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Synthesis and nuclear magnetic resonance spectroscopic properties of some acetylenic tellura fatty acid esters

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Abstract

Five positional isomers of acetylenic tellura stearate (**1**–**5**) have been synthesized by three different routes. The number of methylene groups located between the acetylenic system and the tellurium metal varies from 0 to 4. The ^{1}H and ^{13}C NMR spectroscopic properties have been studied. The tellurium atom induces strong deshielding effects on the adjacent methylene protons, which in combination with the deshielding effects of the acetylenic system allows most of the methylene groups between the tellurium and the triple bond to be identified by ^{1}H NMR spectroscopic analysis. The tellurium causes a very strong shielding effect (ca. -27.1 ppm) on the carbon shift of the adjacent α-methylene carbon atom, but weak deshielding effects on the β-(ca. $+2.6$ ppm) and γ-(ca. $+2.3$ ppm) methylene carbon atoms. Carbon shifts of methylene carbon atoms, especially those which are located between the tellurium atom and the triple bond, are found very much upfield (δ_C 0.65–4.81) and in one case in the negative region ($\delta_C - 17.95$) of the ^{13}C NMR spectrum. Most of the signals of the carbon nuclei of these analogue have been identified and from the results of these analyses the number of methylene groups between the acetylenic system and the tellurium atom can be determined. © 1997 Elsevier Science Ireland Ltd.

Keywords: Acetylenic; NMR spectroscopy; Positional isomers; Synthesis; Unsaturated tellura; Stearate analogues

1. Introduction

We have reported the synthesis of a complete series of position isomers of methyl tellura laurate (Lie Ken Jie et al., 1991), long-chain methyl esters containing a tellurophene system (Lie Ken Jie and Chau, 1995a) and the dichloride derivatives of some methyl tellura laurates (Lie Ken Jie and Chau, 1995b), and have studied the nuclear magnetic resonance spectroscopic (NMR) and mass spectrometric properties of this class of fatty acid ester analogues (Lie Ken Jie and Chau, 1995c). Long-chain fatty acids containing a tellurium atom in the alkyl chain are shown to inhibit the process of β-oxidation of fatty acids in the my-

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ocardium. Such long-chain fatty acids have been used to trap radiolabelled fatty acids in the heart tissues for myocardial imaging purposes (Knapp et al., 1979; Srivastava et al., 1987; Goodman and Knapp, 1982). There are only a few reported cases of unsaturated tellura fatty acids in the chemical literature. Knapp et al. have described the synthesis of unsaturated tellura fatty acid analogues containing an iodo-vinylic system, where the double bond is located at the end of the fatty acid chain (Knapp et al., 1984).

In our continuing effort to study the properties of long-chain fatty acids containing a hetero atom in the alkyl chain, we report in this paper the synthesis of five unsaturated tellura stearate ester analogues containing an acetylenic bond and a tellurium atom in defined positions of the alkyl chain (compounds **1**–**5**).

$CH_3(CH_2)_5-Te-(CH_2)_4-C\equiv C-(CH_2)_4COOEt$ (**1**)

$CH_3(CH_2)_5-Te-(CH_2)_3-C\equiv C-(CH_2)_5COOEt$ (**2**)

$CH_3(CH_2)_5-Te-(CH_2)_2-C\equiv C-(CH_2)_6COOEt$ (**3**)

$CH_3(CH_2)_8-C\equiv C-CH_2-Te-(CH_2)_4COOEt$ (**4**)

$CH_3(CH_2)_6-C\equiv C-Te-(CH_2)_7COOMe$ (**5**)

One of the main objectives of this work is to study the effects of the tellurium atom and the acetylenic system on the shifts of the adjacent methylene group by NMR spectroscopy. For this reason the number of methylene groups between the acetylenic bond and the hetero atom (tellurium) in these fatty acid analogues is varied from 0 to 4.

