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^{1}H–{^{125}Te} Indirect Detection in Nuclear Magnetic Resonance Spectra of Organotellurium Compounds

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^{125}Te was measured by inverse proton detection using multiple-quantum ^{1}H–{^{125}Te} correlation spectroscopy. One- and two-dimensional heteronuclear multiple quantum coherence (HMQC) experiments are reported for dimethyl telluride, dimethyl ditelluride, benzyl tellurocyanate, trimethyltelluronium chloride, telluromethionine, tellurophene, 1,4-thiatellurin and di(*n*-butyl) telluride having a range of ^{125}Te–^{1}H coupling constants from 14.6 to 102.5 Hz. The enhancement for indirect *vs.* direct ^{125}Te detection was estimated for trimethyltelluronium chloride. The theoretical enhancement is 50.7 and that estimated experimentally 46.2. Multiple-quantum ^{1}H–{^{123}Te} correlation spectroscopy is also illustrated for one example. © **1997 John Wiley & Sons, Ltd.**

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INTRODUCTION

Detection of insensitive spin $I = \frac{1}{2}$ nuclei can be enhanced by taking advantage of the high magnetogyric ratio and high natural isotopic abundance of the proton using inverse detection. For instance, it has recently been shown that the sensitivity of ^{77}Se NMR spectroscopy can be enhanced appreciably by inverse proton detection using multiple quantum ^{1}H–{^{77}Se} correlation spectroscopy.[1] Most other $I = \frac{1}{2}$ nuclei have also been observed using multiple quantum spectroscopy.[2] However, tellurium is an attractive atom that has not been studied even though there are two NMR-active nuclei, ^{123}Te and ^{125}Te, both with $I = \frac{1}{2}$. The natural isotopic abundances of ^{123}Te and ^{125}Te are 0.90 and 7.14%, respectively. Indeed, enhancement of tellurium by inverse proton detection may be sizable on account of the $N(\gamma_I/\gamma_S)^{3/2}$ theoretical enhancement,[3] where N is the number of sensitive nuclei, γ_I the magnetogyric ratio for the sensitive nuclei and γ_S the magnetogyric ratio for the insensitive nucleus. This paper describes for the first time inverse proton detection of ^{125}Te in organotellurium compounds employing multiple-quantum ^{1}H–{^{125}Te} correlation spectroscopy. Recently, the use of ^{13}C–{^{125}Te} correlation spectroscopy has also been reported.[4] However, despite the sizable enhancement expected for inverse proton detection of ^{125}Te, the fourfold greater sensitivity of this nucleus over ^{77}Se, due primarily to its higher magnetogyric ratio, should result in less enhancement for ^{125}Te than ^{77}Se. In addition, inverse detection of the less abundant ^{123}Te nucleus is reported for one example.

The methodology reported in this paper may prove especially useful for ^{125}Te NMR spectroscopic studies on biomolecules containing tellurium. Incorporation of tellurium as a heavy atom for x-ray diffraction studies and as an NMR reporter nucleus has attracted substantial interest.[5] It has also been reported that fungi incorporate inorganic tellurium into proteins as telluroamino acids.[6,7] The chemical shift range for ^{125}Te is *ca.* 7000 ppm, rendering it exceptionally sensitive to its environment[8] and, thereby, advantageous for probing biomolecular structure.

EXPERIMENTAL

Trimethyltelluronium chloride (**4**) was purchased from Organometallics (East Hampstead, NH, USA) and di(*n*-butyl) telluride (**8**) was from Pfaltz and Bauer (Waterbury, CT, USA). Dimethyl telluride (**1**),[9] dimethyl ditelluride (**2**)[10] and benzyl tellurocyanate (**3**)[11] were synthesized following published procedures. Tellurophene (**6**) was prepared by a modification of the published method.[12] 1,4-Thiatellurin (**7**)[13] was prepared as follows. Tellurium powder (0.635 g, 5 mmol) was added in portions with stirring to a solution of sodium (0.23 g, 10 mmol) in 10 ml of liquid ammonia at −78 °C

