^1H and ^{13}C NMR Studies on the Positional Isomers of Methyl Selenalaurate and Telluralaurate

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A report is given of the ^1H and ^{13}C NMR spectra of a series of methyl selenalaurates and telluralaurates in which successive methylene groups have been replaced by a selenium or a tellurium atom. The effect on contiguous carbons is a marked upfield shift (shielding) while the protons attached to these carbons are deshielded. The β and γ protons are weakly deshielded.

We have recently reported the synthesis and NMR studies on the positional isomers of methyl thialaurate and methyl thiastearate.[1] An investigation of the effect of the sulphur atom in thiastearic acid on the metabolism of fatty acids in liver cells (hepatocytes) shows that the rate of β-oxidation of fatty acids is decreased, resulting in an increased accumulation of fatty acids in the form of triglycerides in the liver.[2] The replacement of a methylene group in long chain fatty acids by a sulphur atom has been previously found to inhibit dihydrosterculic acid biosynthesis and on the growth of the protozoan species, *Crithidia fasciculata*.[3,4] 7-Thiaarachidonic acid is reported to be a potent and irreversible inhibitor of leukotriene (lipoxin) biosynthesis.[5] In view of these important developments in the biochemistry of thia analogues of long chain fatty acids, we have substituted the sulphur atom by a selenium or tellurium atom in order to compare the effects of the group related elements of sulphur on the metabolism of long chain fatty acids.

Several selena C_{16}–C_{20} long-chain alkanoic acid homologues containing radioactive ^{75}Se in the 3- or 4-position of the alkyl chain have been synthesized to study their potential as myocardial imaging agents.[6] Results of the antimicrobial action of some selena-alkanoic acids against *Streptococcus pyogenes* show that the activity is more effective in the selena C_{14} acid than the corresponding C_{15} or C_{16} homologues; and the position of the selenium atom in the alkyl chain in these alkanoic acids appeared to be more effective when positioned furthest from the carboxyl group.[7] Schwarz and Fredga have studied the biological potency of selena-alkanoic acids and have noted the relation between the structure of aliphatic selena-alkanoic acids in preventing dietary liver necrosis in rats.[8] The nutritional importance of selenium has been extensively researched and many organic compounds containing selenium have been found to be potential chemotherapeutic agents.[9] Of greater interest has been the inhibition of β-oxidation of fatty acids in the myocardium by a tellurium heteroatom in fatty acid molecules, which provides a unique method by which to 'trap' radiolabelled fatty acids in the heart tissue for myocardial imaging purposes.[10] Knapp *et al.* have reported the synthesis of several long chain unsaturated tellura fatty acids for this purpose.[11,12] In view of the increased developments in the biochemistry of organo-selenium and organo-tellurium compounds, we have synthesized the complete series of positional isomers of methyl selenaulaurate and telluralaurate in an effort to study the spectroscopic and biological properties in further detail. In this paper we report on the ^1H and ^{13}C NMR properties of all the positional isomers of methyl selenalaurate and telluralaurate.

The synthesis of the positional isomers of the selenalauric acid was accomplished by preparing the dialkyl diselenide and ditelluride from n-alkyl bromides or iodides with disodium diselenide and ditelluride, respectively. Reduction of the dialkyl diselenide by hydrazine and dialkyl ditelluride by $NaBH_4$ gave the selenide and telluride anions, respectively, which were then condensed with ω-bromoalkanoic acids to furnish the corresponding selenalauric acids (average yield 70%)[13] and telluralauric acids (average yield 35%).[14,15] In the case of the 2-selena and 2-tellura isomers, methyl chloroformate was used in place of the corresponding bromoalkanoic acid, as the 2-selena and 2-telluralauric acids were found to be very unstable at room temperature.[16] For the preparation of the 3-tellura isomer methyl 2-bromozincacetate ($BrZnCH_2CO_2Me$) was employed.[17] Most of the short chain ω-bromoalkanoic acids were commercially available, but could also be readily obtained by partial bromination of α,ω-alkanediols followed by $KMnO_4$ oxidation.[18,19]

The ^1H NMR spectral data for the chemical shifts of the methylene protons attached to the selenium atom of 3-selena C_{15}, C_{17}, C_{19} and 4-selena C_{16}, C_{18}, C_{20} alkanoic acids were found at δ 2.50–2.92 from TMS.[6] The shift of the methyl protons of dimethylselenide appeared at δ 2.26, due to the shielding effect of the selenium atom.[13] In a study of the ^1H NMR behaviour of dialkyl tellurides, the effect of a tellurium atom on the shift of the methylene protons adjacent to the heteroatom was very similar (δ 2.45–2.80) to selenium.[20] ^{13}C NMR chemical shifts in isologous series of ethers, sulphides, selenides and tellurides were reported (with alkyl groups consisting of either a methyl, phenyl, allyl, butadienyl, or a short-chain conjugated diacetylene group), showing the deshielding effects of the oxygen and sulphur, and the shielding effects of selenium and tellurium on the adjacent carbon atoms.[21] The ^{13}C NMR data for a number of phenyl- and *p*-methoxyphenyl-tellurium compounds are also reported, where the tellurium atom exerts a strong shielding effect on the aromatic carbon attached to the heteroatom.[22]