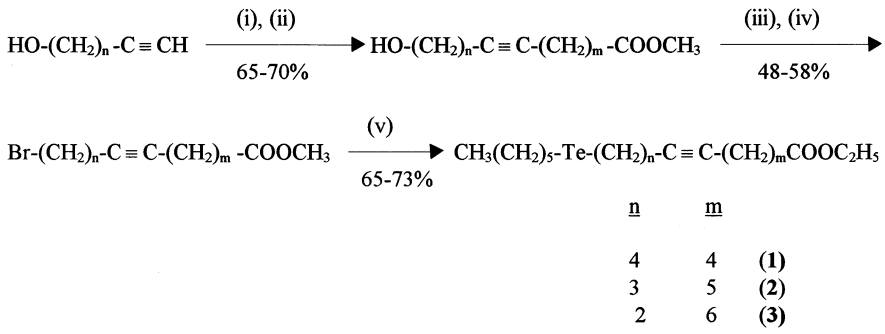
2. Material and methods

Infrared spectra were measured as neat samples on a Shimadzu model IR-470 spectrophotometer (Shimadzu, Kyoto, Japan). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL GSX-270 fourier transformed NMR spectrometer (JEOL, Tokyo, Japan) at an operating frequency of 270 MHz for proton and 67.89 MHz for carbon nuclei from solutions in deuteriochloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal reference standard. Chemical shifts are given in δ_H and δ_C values in ppm downfield from TMS ($\delta_{TMS}=0$). Solvents used in the synthesis were distilled and dried over sodium in benzophenone. 5-Hexyn-1-ol, 4-pentyn-1-ol, 3-butyn-1-ol, 5-bromopentanoic acid, 6-bromohexanoic acid and 8-bromooctanoic acid were purchased from Aldrich (St. Louis, MO).

*2.1. General method for the preparation of di-, tri- and tetra-methylene interrupted acetylenic tellura fatty acid esters (**1**–**3**) as exemplified by the synthesis of ethyl 12-tellura-6-octadecynoate (**1**) (Scheme 1)*

5-Hexyn-1-ol (13.2 g, 0.135 mol) was added to a suspension of lithamide [prepared from lithium (4.0 g, 0.57 mol), Fe(III) nitrate (0.5 g) and liquid ammonia (1 l)] in liquid ammonia and the reaction mixture was stirred for 1 h. 5-Bromopentanoic acid (23 g, 0.13 mol) in tetrahydrofuran (THF, 50 cm^3) was slowly added and the resulting mixture was stirred for 12 h. The ammonia was allowed to evaporate and dilute HCl (2 M, 200 cm^3) was added and the reaction mixture was extracted with diethyl ether (3×100 cm^3). The ethereal extract was washed with water (2×30 cm^3) and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was refluxed with borontrifluoride-methanol complex (15%, w/w, 10 cm^3) and absolute methanol (100 cm^3) for 20 min. Water (150 cm^3) was added and the reaction mixture was extracted with petroleum ether (b.p. 60–80°C, 3×50 cm^3). The petroleum extract was washed with water (30 cm^3) and dried. The filtrate was evaporated under reduced pressure and the residue was chromatographed (100 g silica) using a mixture of petroleum ether: diethyl ether (4:1, vol/vol) as eluent to give methyl 11-hydroxy-6-undecynoate (17.7 g, 65%) as an oil. Infrared analysis (cm^{-1}) 3395, 1733, 1434, 1175, 1063; ^1H NMR (δ_H) 1.4–1.8 (m, 8H, CH_2), 2.0–2.4 (m, 6H, 2-*H*, 5-*H* and 8-*H*), 3.59 (s, 3H,

Synthesis of di-, tri- and tetra-methylene interrupted acetylenic tellura fatty esters (**1-3**)



Reagents: (i) $LiNH_2$, ammonia, $Br(CH_2)_mCOOH$; (ii) BF_3/MeOH; (iii) methanesulfonyl chloride, pyridine, dichloromethane; (iv) LiBr, acetone; (v) $[CH_3(CH_2)_5Te]_2$, $NaBH_4$, ethanol.

