and not the hydrogen-bonded endo-2'-hydroxyaverufin (2b) as previously assumed.

If a nidurufin-type intermediate is indeed involved in the averufin to versicolorin A transformation, it seems likely that this intermediate is the exo-alcohol nidurufin (2a) and not the unknown C-2' endo isomer epinidurufin (2b), since only 2a has the favorable stereochemistry for an AR,3-promoted rearrangement.

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Registry No. 2a, 28458-23-3; 5, 518-83-2; 6, 92762-95-3; 6-oil, 92762-96-4; 6 (chloro derivative), 92762-97-5; 7, 92762-98-6; 8, 92762-99-7; 9, 92763-00-3; 9a, 92763-01-4; 10, 92763-02-5; 11, 92842-94-9; 5 (methoxymethyl ether), 64517-18-6; 5 (allyl ether), 92763-03-6.

Spin Multiplet Enhancement in Two-Dimensional Correlated NMR Spectroscopy

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Two-dimensional (2D) homonuclear correlated spectroscopy is probably the most widely used 2D NMR experiment to date. It has proven to be a convenient and powerful method for tracing the pattern of homonuclear couplings in molecules with a molecular weight of up to 10000 daltons. However, it appears in practice that the intensity of a cross multiplet, indicating spin coupling involved. Sometimes protons that have a large molecular weight of up to 10000 daltons. However, it appears in practice that the intensity of a cross multiplet, indicating spin coupling involved. Sometimes protons that have a large scalar interaction show vanishing intensity for the cross multiplet. We propose a method for enhancing selectively the intensity of nuclear coupling involved. Sometimes protons that have a large molecular weight of up to 10000 daltons. However, it appears in practice that the intensity of a cross multiplet, indicating spin coupling involved.

Figure 1. Cross sections parallel to the F1 axis through the 2D COSY spectra of a sample of amphotericin B, recorded at 500 MHz. The cross sections are taken at the F1 frequency of proton H1. (a) Cross section if no digital filtering is used, (b) cross section if a single sine bell is used in both dimensions, and (c) the cross section obtained if the optimized filter of eq 3 is used in order to emphasize the H1-H2 cross peak.

If the experiment is performed with phase modulation and n-type (coherence-transfer echo) selection, the detected X spin magnetization, originating from A, is then given by

$$s_{AX}(t_1,t_2) = M_{0A}[R_1(t_1)R_2(t_2)\exp(-t_1/\tau_A)\exp(-t_2/\tau_X)] \times \exp(-\delta_H t_1)\exp(\delta_{AX} t_2)$$

(2)

where $M_{0A}$ denotes the longitudinal A spin magnetization just before the first pulse of the COSY experiment, and $\tau_A$ and $\tau_X$ are the transverse relaxation times of A and X. From the terms within the square brackets in eq 2, it is seen that the magnetization transfer from A to X does not only depend on the magnitude of $J_{AX}$ but also on the couplings between A and spins $k$ and between X and spins $n$. Optimal signal to noise for the AX cross multiplet will be obtained for matched filtering, i.e., by multiplying the time domain signal with the function within the square brackets in eq 2. This function is specific for magnetization transferred from A to X and will be nonmatched filtering for other magnetization components. Consequently, diagonal components will be strongly attenuated by such a function, as are other cross peaks that show a different multiplet structure. It is clear from eq 2 that cross peaks between A and X will be hard to observe, if both A and X are coupled to a large number of other spins. However, the use of a filtering function matched for that particular transfer, other all magnetization components are attenuated relative to the magnetization that contributes to the AX cross peak.

In practice, of course, multiplets of protons A and X have usually not been identified in the regular one-dimensional spectrum, and exact values for the spin couplings involved are unknown. However, an approximate guess for those values is sufficient for fruitful use of the "multiplet-selective filter", especially since acquisition times, AT, in the t₁ and t₂ dimensions usually have a duration of only one to several hundred milliseconds.

