Deuterium Isotope Effects on ^{13}C Chemical Shifts in Long-chain Aliphatic Compounds

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Summary After introduction of one or more deuterium atoms into long-chain aliphatic compounds there are measurable upfield shifts of β- and γ-carbon signals and also marked increases in line width probably due to long range ^{13}C–D coupling.

To simplify assignment of signals in an investigation of ^{13}C n.m.r. spectra of C_{18} aliphatic esters we examined spectra of some deuterio-compounds and observed upfield isotope shifts of signals for carbons β and γ to the deuterium in addition to the expected shift of the α-carbon signal. Further, the line width of β- and γ-carbon resonances was increased three- to four-fold apparently due to long range ^{13}C–D coupling. Small (*ca.* 0·1 p.p.m.) second atom isotope induced shifts have been reported for monodeuteriobenzenes[1,2] and for three substituted monodeuterioheptanes[3] but second and third atom isotope effects and long range ^{13}C–D coupling have not previously been observed in the spectra of simple deuterio-aliphatic compounds (Table).

Appreciable upfield shifts were observed for the α-carbon of the monodeuterio-compounds (**1**), (**3**), and (**6**) (see Table), the signal was a triplet with $J(^{13}\text{C–D})$ about 20 Hz, but no

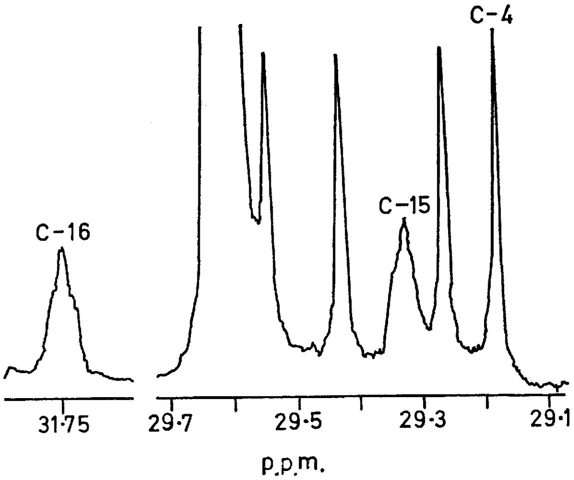

FIGURE. Portion of spectrum (100 Hz sweep width) of methyl 17-deuterio-octadecanoate (**3**).

TABLE. ^{13}C Isotope shifts in long-chain deuterio-compounds

		Isotope shift[a]			
	Compound	α-Carbon	$J(^{13}\mathrm{C{-}D})$ (Hz)	β-Carbon	γ-Carbon
(1)	$\mathrm{Me[CH_2]_{13}CH_2CH_2CH_2CH_2D}$	−0·28	20	−0·08[b]	−0·02[b]
(2)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CH_2CH_2CD_3}$	—	—	−0·36[c]	−0·16[c]
(3)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CH_2CHDMe}$	−0·44	19	−0·12[b](C-16) −0·16 (C-18)	−0·02[b]
(4)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CH_2CD_2Me}$	—	—	−0·24[d](C-16) −0·28 (C-18)	−0·08[d]
(5)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CD_2CH_2CD_3}$	—	—	−0·48[c](C-17) −0·20 (C-15)	[g]
(6)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CH_2CDOHMe}$	−0·52	21	−0·12[e]	—
(7)	$\mathrm{MeO_2C[CH_2]_{13}CH_2CD_2CHOHCD_3}$	—	—	−0·20[e](C-17) −0·24[f](C-15)	[g]
(8)	$\mathrm{MeO_2CCD_2[CH_2]_{13}Me}$	—	—	−0·12[d]	0·04[d]

[a] Measured at 25·2 MHz (Varian XLFT-100-15). [b] $J(^{13}\mathrm{CC{-}D})$ or $J(^{13}\mathrm{CCC{-}D})$ about 0·6 Hz. [c] Fourfold increase in linewidth. [d] Threefold increase in linewidth. [e] No increase in linewidth. [f] Twofold increase in linewidth. [g] γ-Carbon (C-14) obscured by other signals.

signals were observed for di- and tri-deuterio-carbons probably because of increased T_1[4] and decreased nuclear Overhauser enhancement.

Second atom shifts increased from about −0·1 p.p.m. for one β-deuterium to −0·48 p.p.m. [C-17 in (**5**)] for five β-deuteriums. With one β-deuterium (**3**), linewidth increased threefold and the signal resembled an unresolved triplet with $J(^{13}\mathrm{CC{-}D})$ about 0·6 Hz (see Figure). Line width was also greater when more deuterium atoms were present as would be expected if the effect was due to long-range coupling. Third atom shifts were smaller than second atom shifts but the line-width of γ-carbons was almost as large as that of β-carbons. Again coupling appeared to be about 0·6 Hz (see Figure).

Fourth atom effects could not be detected, there appeared to be no change in C-15 of (**2**) and in $\mathrm{MeCD_2[CH_2]_4CHOMe[CH_2]_{10}CO_2Me}$ C-14 was unaffected.

The effects were modified by hydroxy-substitution, in (**6**), with deuterium and hydroxy on C-17, the second atom shift was smaller, there was no third atom shift and no increase in linewidth [though $J(^{13}\mathrm{C{-}D})$, 21 Hz, was unaffected]. In (**7**), with OH on the β-carbon (C-17) there was no linewidth increase for the C-17 signal and the upfield shift was about half that observed in the related (**5**).

Hitherto deuteriation has been used to assign resonances of α-carbons only[4] but in the compounds discussed here several signals can be assigned after deuteriation of one carbon atom.

The third atom effect is particularly useful, since, though the isotope shift is very small, the linewidth increase is quite noticeable. The spectra of (**3**) (see Figure), (**4**), and (**5**) show that the signal at 29·33 p.p.m. is due to C-15 and the spectrum of (**8**) shows that the signal at 29·17 p.p.m. is due to C-4, assignments which could not have been made with any certainty otherwise.

Introduction of deuterium by reduction of a double bond or carbonyl group, *etc.*, could be used to assign resonances in spectra, and so indicate the structures of unknown compounds. ^{13}C N.m.r. investigations of biosynthesis and reaction mechanisms involving suitable deuterio-compounds also appear possible when several signals are affected by one deuterium atom.

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