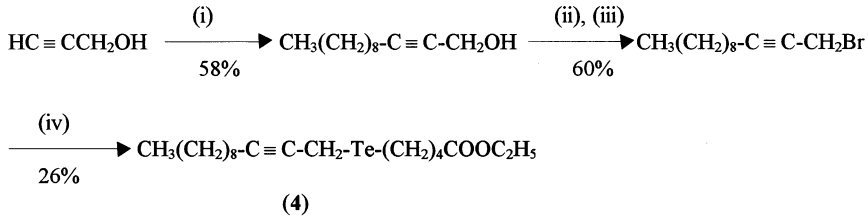
Scheme 1.

$COOCH_3$), 3.72 (t, $J = 6.5$ Hz, CH_2-OH); ^{13}C NMR (δ_C) 18.47 (C-5), 18.58 (C-8), 24.16 (C-3), 25.41 (C-9), 28.52, 29.01, 31.99 (C-10), 33.64 (C-2), 51.49 ($COOCH_3$), 64.43 (C-11), 79.63 (C-6), 80.42 (C-7) and 174.11 (C-1).

A mixture of methyl 11-hydroxy-6-undecynoate (2.0 g, 9.4 mmol), methanesulfonyl chloride (2 g, 17.5 mmol), pyridine (5 cm^3) and dichloromethane (50 cm^3) was stirred at 0–5°C for 30 min and for a further 1 h at room temperature. The reaction mixture was successively washed with dilute HCl (2M, 30 cm^3), water (30 cm^3) and dried (Na_2SO_4). The filtrate was evaporated and a solution of lithium bromide (1.5 g, 17 mmol) in acetone (25 cm^3) was added to the residue. The mixture was refluxed for 1 h and ice water (20 cm^3) was added to the cooled reaction mixture. The reaction mixture was extracted with petroleum ether (3×30 cm^3). The petroleum extract was washed with water (30 cm^3) and dried (Na_2SO_4). The filtrate was evaporated under reduced pressure and the residue was chromatographed on silica gel (40 g) using a mixture of petroleum ether: diethyl ether (9:1, vol/vol) as eluent to give methyl 11-bromo-6-undecynoate (1.5 g, 54%) as an oil. Infrared analysis (cm^{-1}) 1734, 1432,1332, 1251, 1174; ^1H NMR (δ_H) 1.6–1.8 (m, 8H, CH_2), 2.0–2.4 (m, 6H, 2-*H*, 5-*H*, 8-*H*), 3.44 (t, $J = 6.4$ Hz, CH_2Br) and 3.62 (s, 3H, $COOCH_3$); ^{13}C NMR (δ_C) 17.99 (C-8), 18.47 (C-5), 24.92 (C-3), 27.52, 28.52, 31.85, 33.21 (C-11), 33.64 (C-2), 52.44 ($COOCH_3$), 79.69 (C-6), 80.28 (C-7) and 173.87 (C-1); microanalysis: calc. for $C_{12}H_{19}O_2Br$, C, 52.37, H, 6.96, found C, 52.59 and H, 7.04.

A mixture of tellurium (powder, 1.0 g), sodium borohydride (0.2 g, 5.4 mmol) and dimethylformamide (DMF, 20 cm^3) was stirred at 80°C for 2 h under nitrogen. 1-Bromohexane (1.3 g, 7.6 mmol) in DMF (5 cm^3) was added and the reaction mixture was stirred for 2 h. Water (80 cm^3) was added and the reaction mixture was extracted with petroleum ether (3×30 cm^3). The petroleum extract was evaporated under reduced pressure to give crude dihexylditelluride (1.55 g). Sodium borohydride (0.15 g, 4 mmol) and absolute ethanol (30 cm^3) were added to the crude dihexylditelluride and the mixture was stirred for 30 min at room temperature. The temperature of the reaction mixture was raised to 80°C and methyl 11-bromo-6-undecynoate (0.5 g, 1.8 mmol) in ethanol (5 cm^3) was added and the reaction mixture was stirred for 3 h. Water (50 cm^3) was then added to the cooled reaction mixture, which was extracted with diethyl ether (3×30 cm^3). The ethereal extract was washed with water and dried (Na_2SO_4). The filtrate was evaporated and the residue was chromatographed on a silica gel (50

Synthesis of methylene-interrupted tellura-acetylenic fatty ester (**4**).



