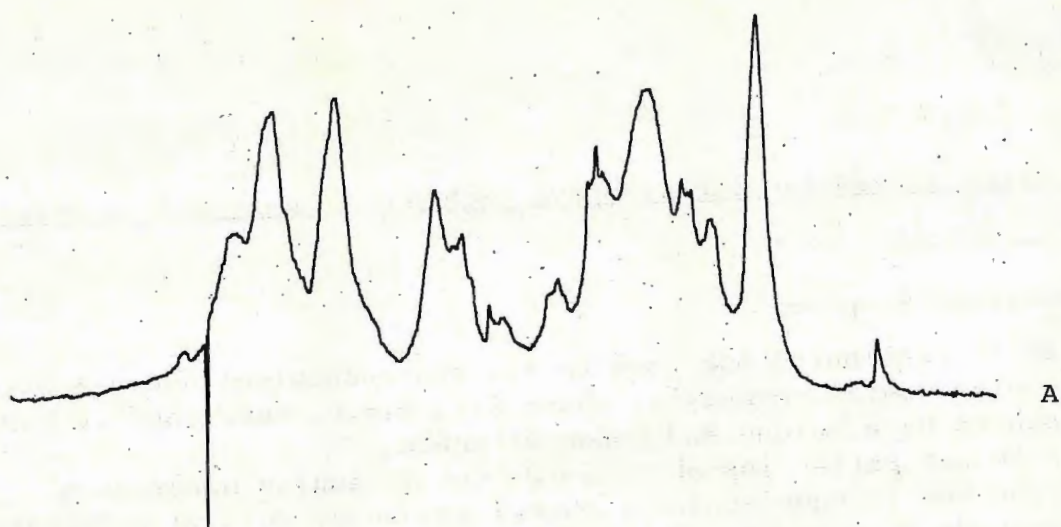
Sincerely yours,


Mark Mattingly


Robert Rowan, III

RR/MM/ssc

1. I.D. Campbell, C.M. Dobson, R.J.P. Williams, and A.V. Xavier, J. Magn. Reson. 11, 172 (1973).
2. W.E. Hull, then at Harvard University, introduced us to the idea of delayed sensitivity enhancement.
3. S.L. Patt and B.D. Sykes, J. Chem. Phys. 56, 3182 (1972).





ISTITUTO CHIMICO

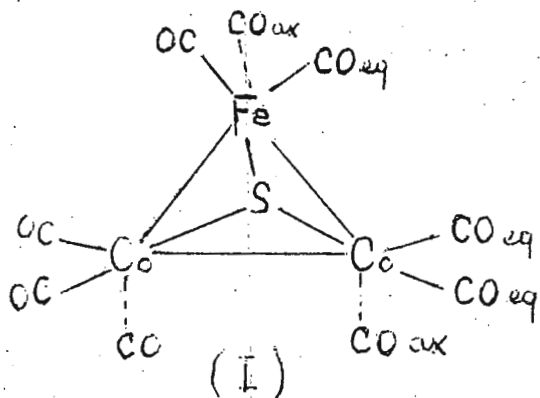
10125 TORINO, 20th July, 1976
 CORSO MASSIMO D'AZEGLIO, 49
 Tel. 65 2102 - 65 28 92 - 65 58 31 - 65 58 32

Multi- steps intramolecular carbonyl exchange in polinuclear metal carbonyl cluster.

Dear Professor Shapiro,

we are still continuing our work on the stereochemical non rigidity in polinuclear metal carbonyls, where C-13 n.m.r. spectroscopy has been shown to be a unique and powerful probe.

In order to get better insight towards the molecular parameters influencing the intramolecular carbonyl exchange, we have undertaken a detailed study of a series of phosphine, phosphite and diphosphine derivatives of (I).



In the parent complex the single broad resonance detected at room temperature splits, at low temperature, into three peaks (intensity ratio 1:2:6), which can easily be assigned to CO_{ax} (1) and CO_{eq} (2) on the iron atom and to six averaged carbonyls on the two Co atoms, respectively.

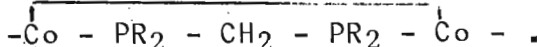
At this stage, of course, it is impossible to decide if localized or delocalized carbonyl scrambling is occurring at the cobalt centres. The substitution of a

CO with L (L=P(n-C₄H₉)₃, P(OPR)₃) ruled out the degeneracy of the signals; in the -133°C spectrum of FeCo₂(CO)₈P(n-C₄H₉)₃S, it is possible to detect six peaks in the intensity ratio 1:1:1:1:1:3. The peak of intensity three shows a remarkable broadening, suggesting that the carbonyl rearrangement is noticeably slowed also at the unsubstituted Co.

