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Note

Determination of one-bond carbon–proton coupling constants through ^{13}C-satellites in ^{1}H-n.m.r. spectra

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For several years, $^{1}J_{C,H}$ values for anomeric carbons have been used to determine the anomeric configuration in pyranosides[1] and particularly in oligo- and polysaccharides[2,3]. These coupling constants have been measured from proton-coupled ^{13}C-n.m.r. spectra using the gated technique[1,2], an approach which is often time-consuming, particularly with small amounts of complex molecules.

We now report that it is possible to determine $^{1}J_{C,H}$ values from the ^{13}C-satellites of high-field ^{1}H-n.m.r. spectra, as shown for the anomeric protons of D-glucose, D-mannose, 1,2,3,4-tetra-*O*-acetyl-β-D-ribopyranose, and methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside in Fig. 1. Each proton signal has two ^{13}C-satellites, each with an intensity that is 0.5% of that of the total proton signal. Except for a small $^{13}C/^{12}C$ isotope effect, which causes an upfield shift of ~0.004 p.p.m., the satellite signals are located symmetrically around the central proton signal and are found 80–85 Hz therefrom. Although the satellite signals are of low intensity, it is possible to obtain a sensitivity sufficient to observe them within 15 min using 3–5-mg samples (Fig. 1). These satellite signals contain information about $^{1}H,^{1}H$ couplings and are not broadened by long-range $^{13}C,^{1}H$ couplings, as in coupled ^{13}C-n.m.r. spectra. Furthermore, the coupling constants can be measured more accurately than those obtained from the coupled ^{13}C spectra, because of the better digital resolution normally used for ^{1}H spectra.

Examples of the measurement of $^{1}J_{C,H}$ values of oligosaccharides and one polysaccharide are shown in Fig. 2. It will not always be possible to observe both satellite signals because of overlap with intense signals from either the solvent or other proton signals. Analysis of the spectra may also be complicated by the presence of small amounts of impurities, which, due to the high sensitivity, may give signals of the same intensity as those of the satellites. However, most signals due to impurities can be neglected and, where overlap with a strong signal occurs, one of the two satellite signals may be observable.

Because of extensive overlap, determination of $^{1}J_{C,H}$ values is normally possible only for the anomeric protons by the present technique.