Reagents: (i) $LiNH_2$, ammonia, Fe(III) nitrate, 1-bromononane; (ii) methanesulfonyl chloride, pyridine, CH_2Cl_2; (iii) LiBr, acetone; (iv) $[Te\text{-}(CH_2)_4COOCH_3]_2$, $NaBH_4$, ethanol

Scheme 2.

g) column using a mixture of petroleum ether: diethyl ether (9:1, vol/vol) as eluent to give ethyl 12-tellura-6-octadecynoate (**1**, 0.55 g, 72%) as an oil.

*2.2. Synthesis of the methylene-interrupted acetylenic tellura fatty acid ester (viz. ethyl 6-tellura-8-octadecynoate, **4**)(Scheme 2)*

1-Bromo-2-decyne was prepared in 58% yield from 2-dodecyn-1-ol (obtained from the dilithio derivative of propargyl alcohol and 1-bromononane) by similar method as described for 11-bromo-6-undecynoate.

A mixture of tellurium (powder, 1.0 g), sodium borohydride (0.2 g, 5.4 mmol) and DMF (20 cm^3) was stirred at 80°C for 2 h under nitrogen. Methyl 5-bromopentanoate (1.5 g, 1.6 mmol) in DMF (5 cm^3) was added to the cooled reaction and the reaction mixture was stirred for 12 h at room temperature. Water (30 cm^3) was added and the reaction mixture was extracted with diethyl ether (3×30 cm^3). The ethereal extract was washed with water (20 cm^3) and dried (Na_2SO_4). The solvent was evaporated and the residue consisting of $CH_3OOC(CH_2)_4$-Te-Te-$(CH_2)_4COOCH_3$ appeared as a red oily residue (1.8 g). A solution of sodium borohydride (0.15 g, 4 mmol) in ethanol (25 cm^3) was added to the red oily residue and the reaction mixture was stirred for 30 min. The reaction mixture was heated to 80°C and 1-bromo-2-dodecyne (1.0 g, 4.1 mmol) in ethanol (5 cm^3) was added and the mixture was stirred for 3 h. Water (100 cm^3) was added to the cooled reaction and the mixture was extracted with diethyl ether (3×50 cm^3). The ethereal extract was washed with water (20 cm^3) and dried (Na_2SO_4). The filtrate was evaporated and the residue was chromatographed on a silica gel (20 g) column using a mixture of petroleum ether: diethyl ether (9:1, vol/vol) as eluent to give ethyl 6-tellura-8-octadecynoate (**4**, 0.43 g, 26%) as an oil.

*2.3. Synthesis of non-methylene interrupted acetylenic tellura fatty acid ester (viz. methyl 9-tellura-10-octadecynoate (**5**) (Scheme 3)*

n-Butyl lithium (2.5 cm^3, 15% solution in *n*-hexane) was added to a solution of 1-nonyne (0.45 g, 3.6 mmol) in THF (15 cm^3) at 0°C under nitrogen and stirred for 15 min. Tellurium (powder, 0.3 g) was added and the reaction mixture was refluxed for 5 h. The reaction mixture was cooled to 0°C and a solution of methyl 8-bromooctanoate (0.45 g, 1.9 mmol) in THF (5 cm^3) was added. The reaction mixture was maintained at 0°C for 12 h. Water (40 cm^3) was then added and the reaction mixture was extracted with diethyl ether (3×30 cm^3). The ethereal extract was washed with water (20 cm^3) and dried (Na_2SO_4). The filtrate was evaporated and silica gel (20 g) chromatographic purification using a mixture of petroleum ether: diethyl ether (9:1, vol/vol) eluent to give methyl 9-tellura-10-octadecynoate (**5**, 0.25 g, 31%).

