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Novel Marine Sponge Alkaloids. 1. Plakinidine A and B, Anthelmintic Active Alkaloids from a *Plakortis* Sponge

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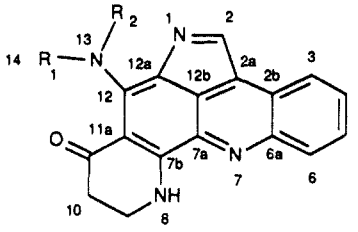
Abstract: Two novel pentacyclic aromatic alkaloids, plakinidine A and B, were isolated from a *Plakortis* sponge. Their structures, which include a pyrrolo[2,3,4-*kl*]acridine, were determined from extensive 2D NMR experiments. The fused aromatic ring system is a structural variation not previously found in aromatic alkaloids of either marine or terrestrial origin. Plakinidine A and B exhibited in vitro activity against *Nippostrongylus brasiliensis*, and plakinidine A showed weak activity against reverse transcriptase.

Our program to discover novel nitrogen-containing natural products from tropical sponges continues to be aided by antiparasitic prescreens.[1] Bioassay-guided isolation of constituents from a Vanuatuan red sponge in the genus *Plakortis*[2] has afforded plakinidine A (**1**) and B (**2**). Both of these novel alkaloids



R_1 = H, R_2 = CH_3 : Plakinidine A = 1

R_1 = CH_3, R_2 = CH_3 : Plakinidine B = 2

exhibited in vitro activity (at 50 μg/mL) against the parasite *Nippostrongylus brasiliensis*.[3] By contrast, in a different assay against reverse transcriptase (at 1 mg/mL), only plakinidine A was active.[4] The fused-ring skeleton of the aromatic chromophore

Table I. ^{1}H and ^{13}C NMR Data for Plakinidine A in $CDCl_3$–TFA-*d* (1:1)

atom	δH	m $^3J_{H-H}$ (±0.3 Hz)	H coupled with H	δC	$^1J_{C-H}$ (Hz)	$^3J_{C-H}$ (Hz)	H coupled with C
2	8.84	s		127.4	200.4		
2a				125.76			H-2, H-3
2b				125.84			H-4, H-6
3	8.64	d, 7.8	H-4	125.3	167.1	6.9	H-5
4	8.23	t, 6.9	H-3, H-5	135.3	167.2	6.9	H-6
5	8.17	t, 7.2	H-4, H-6	133.7	168.1	7.6	H-3
6	8.71	d, 8.4	H-5	124.2	168.0	6.4	H-4
6a				135.8			H-3, H-5
7a				136.7			
7b				153.7			H-9
9	4.24	t, 7.5	H-10	41.2	146.6		H-10
10	3.10	t, 7.5	H-9	34.3	133.2		H-9
11				196.9			H-9, H-10
11a				101.0			H-10
12				152.7			H-14
12a				115.5			H-2
12b				120.1			H-2
14	3.84	s		34.3	141.8		

(1) Most of these have been either unusual amino acid derivatives or nitrogen-containing terpenes. For recent examples and references to this literature, see: Adamczeski, M.; Quiñoá, E.; Crews, P. *J. Am. Chem. Soc.* **1989**, *111*, 647.

(2) C. Diaz has completed a tentative identification on our collection No. 87014 as: *Plakortis* sp. (Fam. Plakinidae, Order Homosclerophorida).

(3) We thank Dr. Tom Matthews (Syntex Research, Palo Alto, CA) and his staff for this data according to the assay described by: Jenkins, D. C.; Armitage, R.; Carrington, T. S. *Z. Parasitenkd.* **1980**, *63*, 261.