Results and Discussion

The ^1H NMR chemical shift values of methyl selenalaurates and telluralaurates are presented in Tables 1 and 2, respectively. From the ^1H NMR analysis of methyl 6-, 7- and 8-selenalaurate, it is evident that the selenium atom in the alkyl chain exerts a strong α-deshielding effect on the protons of the adjacent methylene groups, producing a characteristic signal at δ 2.55 (t, *J* 7 Hz) in the spectrum. The selenium atom also appeared to deshield the protons of the methylene groups at the β- and γ-positions to give a multiplet at δ 1.6–1.8. The effect of the selenium atom in the 2-selena isomer caused the chemical shift of the methyl protons of the ester function to appear at δ 3.82(s), while the C-3 methylene protons were found at δ 2.90, as these protons were additionally affected by the methyl ester function.

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Table 1 Values of δ_H (ppm) for all positional isomers of methyl selenalaurate[a]

	CH_2^a–CH_2^b–CH_2^c–CH_2^d–CH_2^e–CH_2^f–CH_2^g–CH_2^h–CH_2^i–CH_2^j–CH_2^k–$CO_2CH_3^l$ (CH_2 replaceable by Se)											
Selena isomer	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*
2-	0.88(t)				1.2–1.4(a)			1.6–1.8(m)	1.6–1.8(m)	2.90 (t, *J*7.3)	Se	3.82(s)
3-	0.88(t)				1.2–1.4(m)		1.6–1.8(m)	1.6–1.8(m)	2.75 (t, *J* 7.1)	Se	3.15(s)	3.71(s)
4-	0.88(t)			1.2–1.4(m)		1.6–1.8 (m)	1.6–1.8(m)	2.59 (t, *J* 7.5)	Se	2.74(s)	2.74(s)	3.69(s)
5-	0.88(t)		1.2–1.4(m)		1.6–1.8(m)	1.6–1.8(m)	2.3–2.7(m)	Se	2.3–2.7(m)	1.98 (qn, *J* 7.5)	2.3–2.7(m)	3.67(s)
6-	0.89(t)	1.2–1.4(m)		1.6–1.8(m)	1.6–1.8(m)	2.55 (t, *J* 7)	Se	2.55 (t, *J* 7)	1.7(m)	1.7(m)	2.34(t)	3.66(s)
7-	0.90(t)	1.2–1.4(m)	1.6–1.8(m)	1.6–1.8(m)	2.55 (t, *J* 7)	Se	2.55 (t, *J* 7)	1.6–1.8(m)	1.6–1.8(m)	1.6–1.8(m)	2.34(t)	3.66(s)
8-	0.91(t)	1.6–1.8(m)	1.6–1.8(m)	2.54 (t, *J* 7)	Se	2.54 (t, *J* 7)	1.6–1.8(m)	1.6–1.8(m)	1.2–1.4(m)	1.6–1.8(m)	2.32(t)	3.65(s)
9-	0.99 (t, *J* 7.6)	1.6–1.8(m)	2.54 (t, *J* 7)	Se	2.54 (t, *J* 7)	1.6–1.8(m)	1.6–1.8(m)	1.2–1.4(m)		1.6–1.8(m)	2.31(t)	3.66(s)
10-	1.39 (t, *J* 8.3)	2.56 (q, *J* 8.3)	Se	2.56 (t, *J* 7)	1.6–1.8(m)	1.6–1.8(m)	1.2–1.4(m)			1.6–1.8(m)	2.30(t)	3.66(s)
11-	1.97(s)	Se	2.53 (t, *J* 6.8)	1.6–1.8(m)	1.6–1.8(m)	1.2–1.4(m)				1.6–1.8(m)	2.30(t)	3.65(s)

[a] All coupling constant values *J* are given in Hz.