Synthesis of non-methylene interrupted acetylenic tellura fatty ester (**5**)

$$CH_3(CH_2)_6\text{-}C\equiv CH \xrightarrow[31\%]{\text{(i),(ii)}} CH_3(CH_2)_6\text{-}C\equiv C\text{-}Te\text{-}(CH_2)_7COOCH_3$$

(5)

Reagents: (i) *n*-butyl lithium, THF, Te powder, reflux; (ii) methyl 8-bromooctanoate, THF.

Scheme 3.

3. Results and discussion

3.1. Synthesis of acetylenic tellura fatty acid esters (1–5)

To incorporate 2–4 methylene groups between the tellurium atom and the acetylenic bond for the proposed acetylenic tellura analogues (**1**–**3**), ω-alkyn-1-ols [$HO(CH_2)_nC{\equiv}CH$, $n = 2,3$ or 4] were considered as the most suitable starting blocks (Scheme 1). Chain extension from the acetylenic end with esters of ω-bromoalkanoic acids provided hydroxy-acetylenic acid intermediates (average yield of 65%). The hydroxy group of these intermediates was readily transformed to the bromide via the mesyloxy function using lithium bromide in acetone with an average yield of 53%. Subsequent reaction of the bromo-acetylenic ester intermediates with the corresponding sodium alkyltellurolate (RTeNa) (from dialkylditelluride with sodium borohydride in ethanol) furnished the requisite ethyl acetylenic tellura fatty acid esters (**1**–**3**) (average 70% yield) (Scheme 1). Ethyl esters were obtained as the final products, due to the presence of a slight excess of sodium borohydride in ethanol employed during the final step of the synthesis sequence which caused the methyl ester group to be inter-esterified to the ethyl ester. In compounds **1**–**3** the tellurium atom occupied a position between the acetylenic bond and the terminal methyl group.

In the synthesis of the mono-methylene and the non-methylene interrupted acetylenic tellura fatty acid esters (compounds **4** and **5**, repectively), the tellurium atom occupied a position between the acetylenic bond and the carboxylic ester group. This change in the synthesis strategy demonstrated the versatile synthetic approach adopted in this work, which allowed the tellurium atom to be located at any pre-determined position of the alkyl chain of the fatty acid ester molecule. Compound **4** was prepared starting from commercially available propargyl alcohol, which was condensed via its dilithio derivative with 1-bromononane to give 2-dodecyn-1-ol. The latter was transformed to 1-bromo-2-decyne via the mesyloxy intermediate. 1-Bromo-2-decyne was subsequently coupled with the sodium tellurolate derived from methyl 5-bromopentanoate to give ethyl 6-tellura-8-octadecynoate (**4**) in 26% yield (Scheme 2). The yield of this last reaction was persistently low, as the formation of the ditelluride of the bromo-ester (methyl bromopentanoate) appeared to be a low-yielding reaction.

To prepare the non-methylene interrupted acetylenic tellura fatty acid ester (**5**), 1-lithium nonyne was reacted with tellurium metal in tetrahydrofuran (Dabdoub and Comasseto, 1988). The tellurium intermediate was subsequently reacted with methyl 8-bromooctanoate to yield the requisite product (methyl 9-tellura-10-octadecynoate, (**5**) in 31% yield. As no sodium borohydride and ethanol were involved in this reaction, the product obtained was the methyl ester derivative (Scheme 3).

3.2. ^1H NMR properties of acetylenic tellura fatty acid esters (1–5)

The shift effects of an acetylenic system on the chemical shifts of the adjacent methylene protons are reported, the results of which showed that the acetylenic bond imparts a slight deshielding effect (given as a positive on the adjacent α-, β-

Table 1
Results of the ^{1}H-NMR analysis of acetylenic tellura fatty acid esters (**1**–**5**)