0002-7863/90/1512-1$02.50/0

Table II. ^1H and ^{13}C NMR Data for Plakinidine A in DMSO-d_6

atom	δH	m $^3J_{H-H}$ (±0.3 Hz)	H coupled with H	δC	$^1J_{C-H}$, (Hz)	$^3J_{C-H}$, (Hz)	H coupled with C
2	8.47	s		136.0	184.1		
2a				124.38[a]			H-2
2b				124.44[a]			H-4, H-6
3	8.42	d, 7.8	H-4	123.8	167.1	5.5	H-5
4	7.73	t, 7.2	H-3, H-5	128.1	160.1	8.2	H-6
5	7.69	t, 9.3	H-4, H-6	126.2	160.7	9.1	H-3
6	8.27	d, 8.1	H-5	130.3	167.0	7.0	H-4
6a				144.1			H-3, H-5
7a				138.1			
7b				157.9			H-9
8	9.93	br s	H-9				
9	3.82	dt, 7.8, 1.2	H-8, H-10	38.0	141.5		H-10
10	2.72	t, 7.8	H-9	35.5	131.0		H-9
11				194.0			H-9, H-10
11a				100.0			H-10, H-13
12				152.0			H-13, H-14
12a				122.3			H-13
12b				127.7		11.7	H-2
13	11.17	q, 5.4	H-14				
14	3.68	d, 5.7	H-13	33.7	139.5		

[a] Interchangeable

in **1** and **2**, a pyrrolo[2,3,4-*kl*]acridine, represents a new structural variation within an emerging group of polycyclic aromatic alkaloids from marine organisms.

Results and Discussion

The molecular formula of **1**, $C_{18}H_{14}N_4O$, was determined from HREIMS (*m/z* 302.1169, M^+, Δ 0.7 mmu of calcd) and an APT ^{13}C NMR spectrum. COSY experiments in DMSO-d_6 and $CDCl_3$–TFA-*d* (1:1)[5] identified four separate proton spin systems (see Tables I and II). The protons on C-3 to C-6 were part of an ortho-disubstituted benzene ring, protons on N-8 to C-10 were ascribed to a $CH_2CH_2N(H)$ group, and the amino H-13 to methyl H-14 protons comprised an N(H)Me appendage. The remaining proton, H-2, was a low-field singlet (δ 8.84) with a large $^1J_{CH}$ coupling constant (200.4 Hz in $CDCl_3$–TFA-*d*), indicating a nitrogen was adjacent to C-2.[6] The remaining C_9N atoms were assumed to comprise five double bonds based on their ^{13}C chemical shifts; consequently, five rings were required. Long-range ^1H–^{13}C COSY experiments were invaluable for building up larger substructures (see Figure 1, Tables I and II). Three-bond correlations to H-4 and H-5 revealed the location of quaternary carbons C-2b and C-6a, and a three-bond correlation to H-3 suggested the location of C-2a. The existence of a six-membered-ring β-enamino ketone was required by the IR (1624 cm^{-1}) and COSY NMR correlations from H_2-9 to C-7b and from H_2-10 to C-11 and C-11a. This substructure was expanded to include the enamine attached at C-11a due to long-range correlations from H-13 to C-11a, C-12, and C-12a. Both C-12a and C-12b displayed long-range correlations to H-2 and were required to be in the vicinity of the disubstituted imine. Another important long-range COSY correlation was observed from H-2 to C-2a (two-bond coupling) or C-2b (three-bond coupling). The largest chemical shift difference between C-2a and C-2b ($\Delta\delta = 0.08$) was observed in $CDCl_3$–TFA (Table I), and H-2 appeared to be coupled to C-2a. Long-range COSY experiments with **2** in $CDCl_3$ clearly showed a correlation between H-2 and C-2a (see discussion below) and provided conclusive evidence for the H-2 to C-2a two-bond coupling in **1**.[7] At this point, the two six-membered rings and an N(H)Me substituent were fully defined as the terminal groups,[8] and they could be connected as shown in fragment A based on the collective NMR data. The remaining fragment, B, needed to be joined to A to generate three additional rings. The nitrogen in B was joined to C-6a based on the chemical shift of C-6a (δ

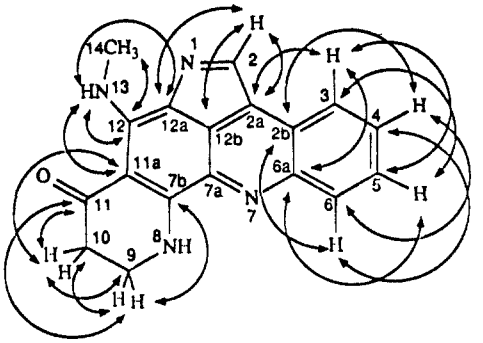
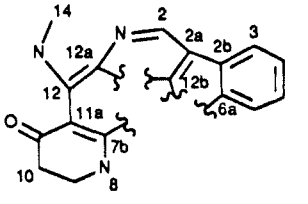
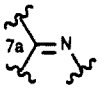


Figure 1. Long-range C–H correlations for **1**.