Table 2 Values of δ_H (ppm) for all positional isomers of methyl telluralaurate[a]

	CH_3^a–CH_2^b–CH_2^c–CH_2^d–CH_2^e–CH_2^f–CH_2^g–CH_2^h–CH_2^i–CH_2^j–CH_2^k–$CO_2CH_3^l$ (CH_2 replaceable by Te)											
Tellura isomers	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*
2-	0.88(t)				1.2–1.4(m)				1.88(m)	2.91 (t, *J* 7.2)	Te	3.84(s)
3-	0.88(t)				1.2–1.4(m)			1.5–1.8(m)	2.90 (t, *J* 7.2)	Te	3.29(s)	3.70(s)
4-	0.88(t)				1.2–1.4(m)		1.5–1.8(m)	2.84 (t, *J* 7.2)	Te	2.84(s) (t, *J* 7.2)	2.68(s) (t, *J* 6.5)	3.69(s)
5-	0.88(t)			1.2–1.4(m)		1.5–1.8(m)		2.63 (t, *J* 7.2)	Te	2.63 (t, *J* 7.2)	2.10 (q, *J* 7.2)	2.40 (t, *J* 6.5)	3.67(s)
6-	0.89(t)		1.2–1.4(m)		1.5–1.8(m)	2.63 (t, *J* 7.2)		Te	2.63 (t, *J* 7.2)	1.5–1.8 (m)		2.35 (t, *J* 6.5)	3.67(s)
7-	0.90(t)	1.2–1.4(m)		1.5–1.8(m)	2.63 (t, *J* 7.2)	Te	2.63 (t, *J* 7.2)		1.5–1.8(m)			2.32 (t, *J* 5.5)	3.66(s)
8-	0.92(t)	1.2–1.4(m)	1.5–1.8(m)	2.63 (t, *J* 7.2)	Te	2.63 (t, *J* 7.2)	1.5–1.8(m)	1.2–1.4(m)		1.5–1.8(m)		2.31 (t, *J* 7.0)	3.66(s)
9-	0.97 (t, *J* 7.0)	1.5–1.8(m)	2.62 (t, *J* 7.2)	Te	2.62 (t, *J* 7.2)	1.5–1.8(m)		1.2–1.4(m)		1.5–1.8(m)		2.30 (t, *J* 7.0)	3.66(s)
10-	1.60 (t, *J* 6.5)	2.65 (q, *J* 6.5)	Te	2.58 (t, *J* 7.2)	1.5–1.8(m)		1.2–1.4(m)			1.5–1.8(m)		2.30 (t, *J* 7.0)	3.66(s)
11-	1.88(s)	Te	2.62 (t, *J* 7.2)	1.5–1.8(m)		1.2–1.4(m)				1.5–1.8(m)		2.30 (t, *J* 7.0)	3.66(s)

[a] All coupling constant values *J* are given in Hz.

The 3-selena isomer gave a characteristic singlet at δ 3.15 due to the resonance shift of the protons at C-2. An intense singlet at δ 2.72 (4 H) appeared in the spectrum of the 4-selena isomer, resulting from the shift of the protons of the C-2 and C-3 methylene groups. The 5-selena isomer was characterized by the appearance of a quintet at δ 1.98, due to the shift of the proton of the C-3 methylene group. In the case of the 9-selena isomer, where the selenium atom was located at the ω-3 position, the γ-effect of the selenium atom on the protons of the terminal methyl group furnished a distinct triplet at δ 0.99 as opposed to the distorted triplet signal at δ 0.89 commonly observed for the terminal methyl protons of long-chain fatty esters. In the 10-selena isomer a quartet at δ 2.56 (due to the protons at C-11) could be clearly differentiated from the triplet at the same chemical shift position due to the protons at C-9, which appeared as a triplet at δ 2.56. Also, in this same isomer the protons of the terminal methyl group were shifted to δ 1.39. In the ω-1 isomer the effect of the selenium atom caused the methyl protons to shift to δ 1.97(s).

The deshielding effect of the selenium atom on the chemical shift of the adjacent methylene protons was slightly larger than that of a sulphur atom as observed from the ^{1}H NMR study of methyl thialaurate and thiastearate isomers.[1] With the heteroatom located in the central section of the alkyl chain, the α-methylene protons were generally shifted to δ 2.55 and 2.50 for the methyl selenalaurate and thialaurate analogues, respectively. In the case of methyl 4-selenalaurate, the methylene protons attached to C-2 and C-3 appeared as a singlet at δ 2.74, while methyl 4-thialaurate gave triplets at δ 2.59 and 2.70 for the protons at C-2 and C-3, respectively. However, where the heteroatom occupied the ω-1 position of the alkyl chain (methyl 11-selenalaurate and 11-thialaurate), the chemical shift of the terminal methyl protons was more downfield in the case of the thia ester (δ 2.08) than in the selena analogue (δ 1.97).