Then, besides the localized scrambling at the unsubstituted Co, three other steps of intramolecular carbonyl exchange can be detected as the temperature is raised, i.e. rearrangement of CO groups on Fe, then average between the carbonyls on the two cobalts and, finally, delocalized CO exchange between iron and cobalt.

It comes out from our studies on this series that the introduction of the phosphine has a two-fold effect: i) the CO exchange rate on the metal where the substitution occurs is decreased and ii) the CO rearrangement rate on the other metals is increased.

Steric and electronic effects are responsible for the observed behaviour. In the diphosphine derivative (where two equatorial CO are substituted on different cobalt atoms) only localized CO scrambling at the iron centre can be detected in the range of temperatures studied (from -100°C up to +30°C): the overall stereochemical rigidity is then related to the formation of the metallo-cycle



(Silvio Aime)

(Luciano Milone)

New 18-mm Probe for the XL-100

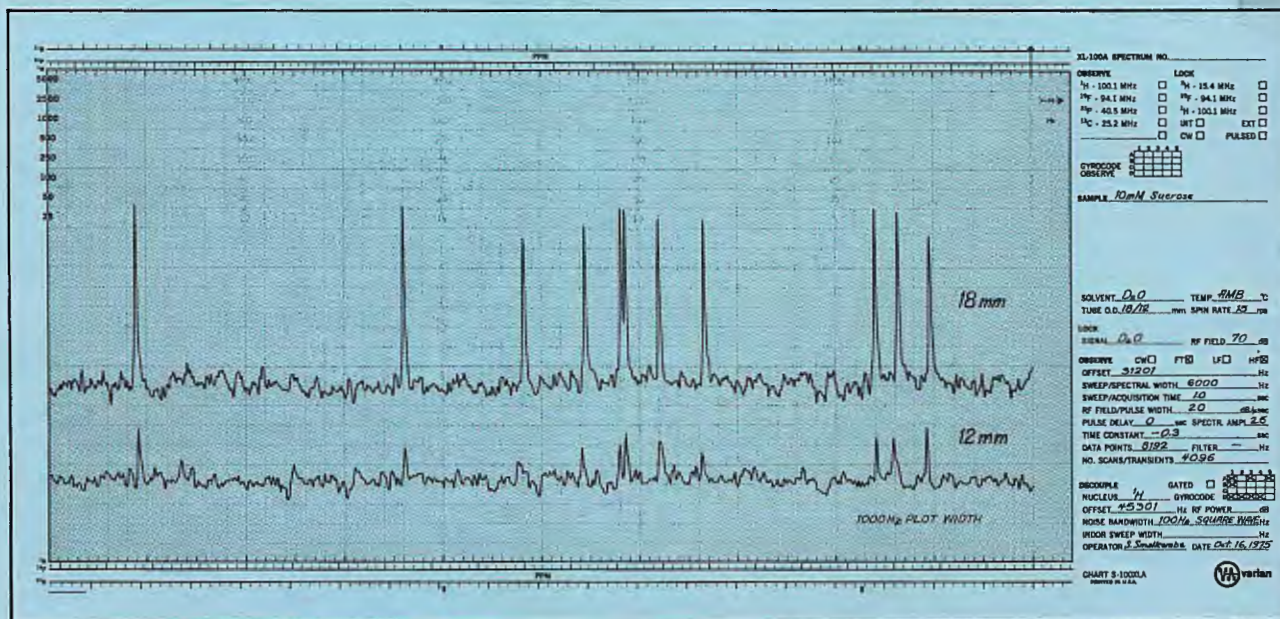
^{13}C Spectra 10 Times Faster

Now Varian XL-100 users can run natural abundance ^{13}C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose—clearly this new probe could extend the application of ^{13}C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs ^{13}C spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10—with results second to none.

Not only is the absolute sensitivity of the V-4418 Probe outstanding, it also offers excellent sensitivity per milliliter of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.



Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D_2O , one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.

For further information contact your local Varian representative or write to:
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Sample tube shown actual size.

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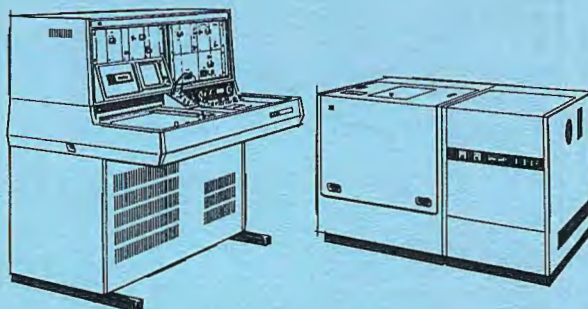


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