A



B

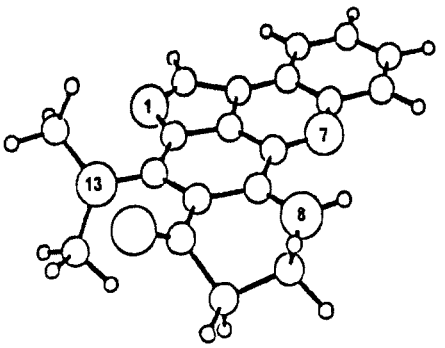
(4) These results were also provided by Dr. Tom Matthews (Syntex Research, Palo Alto, CA) and his staff. Purified cloned HIV-1 reverse transcriptase was assayed by a previously described procedure: Chen, M. S.; Oshana, S. C. *Biochem. Pharm.* **1987**, *36*, 4361. Another assay utilizing a tyrosine kinase tumor model, carried out by Dr. D. Slate (Syntex Reasearch), showed that plakinidine A was not active against this enzyme.

(5) Plakinidine A was only slightly soluble in common organic solvents including trifluoroacetic acid (TFA). This along with the small amount of material thwarted our attempts to obtain INADEQUATE data.

(6) The difference in ^{13}C chemical shift and one-bond C–H coupling ($^1J_{CH}$) for C-2 in the unprotonated vs protonated form of **1** was +9 ppm (upfield shift for protonated **1**) and 16 Hz (increase in $^1J_{CH}$ for protonated **1**), respectively. These values compare favorably to changes in ^{13}C chemical shift and one-bond C–H coupling in pyridine (unprotonated vs protonated) at the position α to N, +8 ppm (upfield shift for protonated pyridine) and 13 Hz, respectively. See: Seel, H.; Gunther, H. *J. Am. Chem. Soc.* **1980**, *102*, 7051. Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 697.

(7) We could not find an example of long-range C–H couplings in a fused aromatic pyrrolo derivative; however, two-bond C–H coupling in pyridine (H is α to N) is typically 5–6 Hz; see: Silverstein, R. M.; Bassler, G. C.; Morrill, J. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; Chapter 4. Two bond C–H coupling in benzene is ≈1.0 Hz and is not observed in the long-range COSY experiments; see: Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1983; p C230.

(8) HREIMS fragments for the loss of the nonaromatic substituents were *m/z* 275.1066 (M^+ – HCN, Δ 0.7 mmu of calcd), 231.0797 (M^+ – C(=O)$CH_2CH_2N(H)$, Δ 0.1 mmu of calcd), and 204.0663 (M^+ – C(=O)CH_2-$CH_2N(H)$ and HCN, Δ 2.5 mmu of calcd).



2

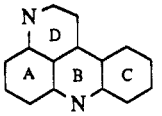
Figure 2. ORTEP plot of plankinidine B (**2**).

144.1/DMSO-d_6)[9] and dictated the final connections shown in **1**. Finally, the polyaromatic chromophore of **1** was consistent with the color and the intense molecular ion observed in the mass spectrum.