In the ^{1}H NMR analysis of the methyl telluralaurate isomers, the tellurium atom exerted a slightly stronger deshielding effect than selenium or sulphur on the protons of the adjacent methylene groups, which gave a characteristic triplet at δ 2.63 (*J* 7.2 Hz) in the case of the 6-, 7- and 8-tellura isomers. The effect of the tellurium atom on the protons of the β-methylene groups was slight with signals found in the range δ 1.5–1.8. On the whole, the spectra of the methyl 6-, 7- and 8-tellura isomers were very similar and differentiation of these positional telluraisomers by this technique was therefore not possible. However, the effect of the tellurium atom in the 2-tellura isomer caused the chemical shift of the methyl protons of the ester function to appear at δ 3.84(s), while the α-methylene protons were located downfield at δ 2.91, being additionally affected by the methyl ester function. The protons of the C-4 methylene group of this isomer were shifted to δ 1.88 (m). The 3-tellura isomer was readily differentiated from the other isomers by the appearance of a singlet at δ 3.29, due to the resonance of the protons of the C-2 methylene group. In spite of the presence of a methylene group between the tellurium atom and the ester group, the combined effects of these two functions on the chemical shift of the protons of the C-4 methylene group gave a downfield signal at δ 2.90 (t, *J* 7.2 Hz). A partially overlapping set of two triplets in the spectrum of the 4-tellura isomer was the result of the signals from the resonances of the protons of the C-2 (δ 2.68, *J* 6.5 Hz, 2 H) and the C-3, C-5 (δ 2.84, *J* 7.2 Hz, 4 H) methylene groups. The 5-tellura isomer was characterized by the appearance of a quintet at δ 2.10 (*J* 7.2 Hz), due to the shift of the protons of the C-3 methylene group. In the case of the 11-tellura isomer, the location of the tellurium atom at the ω-1 position of the alkyl chain caused the methyl protons to shift to δ 1.88 (s), a value which was 0.2 and 0.1 ppm lower than that exhibited in the case of methyl 11-thialaurate and 11-selenalaurate, respectively. The ω-2 isomer gave a characteristic signal at δ 1.60 (t, *J* 6.5 Hz) for the terminal methyl protons, which was partially merged with the signals at δ 1.5–1.8 (m). The tellurium atom in the ω-3 isomer (9-telluralaurate) exerted a unique γ-effect on the protons of the terminal methyl group to furnish a distinct triplet at δ 0.97, as opposed to the distorted triplet signal normally observed for the methyl protons of long-chain fatty esters. This phenomenon was also observed in the case of the methyl 9-thia[1] and 9-selenalaurate analogues. By examining the chemical shifts of the protons of these closely related positional isomers of selena and tellura fatty esters, it was possible to identify seven of the positional isomers in each series by this technique.

The ^{13}C NMR chemical shift values of the series of positional isomers of methyl selenalaurate and those for methyl 12-selenastearate are presented in Table 3. In order to determine the incremental effects due to the selenium atom on the chemical shifts of the adjacent α-, β- and γ-methylene carbon nuclei, methyl 12-selenastearate was prepared so as to eliminate any chemical shift effects on the adjacent carbon nuclei of the selenium atom in the alkyl chain by the terminal Me and the CO_2Me groups of the selena fatty ester molecule. The results of the chemical shifts of the carbon atoms in methyl 12-selenastearate showed that the selenium atom in the alkyl chain induced a strong shielding effect (*ca.* −5.28 ppm, assuming the chemical shift of the carbon atom of an unperturbed CH_2 group to be 29.3 ppm) on the shift of the α-methylene carbon atom located on either side of the selenium linkage. The effect of the selenium atom on the shift of the β-methylene carbon atoms was weakly deshielding (*ca.* +1.47 ppm), while the γ-methylene carbon atoms experienced an even weaker deshielding effect (*ca.* +0.62 ppm). For comparison the sulphur atom in the series of methyl thialaurate analogues displayed a deshielding α-effect (+2.70 ppm) and β-effect (+0.5 ppm), and a weak shielding γ-effect (−0.5 ppm) on the adjacent methylene carbon atoms.

The chemical shift of the carbonyl carbon of the CO_2Me group of methyl 2-selenalaurate was shifted upfield to 168.02 ppm as a result of the shielding effect of the selenium atom (the shift of an unperturbed CO_2Me appeared at *ca.* 174 ppm). However, the shift of the carbon atom at C-3 of 2-selenalaurate appeared at 27.22 ppm and not at a lower shift value as expected, since the chemical shift value for the C-3 carbon atom in a methyl alkanoate appeared at *ca.* 25 ppm from TMS. This unexpected shift value for the C-3 carbon atom in this positional isomer appeared to upset the general trend observed for the contributory shielding or deshielding effects of a selenium atom on the adjacent methylene carbon atoms, making the application of the additivity rule in the estimation of chemical shift values inoperable.