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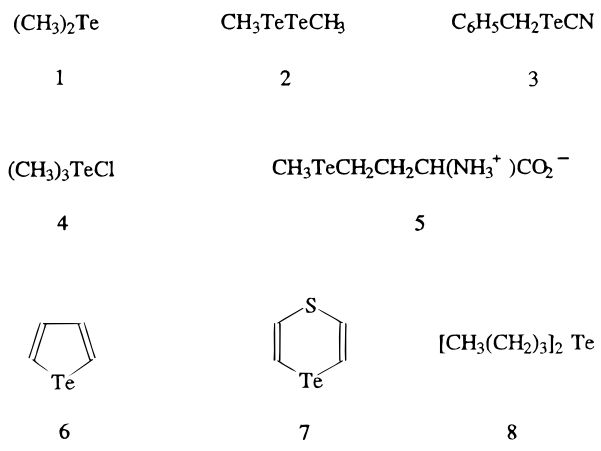
under argon; stirring was continued for 1 h. Methanol (5 ml) was added dropwise followed by bis(trimethylsilylethynyl) sulfide (0.98 g, 4.3 mmol), stirring was continued for 10 min and ammonia was removed at 40 °C. Workup was carried out by cautious addition of ice–water (20 ml) and extraction with 2:1 diethyl ether–pentane (3 × 20 ml). The extracts were washed with brine, dried ($MgSO_4$) and the solvent was removed *in vacuo* to give **7** as a red liquid (0.59 g, yield 65%); ^{1}H NMR, δ 7.39 (d, $J = 7$ Hz, 1), 6.88 (d, $J = 7$ Hz, 1); ^{13}C NMR, δ 106.88, 127.89; EI-MS, *m/z* 214 (M^+, ^{130}Te, 20%), 162 (^{130}Te, 19%), 130 (^{130}Te, 23%), 84 (100%).

NMR samples were prepared at various concentrations using solvents rigorously degassed by the freeze–pump–thaw method and the NMR tubes were sealed under vacuum to exclude molecular oxygen. All spectra were recorded at 302.5 K on a Bruker AMX 500 spectrometer using a broadband inverse probe, in which the inner coil (15 mm in length and 6 mm diameter) was used for the detection of protons and the outer decoupling coil (18 mm in length and 11 mm diameter) was used for the excitation and direct detection of tellurium. The ^{1}H frequency was 500.13 MHz; the ^{125}Te carrier frequency was centered at 157.86 MHz and the ^{123}Te spectral carrier frequency was centered at 130.04 MHz. ^{1}H NMR spectra were referenced to TMS or $CHCl_3$, whereas the ^{125}Te spectra were referenced to external neat dimethyl telluride (31.549 666 *vs.* TMS at 100.000 000 on the absolute Ξ scale of chemical shifts). An ^2H_2O capillary insert was placed inside the 5 mm NMR tube for the deuterium lock signal. In a typical ^{1}H NMR spectrum, a spectral window of 5000 Hz, 16K points, 16–32 transients, a pulse width of 5 μs and no interpulse delay were used. A typical direct tellurium NMR spectrum contained a spectral window of 2000–5000 Hz, collection of 16K data points, 2000 transients, a pulse width of 4 μs and a recycle delay of 1 s.

Pulse sequences were implemented as described by Bax and co-workers [14,15] to optimize either large or smaller couplings of the protons which are scalar coupled to the NMR-active isotopes of tellurium. One-dimensional inverse NMR spectra of the compounds typically used a spectral width of 5000 Hz, 16K data points, 90° pulses (7–10 μs for proton and 16 μs for tellurium), 32 transients and a recycle delay of 1–30 s (depending on T_1). The 90° pulse for ^{125}Te was calibrated using **4**. Two-dimensional inverse spectra had spectral windows of 5000 Hz in the ω_2 dimension and 2000 Hz in the ω_1 dimension; a total of 4K data points were collected for 512 experiments (with the data sets processed by a 1K by 1K matrix). Apodized sine-bell functions in the ω_2 direction and magnitude correction in the ω_1 direction were used. The other parameters were typically the same as in the one-dimensional inverse spectra of each of the respective compounds. For **1**–**5** and **8** the coupling constants were calculated from the ^{125}Te satellites seen in their proton spectra. The coupling constants for **6** and **7** were obtained from the directly detected ^{125}Te NMR spectrum. The T_1 estimation was made using the null seen when a BIRD pulse sequence was applied. The BIRD pulse sequence is the inversion pulse for the spins of protons in molecules containing the NMR-active isotopes of tellurium.