The molecular formula of **2**, $C_{19}H_{16}N_4O$, was determined from HREIMS (m/z 316.1322, M^+, Δ 0.2 mmu of calcd) and APT ^{13}C NMR spectra.[10] The HREIMS of **2** denoted a net gain of CH_2 in comparison with **1**. Furthermore, the similar MS fragmentation patterns[8] and NMR spectra of **1** and **2** indicated the skeletons of both structures were related. Particularly important HREIMS fragments were for the loss of the nonaromatic substituents as indicated by m/z 259.0998 ($M^+ - C(=O)CH_2CH_2$ and H Δ 1.4 mmu of calcd), 245.0933 ($M^+ - C(=O)CH_2CH_2N(H)$, Δ 2.0 mmu of calcd), and 202.0545 ($M^+ - C(=O)CH_2CH_2N$ and $N(CH_3)_2$, Δ 1.4 mmu of calcd). ^{13}C NMR signals of **2** were only resolved in $CDCl_3$, especially the C-2a and C-2b resonances ($\Delta\delta$ = 4.1) which were distinguished by long-range ^1H–^{13}C COSY correlations from H-4 to C-2b and H-3 to C-2a. Most other regular and long-range ^1H–^{13}C COSY correlations measured in **2** were similar to correlations measured in **1**. However, there was a conspicuous absence of a normal methyl resonance expected for both H-14 and C-14 in the NMR spectra of **2** at ambient conditions. A broad absorption (δ 46.2) attributed to a CH or CH_3 group was observed in the ^{13}C APT spectrum. Low-temperature NMR experiments with **2** in $CDCl_3$ revealed the presence of two methyls at N-13. At −40 °C, two sharp resonances were observed in ^{13}C (δ 47.3, 45.0) and ^1H (δ 3.92, 3 H; 3.32, 3 H) spectra, and this assignment completed the overall structure of **2**. The coalescence temperature (T_c) was measured in the ^1H NMR at 10 °C, and the free-energy barrier to rotation at 10 °C was calculated to be 55 kJ/mol (13 kcal/mol).[11] The barrier to rotation was due to the steric interactions between the carbonyl oxygen and methyls. Mechanics calculations (MM2 force field) for **2** predicted the 14–13–12–11a torsion angle was −60° (128° for the alternate methyl) in the global minimum (Figure 2), whereas the 14–13–12–11a torsion angle in **1** was −174° with H-13 hydrogen bonding to the carbonyl oxygen.

Conclusions

The purple color of plakinidine A and B varies according to the pH[12] and is reminiscent of hue fluctuations observed for unique polycyclic aromatic alkaloids from sponges,[13,14] tunicates,[15,16] and an anemone.[17] There are several zoochromic alkaloids that appear to be biogenetically related as they possess the aromatic pyridoacridine (tetracyclic) skeleton C, but their biogenic origin remains



C

a mystery. The tunicate metabolites include the tetracyclic cystodytins[18] and norsegoline[15] with an appendage off the A ring of C, whereas ascididemin,[19] leptoclinidinone,[20] and shermilamine[16] include C with further annulation at the A ring or annulation across the A/B rings as in segolines.[15] The incomplete structure of an anemone pigment, calliactine,[17] incorporates annulation off the A ring of C. Three sponge pentacyclic alkaloids, amphimedine,[13] petrosamine,[14] and dercitin[21] both have the fifth ring appended to the A ring of C. In marked departure to this pattern, the plakinidines have only the A/B/C tricyclic nucleus in common with parent array of C as the D ring is contracted. Moreover, the plakinidines are the first reported structures having the pyrrolo[2,3,4-*kl*]acridine skeleton.[22]

Experimental Section

NMR spectra were recorded on a GN-300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). Multiplicities of ^{13}C NMR peaks were determined from APT data, and two-dimensional COSY NMR experiments were carried out on the GN-300 instrument. Long-range ^1H–^{13}C COSY experiments were carried out by M. O'Neill-Johnson on a Bruker 500 spectrometer (at Bruker Applications lab, San Jose, CA). HREIMS data were obtained at the UC, Berkeley, mass spectrometry lab.

Two-Dimensional NMR Procedures. Standard pulse sequences were used for the ^1H–^1H COSY, ^1H–^{13}C COSY, long-range ^1H–^{13}C COSY experiments.[23]

Computational Methods. Computer modeling was carried out with the MACROMODEL program (version 1.5) on a Vax 11/750 computer with an Evans and Sutherland (PS 330) picture system. Molecular mechanics calculations were performed with the MM2 force field with a distance-dependent dielectric. Structures were energy minimized with the block-diagonal Newton–Raphson algorithm in cartesian coordinate space until the rootmean square energy gradient was less than 0.04 kJ/(mol Å).

Isolation Procedures. The organism was collected by scuba at −10 m off Hideaway Island, Port Vila, Vanuatu. Aqueous methanol extracts of the preserved organism (0.2 kg, wet) yielded a red viscous oil (3.87 g). The crude oil was partitioned between aqueous MeOH and the solvent series of hexanes (B), CCl_4 (α), CH_2Cl_2 (β).[24] The α and β partition fractions were separately column chromatographed (reversed phase and Sephadex LH-20/methanol solvent), and **1** (52 mg, 0.026%

(9) Shamma, M.; Hindenlang, D. M. *Carbon-13 NMR Shift Assignments of Amines and Alkaloids*; Plenum Press: New York, 1979; pp 87–90.