In the next positional isomer, methyl 3-selenalaurate, the selenium at the β-position from the carbonyl carbon of the CO_2Me was expected to cause a deshielding effect (+1.47 ppm) on the carbonyl carbon of the CO_2Me group. In fact, the chemical shift of the carbonyl carbon of the CO_2Me in methyl 3-selenalaurate appeared at a more shielded position (171.86 ppm). The selenium atom did not cause the anticipated strong shielding effect on the shift of the C-2 carbon atom in this isomer, which appeared at 21.72 ppm. The methyl 4- to 7-selenalaurates, gave carbon shift values which agreed with the general trend of effects from the selenium atom on adjacent methylene carbon atoms. There was also a slight combined effect from the terminal Me and CO_2Me groups in these positional isomers, which caused the shift of similarly-positioned methylene carbons on either side of the selenium atom to be distinguishable.

With the selenium atom approaching the terminal Me group of the molecule as in the methyl 8- to 10-selenalaurate isomers,

Table 3 Values of δ_C (ppm) for all positional isomers of methyl selenalaurate and methyl 12-selenastearate

$\overset{12}{C}H_3(CH_2)_n\text{–Se–}(CH_2)_m\overset{1}{C}O_2\overset{13}{C}H_3$

C_{12} Selena isomers	*n*	*m*	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
2-	9	0	168.02	Se	27.22	30.66	29.88	29.61	29.61	29.42	29.17	31.99	22.78	14.14	54.04
3-	8	1	171.86	21.72	Se	25.57	30.07	29.85	29.58	29.36	29.23	31.96	22.75	14.11	52.03
4-	7	2	172.41	35.73	17.39	Se	24.24	30.69	30.04	29.33	29.28	31.96	22.78	14.14	51.52
5-	6	3	173.03	33.80	25.79	22.86	Se	23.86	30.72	30.01	28.96	31.88	22.73	14.11	51.30
6-	5	4	173.49	33.51	25.24	30.15	23.19	Se	24.00	30.69	29.69	31.45	22.62	14.03	51.33
7-	4	5	173.52	33.86	24.54	29.47	30.39[a]	23.48	Se	23.84	30.45[a]	32.23	22.32	14.03	51.25
8-	3	6	173.57	33.91	24.89	28.74	29.63	30.55	23.10	Se	23.65	32.88	23.51	13.65	51.19
9-	2	7	173.90	33.97	24.89	29.04	28.82	29.77	30.63	23.75	Se	26.08	23.94	14.57	51.28
10-	1	8	173.82	33.99	24.95	29.20	29.12	29.04	29.93	30.63	23.32	Se	16.93	15.87	51.25
11-	0	9	173.41	33.91	24.97	29.23	29.23	29.33	29.47	29.90	30.28	25.33	Se	3.58	51.09

C_{18} Selena isomers			C-1	C-2	C-3	C-4/C-8	C-9	C-10	C-11	Se	C-13	C-14	C-15	C-16	C-17	C-18	OCH_3
12-	5	10	174.22	34.16	25.03	29.23–29.55	29.92	30.77	24.02	—	24.02	30.77	29.92	31.50	22.67	14.14	51.44

[a] Interchangeable.

the combined effects of the selenium and the terminal Me group permitted the carbon nuclei located between the two functions to be readily assigned. In methyl 9-selenalaurate the chemical shifts for C-8 (23.75 ppm) and C-11 (23.94 ppm) were confirmed by 2D ^1H-^{13}C NMR techniques, as the protons attached to these carbons atoms had very different shift values in the ^1H NMR spectra. However, in the case of methyl 11-selenalaurate, the shift of the carbon atom of the terminal Me group was found upfield at 3.58 ppm. While it was not possible to establish a uniform set of shielding or deshielding effects due to the selenium atom on the neighbouring carbon atoms, in isomers where the selenium atom occupied positions close to the Me or CO_2Me groups of the alkanoate, the ^{13}C NMR spectral analysis of these compounds showed the possibility of identifying each of the positional isomers of methyl selenalaurate by this technique.