A null for these spins occurs when the longitudinal relaxation time is multiplied by ln 2. The root mean squared experimental signal-to-noise ratio calculations were made measuring the root mean square amplitude for the noise using Bruker xwinnmr software and an ASPECT station (using a convoluted line broadening which was twice the natural linewidth of the signal being observed).[16]

RESULTS AND DISCUSSION

Satisfactory one- and two-dimensional ^{1}H–{^{125}Te} heteronuclear multiple quantum coherence (HMQC) spectra were obtained for compounds **1**–**8**. In addition, the directly detected ^{1}H and ^{125}Te NMR spectra were also measured. The ^{125}Te NMR spectroscopic parameters are listed in Table 1. For compounds **1**, **2**, **5** and **6**, comparison of the ^2J values for the ^{125}Te–^{1}H scalar couplings with the ^2J values for the ^{77}Se–^{1}H scalar couplings of the corresponding selenium compounds[1] reveal that those involving tellurium are *ca.* 2–3 times greater. The larger coupling constants of the tellurium compounds means that the delays used for the evolution due to the ^{1}H–^{125}Te scalar coupling and also the refocusing delays are necessarily shorter than those of the corresponding selenium compounds. Thus, the loss of signal due to spin–lattice and spin–spin relaxation is less, and the observed signal is enhanced for the tellurium compound relative to the corresponding selenium compound. The relatively long spin–lattice relaxation times for the tellurium compounds estimated in Table 1 mean that little magnetization transfer is lost due to longitudinal relaxation. This is because the delays used ($1/2J$) are significantly shorter than the T_1 relaxation times. The relatively narrow lines in the tellurium NMR spectra indicate that the T_2 relaxation times are also relatively long, and thus little magnetization transfer should be lost by this relaxation mechanism.

To illustrate the indirect detection of ^{125}Te, results for **2** are shown in Fig. 1. The proton spectrum of **2** in Fig. 1(a) shows a large peak at 2.65 ppm, which results from the methyl protons that are on molecules which do not contain the NMR-active isotopes of tellurium. On each side of this peak there appear two satellite signals resulting from the protons in molecules containing a ^{125}Te nucleus (at 2.62 and 2.67 ppm). The satellites from ^{123}Te are obscured owing to the low natural

Table 1. ^{125}Te NMR spectroscopic parameters from HMQC experiments for organotellurium compounds 1–8

Compound	Concentration (mM)	Solvent	$\delta(^{125}\text{Te})$ (ppm)[a]	$^2J(^{125}\text{Te},^1\text{H})$ (Hz)	$^3J(^{125}\text{Te},^1\text{H})$ (Hz)	T_1 (s)[b]
1	Neat	None	0.0[c]	20.9	—	8.3
2	351	C^2HCl_3	44.2	23.8	Not observed	6.1
3	123	C^2HCl_3	1930.3	29.3	—	4.3
4	1923	^2H_2O	416.8	23.6	—	5.8
5	58	^2H_2O	114.3	19.2[d]		4.9
6	1336	C^2HCl_3	775.1	102.5	20.5	—
7	227	C^2HCl_3	476.4	92.4	14.6	28.8
8	828	C^2HCl_3	234.3	21.6		0.3

[a] $\delta(^{125}\text{Te}$, ppm) relative to neat dimethyl telluride (**1**).
[b] Estimated from the null point using a BIRD pulse sequence.
[c] Reference standard.
[d] Coupling constant for H-5.