As an example, Figure 1 compares absolute value mode cross sections taken parallel to the F₁ axis at the F₁ frequency of proton H₁ through three COSY spectra, all obtained from the same set of acquired data, for a sample of amphetamine B in Me₃SO-d₆. Figure 1a shows the cross section obtained if no digital filtering is used. The diagonal peak shows a broad base due to the absolute value mode and the in-phase nature of the unresolved multiplet components. The cross peak with Me₃8 is strong, but the cross peak with proton H₂ has very low intensity. The noise in this trace is partly so-called t₁ noise and arises from instabilities in the spectrometer system which cause some of the signal energy of the intense peaks (H₁ and Me₃8) to be distributed over the entire trace. Figure 1b shows the trace that is obtained if the commonly used sine-bell function is applied in both dimensions. The line shape is improved and the diagonal peak (H₁) is attenuated compared with Figure 1a, but the H₁–Me₃8 cross peak is still a factor of about 60 stronger than the H₁–H₂ cross peak. Figure 1c shows the cross section that is obtained if the multiplet selection procedure, described earlier, is applied in order to emphasize the H₁–H₂ cross peak. The signal-to-noise ratio for the H₁–H₂ cross peak has improved dramatically, mainly because of the matched filtering in both dimensions but also because the intense resonances in this F₁ section, which are the major contributors to t₁ noise, are attenuated. Note that the use of the multiplet-selective filter introduces a broadening of the multiplet structure in both frequency dimensions.

The H₁–H₂ cross peak has been enhanced to within about a factor of 2 relative to the H₁–Me₃8 cross peak. Both H₁ and H₂ are coupled to methyl groups, and this coupling is estimated to be 7 Hz. The H₁–H₂ coupling is unknown but is estimated at 5 Hz. The H₂–H₃ coupling is unknown and is not incorporated in the filtering function. The total filtering function, G(t), used in both dimensions for a duration of the acquisition time, AT, is given by

\[ G(t) = \cos \left( \frac{\pi}{\text{AT}} \right) \sin \left( \frac{5\pi t}{\text{AT}} \right) \sin \left( \frac{\pi t}{\text{AT}} \right) \]

The last factor of this function denotes a sine bell, added to the optimized filter in order to avoid truncation of the time domain data at the end of the FID.

We have shown that the relative intensity and sensitivity of cross peaks in homonuclear correlated spectra can be increased dramatically by use of digital filtering procedures optimized for this purpose. This approach is particularly important for the common case where small impurities are present in the sample, and low contour levels in a regular COSY spectrum show a jumble of corresponding cross peaks. Also, by trying a number of different filtering functions one is able to distinguish between cross peaks due to relatively large couplings and small long-range couplings. The method is also applicable in heteronuclear and homonuclear relayed coherence transfer spectroscopy and in proton double-quantum spectroscopy.

In view of improvements in computer technology and incorporation of array processors in commercial spectrometers, we expect that the extra data processing time, needed for reprocessing the same set of time domain data several times, will not be a major factor in the near future.

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Fluoride Ion Induced Rearrangements of Chloromethyl-Substituted Silanes: Carbanionic Character of Groups Undergoing Migration

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We have discovered that chloromethyl-substituted silanes undergo alkyl- and aryl-group rearrangement induced by fluoride ion solubilized by 18-crown-6. This migration is largely controlled by the ability of the migrating group to bear the negative charge which develops in the transition state.

Considerable recent activity has focused on the degree of anionic character associated with groups cleaved from silicon by nucleophiles, particularly in cases where the pKa values of the groups undergoing cleavage are less than 37. Such reactions are induced both by basic and fluoride ion catalysis, generally from trialkylsilyl-substituted derivatives. A variety of correlations between substituent and acidity constants and rates or relative rates of cleavage has made it clear in such reactions that the cleaved carbon fragment has substantial carbanionic character. Quite recently we have measured the gas-phase acidities of some weakly acidic hydrocarbons by reaction of hydroxide ion with several trialkylsilyl-substituted alkanes. Indeed, we have found a remarkable correlation between the gas-phase acidities of RH (AHoacid) and the product ratio (1/2) resulting from competitive cleavage producing CH₃H and RH in eq 1.

\[ (\text{CH}_3)_2\text{SiR} \xrightarrow{\text{OH}^-} (\text{CH}_3)_2\text{SiO}^- + \text{R-H} \]
\[ \rightarrow (\text{CH}_3)_2\text{SiR}_2\text{O}^- + \text{CH}_3\text{H} \]

We report here on some solution-phase work involving the rearrangement of alkyl and aryl groups. This work is particularly important because it occurs in condensed phase with the migration of groups that are weakly acidic. Thus, it partially bridges a gap between the studies just discussed. We have found that (chloromethyl)trimethylsilane reacts with potassium or cesium fluoride in the presence of 18-crown-6 in aromatic hydrocarbon solvents to give exclusively dimethylfluorosilane (eq 2). Although we have discovered that chloromethyl-substituted silanes undergo alkyl- and aryl-group rearrangement induced by fluoride ion solubilized by 18-crown-6. This migration is largely controlled by the ability of the migrating group to bear the negative charge which develops in the transition state.


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