The ^{13}C NMR chemical shift values of the series of methyl telluralaurate are presented in Table 4. In this series, the tellurium atom exerted a much stronger shielding effect (*ca.* −28.0 ppm) on the carbon atoms of the adjacent methylene groups than selenium. The two α-methylene carbon atoms in the 7-tellura isomer appeared at 2.10 and 2.70 ppm from TMS, as compared with 23.48 and 23.84 ppm for the similarly-positioned carbon atoms of the 7-selena analogue, and at 32.10 and 32.30 ppm in the case of 7-thialaurate. Furthermore, the tellurium atom induced deshielding effects of *ca.* +2.5 and +2.1 ppm on the shifts of the β- and γ-methylene carbon atoms located on either side of the telluride linkage. Methylene groups located at the δ-position from the tellurium atom were also affected, as this heteroatom caused a weak shielding effect (*ca.* −0.6 ppm) on these carbon atoms. In the case of the 2-isomer the effect of the tellurium atom on C-1 caused this carbon atom to shift to 155.87 ppm, while C-3 appeared at 11.75 ppm. In the spectrum of the 3-tellura isomer, the chemical shifts for C-2 and C-4 were found at 6.47 and −1.79 ppm, respectively, resulting from the combined effects of the tellurium and the ester group. It was interesting to note that in spite of the presence of a tellurium atom between C-2 and C-4, the ester group was not prevented from exerting its normal shielding effect on the methylene carbon atom at C-4. Also, in this same isomer, an unexpected strong shielding effect from the tellurium on the shift of C-1 was observed giving a signal at 160.89 ppm, instead of an anticipated weak deshielding effect on this carbon atom. In the 4-isomer the chemical shifts for the methylene carbons at C-3 and C-5 appeared at −5.92 and 3.60 ppm respectively. The effect of the ester group allowed the peak at 1.30 ppm to be assigned to C-4, and the signal at 3.11 ppm to C-6 in the 5-tellura isomer. The 6-isomer furnished shift values for the C-5 and C-7 at 1.68 and 3.06 ppm, respectively. In the 7-isomer, where the tellurium atom was located in the middle of the alkyl chain, the chemical shifts of the carbons of the α-methylene groups were found at 2.10 (C-6) and 2.70 (C-8) ppm, being least perturbed by the terminal methyl and ester group. A significant shielding effect of the tellurium atom caused the shift of the carbon atom of the terminal methyl group of the 11-isomer (with the tellurium atom at the ω-1 position) to appear at −22.90 ppm from TMS. In the case of the ω-2 and ω-3 isomers, the chemical shifts of the carbon atoms of the methylene groups located between the tellurium atom and the terminal methyl group were readily differentiated from those on the other side of the tellurium linkage by their chemical shifts, due to the combined effects of the tellurium atom and the terminal methyl function on these carbon atoms. While it was not possible to establish a consistent set of additive shift value parameters for the shielding or deshielding effects due to the tellurium atom on the neighbouring carbon atoms, the ^{13}C NMR spectral analysis of these compounds furnished unique spectral features enabling each of the methyl telluralaurate isomers to be identified.

Experimental

^{13}C NMR spectra were obtained with a JEOL FX90 instrument operating at 22.62 MHz with proton noise decoupling. The spectra (3000–6000 accumulations; 27° pulse; 30 °C) were obtained from solutions in $CDCl_3$ (0.2–0.3 mol dm^{-3}), which also served as an internal deuterium lock. All spectra were calibrated against $SiMe_4$ as internal standard. 2D NMR spectral analysis was conducted on a JEOL GSX270 instrument. TLC analysis was performed on microscope glass plates coated with silica (*ca.* 0.1 mm thickness) and a mixture of 20% diethyl ether–hexane used as the developer. GC analysis was carried out on a Hewlett Packard 5970 gas chromatograph fitted with a 10 m microbore glass column (0.53 mm diameter, 2.65 μm film thickness SE-30) using nitrogen (20 cm^3 min^{-1}) as the carrier gas under isothermal condition (140 °C) with a flame ionization detector. External methyl ester standards (12:0, 14:0, 16:0 and 18:0) were used as reference compounds and the equivalent chain length (ECL) values calculated accordingly for each isomer.

General Method for the Preparation of Methyl 3- *to* 11-*Selenalaurate Isomers. Synthesis of Methyl* 11-*Selenalaurate.*—A mixture of selenium (1 g, 12.7 mmol), NaOH (0.76 g, 19 mmol), $NH_2NH_2{\cdot}H_2O$ (0.64 g, 13 mmol) and MeOH (20 cm^3) was stirred for 6 h. Iodomethane (1.8 g, 12.7 mmol) was then added. After the reaction mixture became yellow in colour, NaOH pellets (1 g, 25.4 mmol) were added followed by $NH_2NH_2{\cdot}H_2O$ (0.76 g, 19.1 mmol). The reaction mixture was stirred for 3 h. 10-Bromodecanoic acid (1.6 g, 6.4 mmol) in MeOH (5 cm^3) was added and the reaction mixture was stirred at 50 °C for 8 h. The cooled reaction mixture was poured into water (100 cm^3), and extracted with diethyl ether (2 × 30 cm^3). The aqueous layer was acidified with dilute HCl (2 mol dm^{-3}; 30 cm^3) and extracted with diethyl ether (2 × 50 cm^3). The ethereal extract was washed with brine and dried (Na_2SO_4). Evaporation of solvent gave crude 11-selenalauric acid. The latter was refluxed with methanol (25 cm^3) and BF_3·MeOH (15%, w/w; 5 cm^3) for 15 min. Water (50 cm^3) was added to the cooled reaction mixture and the whole was extracted with hexane (2 × 30 cm^3). The extract was washed, dried and evaporated to dryness. Chromatography on silica gel with hexane–diethyl ether (95:5) as eluent gave methyl 11-selenalaurate (1.3 g, 73%) as an oil.