isotopic abundance of that nucleus and the natural linewidth of the proton spectrum. For dimethyl ditelluride one linewidth at half-height is 12.2 Hz and for the other compounds it varies between 3 and 90 Hz. Figure 1(b) shows the directly detected ^{125}Te NMR spectrum of the same compound, in which the tellurium signal is split into a quartet by the three methyl protons (two-bond scalar coupling). The three-bond scalar coupling resulting from the protons on the other methyl group are not seen because they are obscured by the natural linewidth of the tellurium signal. For dimethyl ditelluride the linewidth at half-height is 12.2 Hz and for the other compounds it varies between 3 and 90 Hz. Figure 1(c) shows a one-dimensional ^{1}H–$\{^{125}\text{Te}\}$ NMR indirect spectrum of the same compound; here, the satellites due to those protons spin coupled to ^{125}Te resulting in a doublet are detected. The large center peak due to those protons in molecules not containing ^{125}Te has been suppressed by first nulling the center signal using the BIRD pulse sequence and then averaging away any residual signal from the center peak by alternating the phase of the receiver. Finally, Fig. 1(d) shows a two-dimensional ^{1}H–$\{^{125}\text{Te}\}$ NMR indirect spectrum of **2**, where the horizontal of ω_2 dimension represents the ^{1}H projection and the vertical or ω_1 dimension represents the ^{125}Te projection. A doublet is obtained in the contour plot which shows the correlation between the ^{125}Te nucleus and the scalar-coupled ^{1}H nuclei on the adjacent methyl groups. Similar results involving indirect detection of ^{125}Te were obtained for **1** and **3–8** the NMR parameters are summarized in Table 1.

To demonstrate that both a large coupling constant and a small coupling constant could be observed in the same molecule, **7** was chosen for further study (Fig. 2). The ^{1}H NMR spectrum of **7** is shown in Fig. 2(a) and reveals doublets centered at 7.37 and 6.84 ppm due to the protons that are α and β to the tellurium atom, with coupling constants of $^3J(^1\text{H},^1\text{H}) = 7.3$ Hz. The ^{125}Te satellites can also be seen as doublets centered at 7.28 and 7.47 ppm. The ^{123}Te satellites are not observed owing to the low natural isotopic abundance of this isotope. Figure 2(b) shows the directly detected ^{125}Te NMR spectrum of **7**. The tellurium signal is split into a triplet by the two adjacent α-protons, which are further split into triplets by the two β-protons, resulting in a triplet of triplets. The corresponding indirectly detected 1D ^{1}H–$\{^{125}\text{Te}\}$ NMR spectra of **7** are shown in Fig. 2(c) and (d). The effect of varying the mixing time on the respective intensities of the proton signal in indirect detection is seen by comparison of Fig. 2(c) and (d). In Fig. 2(c), a short delay time of 5.4 ms optimized for the large coupling constant was used to enhance the signal seen from the α-protons, whereas in Fig. 2(d) the longer delay of 34.2 ms optimized for the smaller coupling constant was used to enhance the less sensitive β-protons. Similar results (not shown) were obtained with tellurophene (**6**), which also has a large and a small coupling constant.

The *theoretical* enhancement seen in indirectly detected ^{1}H–$\{^{125}\text{Te}\}$ HMQC NMR spectroscopy *vs.* directly detecting ^{125}Te is dependent on the number of protons which are scalar coupled to ^{125}Te and the ratio of the respective magnetogyric ratios, as given by

$$S/N \propto N_I(\gamma_I/\gamma_S)^{3/2} \tag{1}$$

where N_I is the number of sensitive ^{1}H nuclei which are scalar coupled to the insensitive ^{125}Te nucleus, and γ_I and γ_S are the magnetogyric ratios of the sensitive and insensitive nuclei, respectively. To investigate the enhancement observed in indirect detection of ^{125}Te in organotellurium compounds, **4** was selected (Fig. 3). Figure 3(a) is the direct detection ^{125}Te NMR spectrum of **4** with proton decoupling, and yields $S/N = 24.09$. The corresponding 1D ^{1}H–$(^{125}\text{Te}\}$ indirectly detected HMQC spectrum is shown in Fig. 3(b) and has $S/N = 466.6$. Note that the indirect NMR spectrum is not decoupled to ensure that all of the observed signal is due to those protons which are spin coupled to ^{125}Te. With proton decoupling, the signal would collapse into a singlet. This could lead to an artificially large signal-to-noise ratio (S/N), because some of the resultant signal might come from protons in molecules with other isotopes of tellurium. The *experimental* enhancement is obtained by comparison of the signal to noise of these respective spectra (see the figure captions for the experimental NMR parameters) and is given by