(10) **2** ^1H NMR ($CDCl_3$, δ in ppm, multiplicities, J (Hz), atom number): 8.49 (s, H-2), 8.32 (dd, 8.1, 1.5, H-3), 7.67 (dt, 6.6, 1.2, H-4), 7.61 (dt, 6.6, 1.2, H-5), 8.19 (dd, 8.4, 1.2, H-6), 3.77 (dt, 6.9, 1.8, H_2-9), 2.71 (t, 6.9, H_2-10), 3.64 (brs, H_3-14a and H_3-14b) [at −40 °C: 3.32 (s, H_3-14a), 3.92 (s, H_3-14b)]. ^{13}C NMR ($CDCl_3$, δ in ppm, multiplicity, atom number): 137.7 (d, C-2), 129.4 (s, C-2a), 125.3 (s, C-2b), 124.1 (d, C-3), 128.3 (d, C-4), 126.5 (d, C-5), 130.5 (d, C-6), 144.7 (s, C-6a), 137.5 (s, C-7a), 159.5 (s, C-7b), 39.3 (t, C-9), 37.9 (t, C-10), 188.2 (s, C-11), 106.7 (s, C-11a), 152.6 (s, C-12), 124.9* (s, C-12a), 126.9* (s, C-12b), 46.2 (q, C-14a and C-14b) [at −40 °C: 47.3 (q, C-14a), 45.0 (q, C-14b)]. (* = interchangeable).

(11) The free energy of activation (ΔG_c^*) at the temperature of coalescence (T_c) was calculated with the equation, $\Delta G_c^* = 2.3RT_c(10.32 + \log(T_c/k_c))$ where the rate constant at coalescence, $k_c = \pi\Delta\nu/2^{1/2}$. See Chapter 7 in: Lambert, J. B., Shurvell, H.; Verbit, L.; Cooks, R.; Stout, G. *Organic Structural Analysis*; Macmillan Publishing: New York, 1976.

(12) The color of plakinidine A and B changes from purple in $CDCl_3$ to dark green in acidic media ($CDCl_3$–TFA).

(13) Schmitz, F. J.; Agarwal, S. K.; Gunasekera, S. P.; Schmidt, P. G.; Shoolery, J. N. *J. Am. Chem. Soc.* **1983**, *105*, 4835.

(14) Molinski, T. F.; Fahy, E.; Faulkner, D. J.; Van Duyne, G. D.; Clardy, J. *J. Org. Chem.* **1988**, *53*, 1340.

(15) Rudi, A.; Benayahu, Y.; Goldberg, I.; Kashman, Y. *Tetrahedron Lett.* **1988**, *29*, 3861.

(16) Cooray, N. M.; Scheuer, P. J.; Parkanyi, L.; Clardy, J. *J. Org. Chem.* **1988**, *53*, 4619. Carroll, A. R.; Cooray, N. M.; Poiner, A.; Scheuer, P. J. *J. Org. Chem.* **1989**, *54*, 4231.

(17) Cimino, G.; Crispino, A.; De Rosa, S.; De Stefano, S.; Gavagnin, M.; Sodano, G. *Tetrahedron* **1987**, *43*, 4023.

(18) Kobayashi, J.; Cheng, J.; Wälchli, M. R.; Nakamura, H.; Hirata, Y.; Sasaki, T.; Ohizumi, Y. *J. Org. Chem.* **1988**, *53*, 1800.

(19) Kobayashi, J.; Cheng, J.; Nakamura, H.; Ohizumi, Y.; Hirata, Y.; Sasaki, T.; Ohta, T.; Nozoe, S. *Tetrahedron Lett.* **1988**, *29*, 1177.

(20) Bloor, S. J.; Schmitz, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 6134. Revised structure: de Guzman, F. S.; Schmitz, F. J. *Tetrahedron Lett.* **1989**, *30*, 1069.

(21) Gunawardana, G. P.; Kohmoto, S.; Gunasekera, S. P.; McConnell, O. J.; Koehm, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 4856.

(22) A search of *Chemical Abstracts* failed to give any examples of this ring system.

(23) For reviews see: (a) Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490. (b) Schoolery, J. N. *J. Nat. Prod.* **1984**, *47*, 226.

(24) Kupchan, S. M.; Britton, R. W.; Ziegler, M. F.; Sigel, C. W. *J. Org. Chem.* **1973**, *38*, 178.

wet weight) was isolated as deep purple solid from methanol (mp 248-250 °C),[25] and **2** (24 mg, 0.012% wet weight) was isolated as a purple oil.