Preparation of Methyl 2-*Selenalaurate.*—A mixture of selenium (1 g, 12.7 mmol), NaOH (0.8 g, 20 mmol), $NH_2NH_2{\cdot}2H_2O$ (0.64 g, 13 mmol) and MeOH (20 cm^3) was stirred for 6 h. 1-Bromodecane (2.8 g, 12.7 mmol) was added and stirred at 50 °C for 4 h. The cooled reaction mixture was poured into water (100 cm^3) and extracted with dichloromethane (2 × 30 cm^3). The organic extract was washed with brine and dried (Na_2SO_4). Evaporation of the solvent gave crude didecyl diselenide (2.5 g, 90%).

Sodium borohydride (0.17 g, 4.6 mmol) was added to a solution of didecyl diselenide (1 g, 2.3 mmol) in MeOH (20 cm^3) and the reaction mixture was stirred at room temperature for 4 h. Methyl chloroformate (0.43 g, 4.6 mmol) in MeOH (5 cm^3) was added and the mixture was stirred at 50 °C for 8 h. Cold water (100 cm^3) was added and the reaction mixture was extracted with diethyl ether (2 × 30 cm^3). The ethereal extract was washed with brine (20 cm^3) and dried (Na_2SO_4). Chromatography on silica gel with hexane–diethyl ether (95 : 5) as eluent gave methyl 2-selenalaurate (0.89 g, 69%) as an oil.

All positional isomers of methyl selenalaurate gave a single spot on TLC with R_F (20% diethyl ether–hexane) 0.6, and a single peak on GC (SE-30, ECL = 13.9–14.9) (Found: 2-isomer, C, 51.7; H, 8.8; 3-isomer, C, 51.6; H, 8.80; 4-isomer, C,

Table 4 Values of δ_C (ppm) for all positional isomers of methyl telluralaurate

$$CH_3(CH_2)_n\text{-}Te\text{-}(CH_2)_m\overset{1}{C}O_2\overset{13}{C}H_3$$

C_{12} Tellura isomers	*n*	*m*	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
2-	9	0	155.87	Te	11.75	32.07	31.85[a]	28.96	29.31	29.51	29.57	31.90[a]	22.69	14.12	53.86
3-	8	1	160.89	6.47	Te	−1.79	31.96	31.77	28.98	29.50	29.28	31.88	22.67	14.09	52.11
4-	7	2	173.34	37.29	−5.92	Te	3.60	32.24	32.05	28.94	29.20	31.86	22.64	14.07	51.59
5-	6	3	173.33	36.11	27.47	1.30	Te	3.11	32.21	31.99	28.66	31.75	22.62	14.06	51.52
6-	5	4	173.82	33.40	27.28	32.21	1.68	Te	3.06	31.77	31.72	31.20	22.56	14.03	51.49
7-	4	5	173.92	33.94	24.29	31.50	31.75[a]	2.10	Te	2.70	31.90[a]	34.24	22.05	13.98	51.38
8-	3	6	174.0	33.99	24.84	28.47	31.64	32.07	2.36	Te	2.55	34.42	25.11	13.41	51.33
9-	2	7	174.14	34.05	24.92	29.01	28.60	31.83	32.23	2.49	Te	5.23	25.54	16.63	51.38
10-	1	8	174.06	34.05	24.92	29.09	29.09	28.77	31.96	32.05	2.30	Te	−5.90	17.71	51.33
11-	0	9	174.18	34.11	24.92	29.20	29.10	29.30	28.91	31.86	31.86	3.41	Te	−22.9	51.39

[a] Interchangeable.

51.5; H, 8.70; 5-isomer, C, 51.8; H, 8.6; 6-isomer, C, 51.7; H, 8.5; 7-isomer, C, 51.65; H, 8.60; 8-isomer, 51.65; H, 8.7; 9-isomer, C, 51.6; H, 8.65; 10-isomer, C, 51.7; H, 8.6; 11-isomer, C, 51.6; H, 8.7. $C_{12}H_{24}O_2Se$ requires C, 51.61, H, 8.66%).