$$\text{enhancement} = \frac{(S/N)_{\text{indir}}(N_s)_{\text{dir}}{}^{1/2}\eta_{\text{dir}}}{(S/N)_{\text{dir}}(N_s)_{\text{indir}}{}^{1/2}\eta_{\text{indir}}} \tag{2}$$

$$\eta_{\text{dir, indir}} = \frac{d_s{}^2}{2D_c{}^2} \tag{3}$$

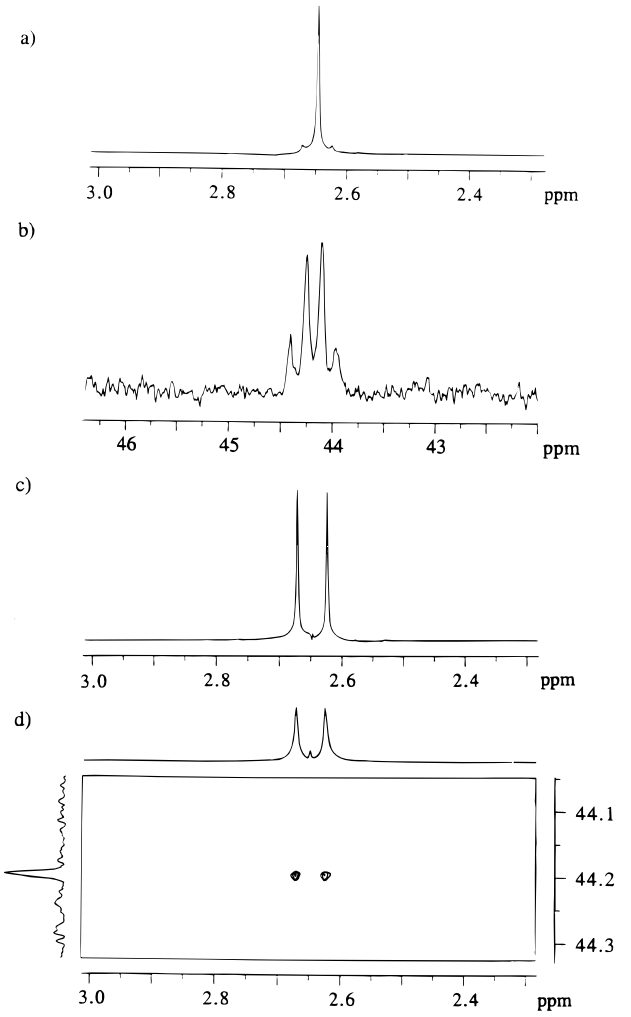


Figure 1. (a) ^{1}H NMR spectrum of dimethyl ditelluride (**2**) at 500.13 MHz. (b) Directly detected ^{125}Te NMR spectrum of **2** at 157.80 MHz. (c) Indirectly detected 1D ^{1}H–{^{125}Te} HMQC spectrum of **2** obtained from eight transients with a mixing time of 21.0 ms, a spectral width of 1500 Hz, a 7 μs 90° ^{125}Te pulse and an interpulse delay of 10 s. (d) Indirectly detected 2D ^{1}H–{^{125}Te} HMQC spectrum of **2** acquired with a mixing time of 21.0 ms, 128 experiments of eight transients each, 4K data points and spectral widths of 1500 Hz in the ω_2 dimension and 250 Hz in the ω_1 dimension. The 2D NMR spectrum was processed with a 1K by 1K data matrix, with exponential multiplication in the ω_1 dimension and sine-bell multiplication in the ω_2 dimension. The ^{1}H projection is shown in the ω_2 dimension and the ^{125}Te projection is shown in the ω_1 dimension.