Nucleus (protons)	Compound (δ_H)				
	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
2-H	2.34(t) ($J = 7.2$)	2.32(t) ($J = 7.2$)	2.30(t) ($J = 7.2$)	2.34(t) ($J = 7.2$)	2.31(t) ($J = 7.2$)
3-H	a	a	a	a	a
4-H	a	a	a	a	a
5-H	2.10(m)	a	b	2.87(t) ($J = 6.8$)	b
6-H	—	2.10(m)	a	Te	a
7-H	—	—	2.10(m)	3.27(s)	a
8-H	2.10(m)	—	—	—	2.77(t) ($J = 6.8$)
9-H	a	2.10(m)	—	—	Te
10-H	a	2.10(m)	2.70(s)	2.10(m)	—
11-H	2.64 (t, $J = 6.8$)	2.71(t) ($J = 6.8$)	2.70(s)	2.10(m)	—
12-H	Te	Te	Te	a	2.48(t) ($J = 7.0$)
13-H	2.64 (t, $J = 6.8$)	2.63(t) ($J = 6.8$)	2.61(t) ($J = 6.8$)	b	a
14-H	a	a	a	b	a
15-H	b*	b	b	b	b
16-H	b	b	b	b	b
17-H	b	b	b	b	b
18-H	0.89(t) ($J = 7.0$)	0.89(t) ($J = 7.0$)	0.90(t) ($J = 7.0$)	0.90(t) ($J = 7.0$)	0.89(t) ($J = 7.0$)
Ethyl ester	1.25(t) 4.12(q)	1.25(t) 4.12(q)	1.25(t) 4.12(q)	1.25(t) 4.12(q)	—
Methyl ester	—	—	—	—	3.67(s)

a = 1.50–1.80; b = 1.20–1.40.
$CH_3(CH_2)_5$-Te-$(CH_2)_4$-C≡C-$(CH_2)_4$COOEt (**1**)
$CH_3(CH_2)_5$-Te-$(CH_2)_3$-C≡C-$(CH_2)_5$COOEt (**2**)
$CH_3(CH_2)_5$-Te-$(CH_2)_2$-C≡C-$(CH_2)_6$COOEt (**3**)
$CH_3(CH_2)_8$-C≡C-CH_2-Te-$(CH_2)_4$COOEt (**4**)
$CH_3(CH_2)_6$-C≡C-Te-$(CH_2)_7$COOMe (**5**)

and γ-methylene protons of $+0.82$, $+0.16$ and $+0.13$ ppm, respectively (Frost and Gunstone, 1975). Such values (shift parameters) when added to a basic value (1.255) for the shift of unperturbed methylene protons would give a fairly accurate estimation of the proton shifts of a particular proton(s) under those effects. From our study of the ^{1}H NMR properties of methyl telluralaurates, the tellurium nucleus shows strong deshielding effects (positive values for the shift parameters) on the shifts of the adjacent methylene protons: $+1.395$, $+0.495$ and $+0.145$ ppm for the α-, β- and γ-methylene protons, respectively (Lie Ken Jie et al., 1991). By taking the combined shift effect of the acetylenic system and that of the tellurium nucleus into consideration, the assignments of the various shifts of the adjacent methylene protons in the acetylenic tellura fatty acid esters could be readily accomplished. The results of the ^{1}H NMR chemical shifts of compounds **1**–**5** are summarized in Table 1.

The presence of four methylene groups between the acetylenic bond and the tellurium atom in the alkyl chain of compound **1** prevented the acetylenic system to exercising any additional shift effect on the methylene group adjacent to the tellurium atom and vice versa. As a result the shifts of the protons of the methylene groups (5-*H*, 8-*H*) adjacent to the acetylenic bond appeared at the anticipated region of the spectrum δ_H 2.10 (multiplet), while the shifts of the methylene protons adjacent to the tellurium atom (11-*H*, 13-*H*) appeared as a triplet at δ_H 2.64 (t, $J = 6.8$ Hz). In the trimethylene-interrupted isomer (compound **2**) the shifts of the methylene protons adjacent the tellurium atom were resolved into two overlapping triplets at δ_H 2.63

(13-*H*) and 2.71 (11-*H*) due to the γ-effect of the acetylenic system on the 11-*H* protons. However, the γ-effect from the tellurium on the methylene adjacent to the acetylenic bond was not obvious, as the signals for these protons were not further differentiated as they appeared unresolved in the region δ_H 2.10 (m) of the spectrum.