General Method for the Preparation of Methyl 4- *to* 11-*Telluralaurate Isomers. Synthesis of Methyl* 6-*Telluralaurate.*—A mixture of tellurium powder (0.5 g, 3.75 mmol), sodium borohydride (0.1 g, 2.5 mmol) and DMF (20 cm^3) was maintained at 80–90 °C for 1.5 h under nitrogen. 1-Bromohexane (0.49 g, 3.5 mmol) in DMF (5 cm^3) was added and the reaction mixture was stirred for 2 h at 80–90 °C. Sodium borohydride (0.3 g, 7.5 mmol) in ethanol (15 cm^3) was added to the cooled reaction mixture and allowed to react for a further 1.5 h. The reaction mixture was then heated to 80 °C and 5-bromopentanoic acid (0.54 g, 3.0 mmol) in DMF (5 cm^3) was added and the mixture was stirred for 2 h. Water (20 cm^3) was added and the cooled reaction mixture was acidified with dil. HCl (2 mol dm^{-3}; 10 cm^3) and extracted with Et_2O (3 × 30 cm^3). The ethereal extract was washed with brine (20 cm^3) and dried ($MgSO_4$). The solvent was distilled and the residue refluxed with methanol (20 cm^3) and BF_3·MeOH complex (15%, w/w; 4 cm^3) for 15 min. Water (40 cm^3) was added and the reaction mixture was extracted with light petroleum (b.p. 60–80 °C) (3 × 20 cm^3). The extract was washed with brine (20 cm^3) and dried ($MgSO_4$). Silica column chromatographic purification using a mixture of light petroleum (b.p. 60–80 °C) – Et_2O (9:1, v/v) as eluent gave pure methyl 6-telluralaurate (0.45 g, 32%) as an oil.

Preparation of Methyl 3-*Telluralaurate.*—A mixture of tellurium powder (0.3 g, 2.3 mmol), $NaBH_4$ (60 mg, 1.5 mmol) and DMF (10 cm^3) was heated at 80–90 °C for 1.5 h under nitrogen. 1-Bromononane (0.42 g, 2 mmol) in DMF (5 cm^3) was added and the reaction mixture was stirred for a further 2 h at the same temperature. A solution of iodine (0.25 g, 1 mmol) in THF (5 cm^3) was added to the cooled reaction mixture. After being stirred at room temperature for 2.5 h, methyl 2-bromozincacetate [prepared by refluxing methyl bromoacetate (0.4 g), zinc (0.2 g) and THF (10 cm^3) for 2 h] was added and the reaction mixture was stirred for 1 h. Water (20 cm^3) was added and the mixture was extracted with Et_2O (3 × 20 cm^3). The extract was washed with water (20 cm^3) and dried (Na_2SO_4). The solvent was removed and silica-gel column chromatography of the residue gave methyl 3-telluralaurate (0.23 g, 28%) as an oil.

Preparation of Methyl 2-*Telluralaurate.*—A mixture of tellurium powder (0.5 g, 3.75 mmol), $NaBH_4$ (0.1 g, 2.5 mmol) and DMF (20 cm^3) was heated at 80–90 °C for 2 h under nitrogen. 1-Bromodecane (0.75 g, 3.4 mmol) in DMF (5 cm^3) was added and the mixture was stirred for a further 2 h. $NaBH_4$ (0.3 g, 7.5 mmol) in ethanol (15 cm^3) was added to the cooled reaction mixture and allowed to stir at ambient temperature for 1 h. The reaction mixture was then cooled to 0–5 °C and methyl chloroformate (0.4 g, 4.2 mmol) in DMF (5 cm^3) was added. After being stirred for 15 min, the reaction mixture was allowed to rise to room temperature and was then stirred for a further 15 min. Water (20 cm^3) was added and the product was extracted with Et_2O (3 × 20 cm^3). Chromatographic purification gave methyl 2-telluralaurate (0.46 g, 30%) as an oil.

All positional isomers of methyl telluralaurate gave a single spot on TLC with R_F (10% diethyl ether–hexane) 0.5, and a single peak on GC (SE-30, ECL = 15.2–15.6) (Found: 2-isomer, C, 44.1; H, 7.6; 3-isomer, C, 44.20; H, 7.45; 4-isomer, C, 44.0, N, 7.60; 5-isomer, C, 43.8, H, 7.60; 6-isomer, C, 44.2, H, 7.40; 7-isomer, C, 43.7, H, 7.20; 8-isomer, C, 44.05, H, 7.35; 9-isomer, C, 43.85, H, 7.6; 10-isomer, C, 43.9, H, 7.15; 11-isomer, C, 44.10, H, 7.6. $C_{12}H_{24}O_2Te$ requires C, 43.95, H, 7.4%).

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