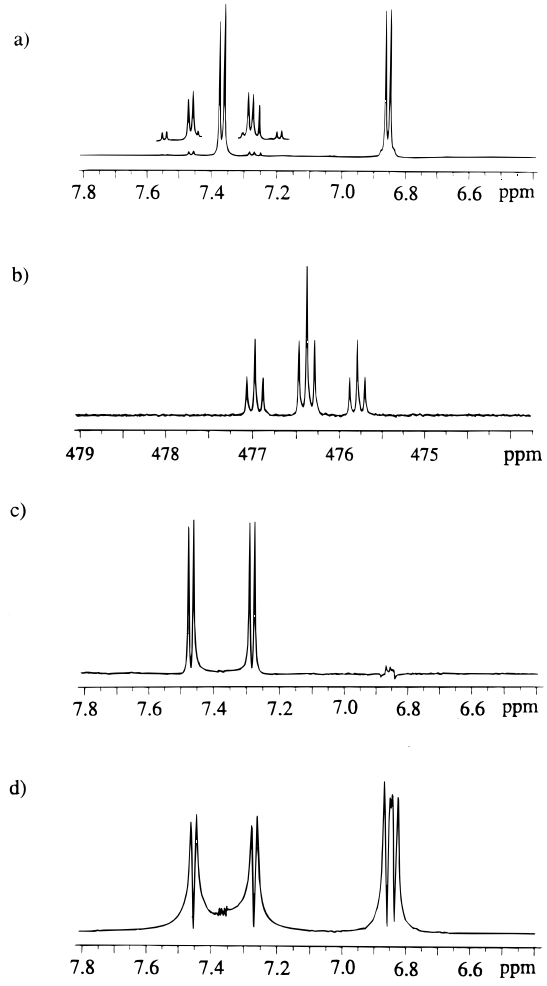


Figure 2. (a) ^{1}H NMR spectrum of 1,4-thiatellurin (**7**) at 500.13 MHz with 10× enlargement inserted. The outer doublet at δ 7.56 and 7.18 ppm is due to ^{13}C satellites and the ^{123}Te satellites are visible inside the inner doublet. (b) Directly detected ^{125}Te NMR spectrum of **7** at 157.86 MHz. (c), (d) Indirectly detected 1D ^{1}H–{^{125}Te} HMQC spectra of **7** using mixing times of 5.4 and 34.2 ms, respectively. In (c) 96 and in (d) 256 transients were acquired; a spectral width of 6000 Hz and 16K data points were used in both cases.

The diameters of the coils were measured and the filling factors were calculated.[17] Here S/N denotes the signal-to-noise ratio of the experimental NMR spectra, N_s the number of scans, η the respective filling factors, d_s the inside diameter of the NMR tube and D_c the coil diameter. The filling factor is included in the equation to correct for the use of an inverse probe. However, it should be noted that the calculated enhancement value is probe specific and that a modified probe was used which was not designed to detect ^{125}Te directly. The Q factors for each of the respective coils were not considered in the calculation. Because the signal-to-noise ratio varies as a function of the line broadening, S/N values were calculated from the NMR spectra by applying a line broadening which doubled the linewidth in the frequency domain.[16] It has been demonstrated mathematically that a line broadening which employs this 'matched filter' gives the maximum signal-to-noise ratio.[18] The experimental enhancement value thus obtained is 46.2, which compares favorably with the theoretical value of 50.7 obtained using Eqn (1).

Finally, the other NMR-active nucleus of tellurium (^{123}Te) was also successfully detected using ^{1}H–{^{123}Te} HMQC NMR spectroscopy. Since ^{123}Te has a much lower isotopic abundance than ^{125}Te, indirect detection of this nucleus is more challenging than in the case of the ^{125}Te nucleus. In addition, the ^{123}Te nucleus suffers from a smaller scalar coupling constant, $^{2}J(^{123}\text{Te},^{1}\text{H}) = 77$ Hz *vs.* $^{2}J(^{125}\text{Te},^{1}\text{H}) = 92$ Hz, which potentially also reduces the efficiency of the magnetization transfer owing to the longer evolution delays required. A representative one-dimensional inverse detected ^{1}H–{^{123}Te} NMR spectrum of **7** is shown in Fig. 4.