For compound **3** the shifts of the two methylene groups between the acetylenic bond and the tellurium atom were clearly being affected by the these groups. The shifts of these protons appeared as a singlet at δ_H 2.70 (4H, 10-*H*, 11-*H*), which reflected the chemical equivalence of these protons. The shifts of the 13-*H* (methylene protons adjacent to the tellurium atom) and that of 7-*H* were found at δ_H 2.61 (triplet) and 2.10 (multiplet), respectively. Compound **4** could be readily differentiated from the other isomers from the singlet at δ_H 3.27, which was due to the shift of the protons of the methylene group between the acetylenic bond and the tellurium atom. A significant downfield effect from the acetylenic system on the other methylene group adjacent to the tellurium atom was also observed as the shifts of these protons (5-*H*) appeared at δ_H 2.87 (t). However, the tellurium atom appeared not to cause any significant deshielding effect on the protons of the remaining methylene group adjacent (10-*H*, δ_H 2.10) to the acetylenic bond.

In the analysis of compound **5**, where the acetylenic group and the tellurium atom are bonded together, the interaction of the metal and the acetylenic system caused the methylene protons adjacent to the acetylenic bond and that adjacent to the tellurium atom to be clearly resolved. The shifts of the 8-*H* and 12-*H* protons appeared as distinct triplets at δ_H 2.77 and 2.48, respectively. From this study of the ^{1}H NMR properties of acetylenic tellura fatty acid esters, it was possible to characterise the non-methylene, mono- and di-methylene from the tri- and tetramethylene interrupted isomers from their ^{1}H NMR spectral properties.

3.3. ^{13}C NMR properties of acetylenic tellura fatty acid esters (1–5)

In the study of ^{13}C NMR properties of acetylenic fatty esters, the shielding shift effects (given as negative values) of an acetylenic system on the carbon shifts of methylene groups have been determined as: -11.00, -0.65 and -0.80 for the adjacent α-, β- and γ-methylene carbon nuclei, respectively (Bus et al., 1976). We have also determined the effects of a tellurium atom on the shifts of the adjacent methylene carbon atoms as: -27.10 (shielding), $+2.62$ (deshielding) and $+2.34$ (deshielding) for the α-, β- and γ-methylene carbon nuclei, respectively (Lie Ken Jie et al., 1991). The shift value of an unperturbed methylene carbon atom was assumed at 29.75 ppm. Taking the combined effects of the acetylenic system and the tellurium nucleus into consideration, the assignments of the shifts of the various methylene carbon atoms were accomplished. The results of the ^{13}C NMR chemical shifts of compound **1**–**5** are summarized in Table 2.

In compounds **1**–**4** the presence of less perturbed triple bond was readily confirmed by the signals in the region of δ_C 79–82 for the shifts of the acetylenic carbon atoms, but not in the case of compound **5** where the tellurium atom is bonded to the triple bond. The strong shielding effect of the acetylenic system on the adjacent methylene carbon atoms caused these carbon atoms to appear at δ_C 18–22, unless the nuclei were being further affected by the tellurium atom. The very strong shielding α-effects exhibited by the tellurium atom caused many of the shifts of the adjacent methylene carbons to appear close to the zero value of the spectrum ($\delta_C = 0$, tetramethylsilane) and in one instance (compound **4**) the shift of one of the adjacent methylene carbons appeared in the negative range of the ^{13}C NMR spectrum.

