The Angular Dependencies of Long-range ^{19}F–^{1}H Coupling Constants

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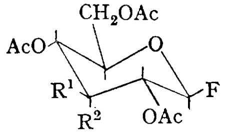
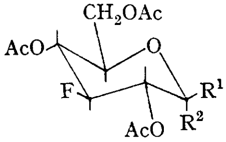
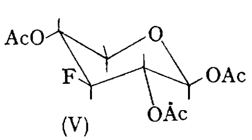
RECENT studies of specifically fluorinated carbohydrate derivatives have shown that the angular and configurational dependencies of *vicinal*[1] and *geminal*[2] fluorine–proton couplings parallel those of the corresponding proton–proton parameters. We have now shown that the steric requirements for *long-range* ^{19}F–^{1}H couplings across four saturated bonds (^{4}J) are also similar to those of the corresponding ^{1}H–^{1}H couplings.



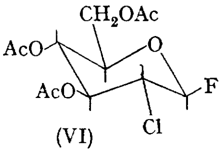


(I) R^1=H, R^2=OAc
(II) R^1=OAc, R^2=H

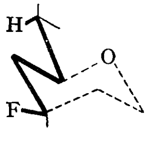
(III) R^1=H, R^2=OAc
(IV) R^1=OAc, R^2=H



(V)



(VI)



(VII)

β-D-Allopyranosyl fluoride tetra-acetate {(I), m.p. 149—151°, $[\alpha]_D$ $-1{\cdot}3°$ ($CHCl_3$)} shows† a long-range coupling of $+3{\cdot}6$ Hz. between F_{1e} and H_{3e} whereas the corresponding β-D-glucopyranosyl fluoride tetra-acetate[3] (II) shows no resolvable coupling between F_{1e} and H_{3a}. Similarly, 3-fluoro-3-deoxy-α-D-glucopyranose tetra-acetate {(III), m.p. 109—111°, $[\alpha]_D$ $+88°$ ($CHCl_3$), prepared from the β-anomer[4] by equilibration using zinc chloride and acetic anhydride[5]} shows a 4 Hz. coupling between F_{3e} and H_{1e} whereas the corresponding β-anomer[4] (IV) shows no resolvable coupling between F_{3e} and H_{1a}. In like fashion, H_{5e} of 3-fluoro-3-deoxy-β-D-xylopyranose triacetate {(V), m.p. 109—110°, $[\alpha]_D$ $-26°$ ($CHCl_3$)} is coupled by $+4{\cdot}2$ Hz. with F_{3e} whereas H_{5a} is not detectably coupled. In several instances, however, $^{4}J_{e,a}$ couplings have been resolved. Thus, for 3-fluoro-3-deoxy-β-D-glucopyranose tetra-acetate (IV), F_{3e} is coupled by $1{\cdot}1$ Hz. with H_{5a} whereas, for 2-chloro-2-deoxy-β-D-glucopyranosyl fluoride triacetate {(VI), m.p. 149—151°, $[\alpha]_D$ $+124°$

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† All spectra were measured with a Varian HA-100 spectrometer operating in the "frequency-sweep" mode for ^{1}H resonances and (at 94 MHz.) in the "locked, field-sweep" mode for ^{19}F resonances.

($CHCl_3$)} F_{1e} is coupled by $-0{\cdot}8$ Hz. with H_{3a} and by 0·7 Hz. with H_{5a}.

These results demonstrate that *long-range* ^{19}F–^1H couplings occur *preferentially* when the two nuclei have a 1,3-diequatorial relationship, or, more generally, when they have the "planar-M" relationship, which has previously[6] been postulated as the *preferred*[7] pathway for ^4J, ^1H–^1H couplings.

In accord with recent findings[7–9] for ^1H–^1H couplings, the signs of ^4J, ^{19}F–^1H couplings exhibit a configurational dependence, the $^4J_{e,e}$ couplings being *absolutely positive* and the $^4J_{e,a}$ couplings *absolutely negative* in sign. The signs were determined relative to *vicinal* ^1H–^1H coupling constants by the "spin-tickling" technique.[10]

Several derivatives exhibit long-range ^{19}F–^1H couplings across five bonds (^5J). Most notable is a coupling of 1·5 Hz. in the spectrum of 3-fluoro-3-deoxy-β-D-glucose tetra-acetate (IV) which occurs between F_{3e} and one of the C_6-protons; no resolvable coupling was detected for the other C_6-proton. The H_5–H_6 couplings in compound (IV) were 2·5 and 4·3 Hz. On the basis of the known[10] configurational dependence exhibited by vicinal couplings, the C_6-proton which has the higher residence time antiparallel to the C_5–O bond may be assigned the smaller J value and since this proton is also coupled to F_{3e} the conformation (VII) may be assigned to compound (IV). The stereochemical dependence of ^5J couplings is being further investigated but preliminary data for other fluorinated carbohydrates indicate that the favoured pathway closely approximates to that depicted in formula (VII).

The results reported herein emphasise the value of fluorinated carbohydrates of defined stereochemistry in studying F–H couplings.

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