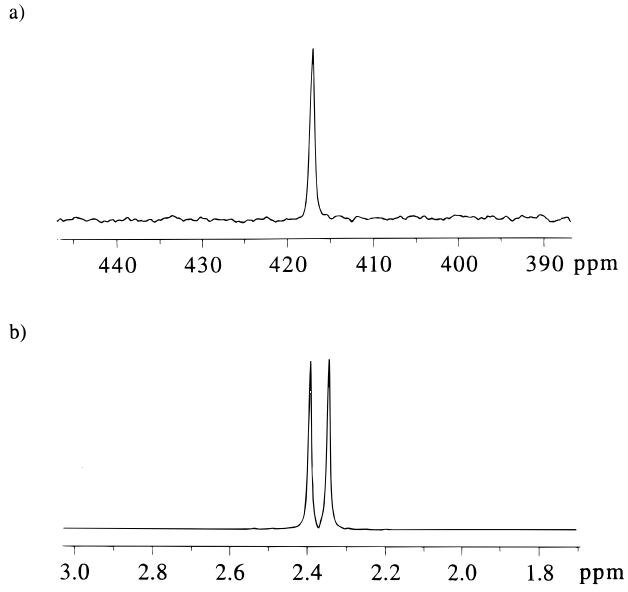


Figure 3. (a) Directly detected ^{125}Te NMR spectrum of a 530 mM solution of trimethyltelluronium chloride (**4**) in $^{2}H_2O$ at 157.86 MHz with proton decoupling. A total of 32 transients were acquired with a spectral width of 6000 Hz, 16K data points, an interpulse delay of 5 s and a line broadening of 60 Hz. Integration of the spectrum gave a resultant signal-to-noise ratio of 24.09. (b) Indirectly detected 1D ^{1}H–{^{125}Te} HMQC spectrum of **4** in $^{2}H_2O$ acquired with a mixing time of 21.2 ms, 64 transients, a spectral width of 6000 Hz, 16K data points, an interpulse delay of 4 s, and a line broadening of 0.2 Hz. The resultant signal-to-noise ratio of the integrated spectrum was 466.6. Comparison of (b) with (a) yielded an enhancement of 46.2 due to indirect detection of ^{125}Te (see text).

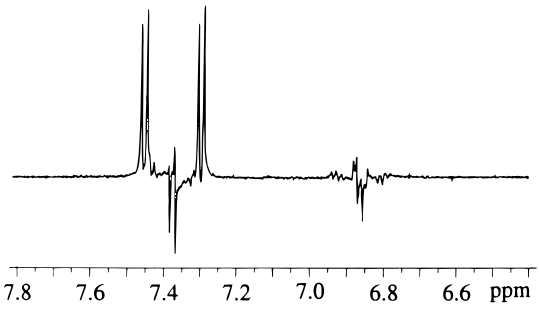


Figure 4. Indirectly detected 1D ^{1}H–{^{123}Te} HMQC spectrum of 1,4-thiatellurin (**7**) at 130.04 MHz. The ^{1}H–{^{123}Te} spectrum was acquired with mixing time of 6.6 μs, employing 64 transients, a spectral width of 2000 Hz, 8K data points, a 16 μs 90° ^{123}Te pulse and an interpulse delay of 30 s.

In conclusion, both ^{1}H–{^{125}Te} and ^{1}H–{^{123}Te} indirect detection NMR experiments were successfully performed. Because of the higher natural isotopic abundance of ^{125}Te relative to ^{123}Te, inverse experiments with ^{125}Te yield higher sensitivity than those with ^{123}Te. Thus indirect detection of ^{125}Te by using the inherent sensitivity and high natural abundance of the proton should prove generally useful in the detection of dilute tellurium samples. Because advances in molecular biology allow the incorporation of unnatural amino acids at any site in a protein, use of ^{125}Te as a 'reporter' nucleus in proteins into which a telluroamino acid has been incorporated may prove to be very important. Its effectiveness is greatly enhanced by the inverse detection of ^{125}Te by the HMQC methods reported in this paper.

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