In compound **1** (a tetramethylene interrupted acetylenic tellura isomer) the combined effects of the tellurium and acetylenic system made it difficult to differentiate the shifts of the β-methylene carbon atoms (C-9 and C-10) as the shifts appeared at δ_C 31.35 and 31.45 for these two nuclei. However, in this narrow region of the spectrum, the signals at δ_C 31.27 and 31.75 could be assigned to the C-15 and C-16 carbon nuclei,

Table 2
Results of the ^{13}C NMR analysis of acetylenic tellura fatty acid esters (**1**–**5**)

Nucleus (carbon)	Compound (δ_C)				
	(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
C-1	173.87	173.30	173.63	173.60	174.06
C-2	33.67	34.02	34.35	33.72	34.08
C-3	24.20	24.54	24.89	27.34	24.92
C-4	28.20	28.41[a]	28.77[a]	31.57	29.12
C-5	18.53	28.76[a]	28.50[a]	4.81	28.58
C-6	79.91	18.66	28.68[a]	Te	31.42
C-7	80.18	80.80	18.77	−17.95	31.50
C-8	18.15	79.20	80.93	82.99	8.90
C-9	31.45[a]	21.07	81.04	78.23	Te
C-10	31.35[a]	31.61	22.56	19.05	34.34
C-11	1.79	1.44	0.65	29.09[a]	112.73
C-12	Te	Te	Te	28.97[a]	21.02
C-13	2.79	2.95	3.11	29.27[a]	28.82[a]
C-14	32.29	32.26	32.34	29.56[a]	28.82[a]
C-15	31.27	31.26	31.23	29.23[a]	29.12[a]
C-16	31.75	31.75	31.75	31.93	31.77
C-17	22.59	22.56	22.69	22.70	22.64
C-18	14.03	14.00	14.00	14.00	14.06
Ethyl ester	14.30 60.25	14.28 60.28	14.27 60.11	14.30 60.20	—
Methyl ester	—	—	—	—	51.38

[a] Interchangeable.
$CH_3(CH_2)_5$-Te-$(CH_2)_4$-C≡C-$(CH_2)_4COOEt$ (**1**)
$CH_3(CH_2)_5$-Te-$(CH_2)_3$-C≡C-$(CH_2)_5COOEt$ (**2**)
$CH_3(CH_2)_5$-Te-$(CH_2)_2$-C≡C-$(CH_2)_6COOEt$ (**3**)
$CH_3(CH_2)_8$-C≡C-CH_2-Te-$(CH_2)_4COOEt$ (**4**)
$CH_3(CH_2)_6$-C≡C-Te-$(CH_2)_7COOMe$ (**5**)

respectively. The α-methylene carbons to the acetylenic system and those adjacent to the tellurium atom were readily identified. In this isomer, where the acetylenic bond is located between the C-6/C-7 position of the fatty acid ester chain, the long range effect from the ethyl ester function on the shift of the acetylenic carbon atoms permitted the acetylenic carbon atoms to be resolved with the result that the shifts of the C-6 and C-7 carbon nuclei appeared at δ_C 79.91 and 80.18, respectively.

The carbon shifts of the methylene carbon atom(s) of the mono-, di- and tri-methylene interrupted acetylenic tellura isomers (compounds **2**–**4**) were readily assigned. The effect of the tellurium atom on the shifts of the acetylenic system also allowed the acetylenic carbon atoms to be identified. Of interest was the large negative shift value (δ_C −17.95) observed for the shift of the methylene carbon atom (C-7) of compound **4**, which is located between the acetylenic system and the tellurium atom.

In compound **5**, where the tellurium atom is bonded to the acetylenic system, the shifts of the acetylenic carbon atoms were unique and appeared at δ_C 34.34 and 112.73 for C-10 and C-11, respectively. However, the shift of the methylene carbon atom adjacent to the tellurium nucleus (C-8) appeared much more downfield (at δ_C 8.90) than expected (at about δ_C 2.00–3.00 region) of this nucleus. Similarly the methylene carbon adjacent to the acetylene system (C-12) appeared at δ_C 21.02 instead of about δ_C 18.00 had there been no tellurium atom bonded to the triple bond

From the study of the NMR properties of these acetylenic tellura fatty acid esters, it was possible

to use this technique to identify each isomers as either the non-, mono-, di-, tri- or tetra-methylene interrupted isomer acetylenic tellura fatty ester analogue.

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