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(25) All attempts to crystallize **1** did not yield X-ray quality crystals; however, long, thin branched needles were obtained.

Principal Values of Carbon-13 NMR Chemical Shift Tensors for a Collection of Substituted Benzenes

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Contribution from the Chemistry Division, DSIR, Private Bag, Petone, New Zealand.
Received December 23, 1988

Abstract: Principal values of 63 NMR chemical shift tensors were determined for atomic carbon atoms in 12 di-, tri-, and tetrasubstituted benzenes. The values were calculated from CP/MAS carbon-13 NMR spectra with the Herzfeld-Berger method. An empirical chemical shift additivity relationship was established for substitution by hydroxyl, methoxyl, aldehyde, carboxylic acid, and substituted alkyl functional groups. This relationship was successful in predicting principal values, usually within ±5 ppm.

Knowledge of spinning side-band (SSB) intensity patterns can be useful in any attempt at quanitative CP/MAS NMR, particularly if a high-field or medium-field magnet is involved. This is well illustrated by calculations for an aromatic CH group, based on typical chemical shift tensor (CST) data reviewed by Veeman[1] and graphs provided by Herzfeld and Berger.[2] For carbon-13 NMR at 50 MHz, it would be necessary to spin the sample at 12 kHz to confine 95% of the signal in the center band or at 20 kHz to confine 98% in the center band. Until these goals can be achieved in routine work, it would seem more reasonable to run spectra at more readily attainable spinning speeds and use correction factors to allow for signal strength lost in the side bands. This approach has been used, for example, in CP/MAS NMR experiments for quantitative determination of lignin in wood.[3]

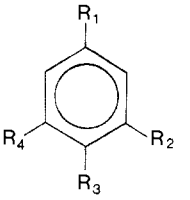
Such applications of the Herzfeld-Berger SSB theory[2] depend on the availability of an adequate database for CST principal values. Recent reviews by Veeman[1] and Duncan[4] tabulate data for aromatic carbon in benzene and derivatives, with only a few examples of oxygen-substituted rings. We have now expanded the available data by determining CST principal values for 12 more substituted benzenes, all substituted by oxygen at 1 or more ring sites. We set out to generate a chemical shift additivity relationship so that we could predict CST principal values for generalized substitution patterns such as may be found in lignin or low rank coals.

A paper by Carter et al.,[5] published since this work was completed, has described similar substitutional effects for a series of three methoxyl benzenes. In this case, chemical shift tensors were determined by single-crystal studies.

Substituent chemical shift effects are most easily obtained from spectra of the monosubstituted benzene. This approach was not used in our solid-state NMR study because most of the substances are liquids at normal probe operating temperatures. We chose instead to use di-, tri-, and tetrasubstituted benzenes, followed by a regression analysis of the observed chemical shifts. All of the compounds in the collection contained at least one methoxyl group. The rotational motion of methoxyl groups provided an efficient proton spin-lattice relaxation mechanism, ensuring that reasonably short recovery delays could be used.

Scheme I

Compound	R_1	R_2	R_3	R_4
1	CO_2H	H	OCH_3	H
2	CO_2H	OCH_3	OH	H
3	CO_2H	OCH_3	OCH_3	H
4	CO_2H	OCH_3	OH	OCH_3
5	CHO	OCH_3	OH	H
6	CHO	OCH_3	OCH_3	H
7	CHO	OCH_3	OH	OCH_3
8	H	OCH_3	OH	OCH_3
9	H	OCH_3	OCH_3	OCH_3
10	CH_2OH	OCH_3	OH	H
11	$CH(CH_3)_2$	H	OH	H
12	$(CH_2)_3OH$	OCH_3	OH	H



Several methods have been used to obtain CST principal values from ^{13}C NMR spectra of solids; these have been reviewed by Veeman.[1] We avoided the use of single crystals because of the difficulty involved in producing crystals of adequate size and because of the number of spectra required for a full description of the angular dependence of resonance frequencies. We also avoided simulation of spectra of static powders, because of the number of overlapping patterns in the spectra of our selected compounds and the consequent chances of errors. Even for a relatively simple aromatic compound such as xylene, the CST principal values measured from powder spectra[6] differed with a

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