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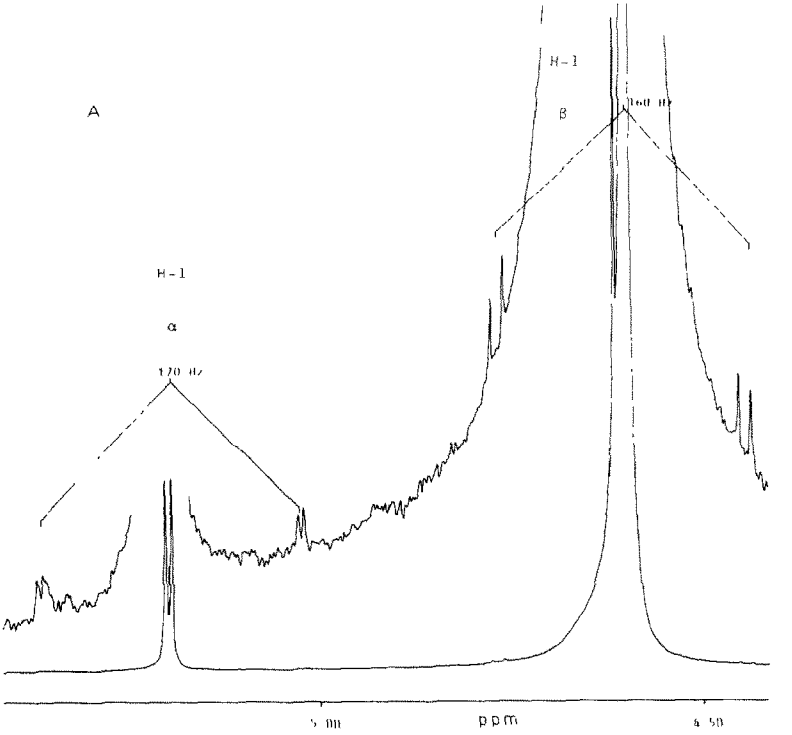
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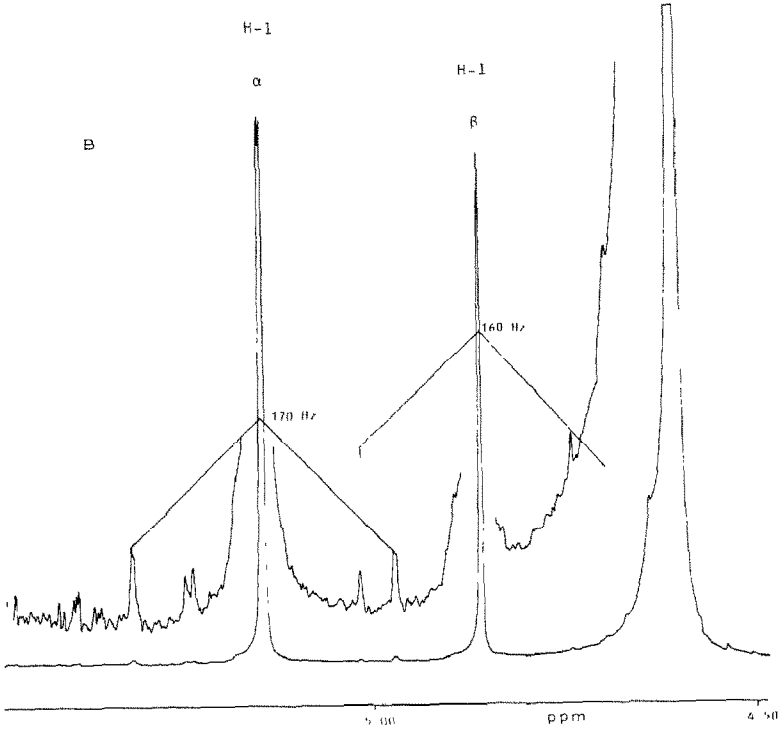
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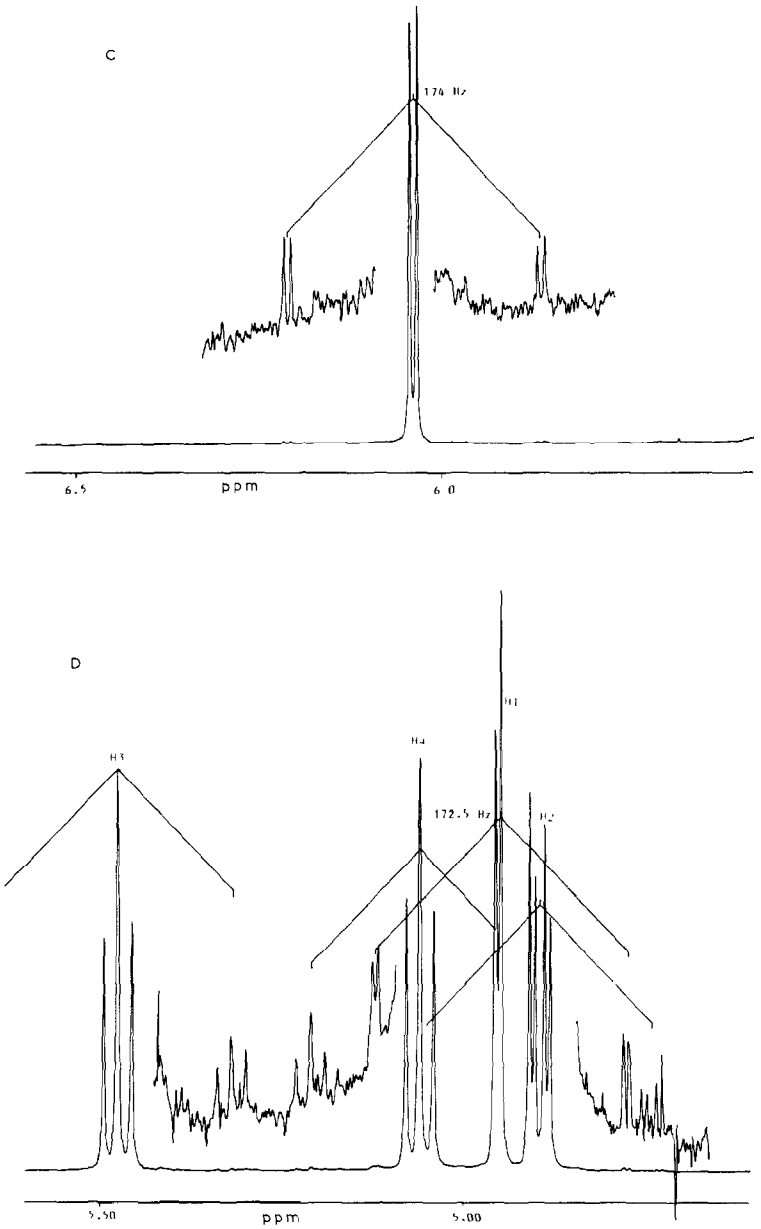
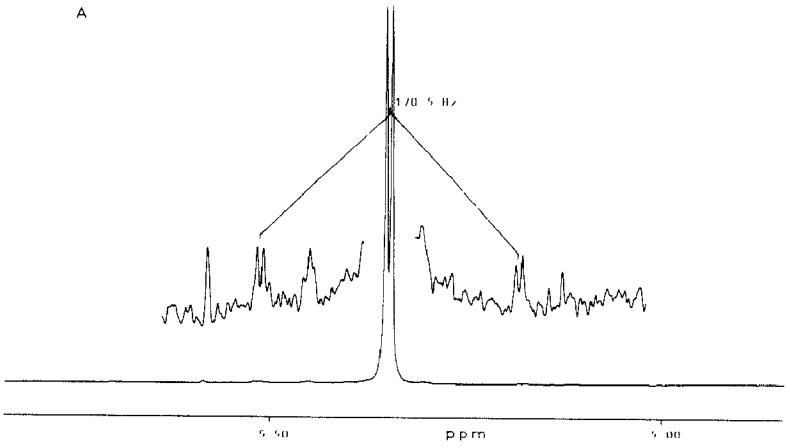


Fig. 1. Partial ^{1}H-n.m.r. spectra (500 MHz) of anomeric protons measured in 5-mm sample tubes at 310 K: A, D-glucose (5 mg in 0.5 mL of D_2O) after 50 transients (2 min); B, D-mannose (4 mg in 0.5 mL of D_2O) after 172 transients (6 min); C, 1,2,3,4-tetra-*O*-acetyl-β-D-ribopyranose [3 mg in 0.5 mL of $(CD_3)_2CO$] after 300 transients (12 min); D, methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (3 mg in 0.5 mL of $CDCl_3$) after 700 transients (28 min).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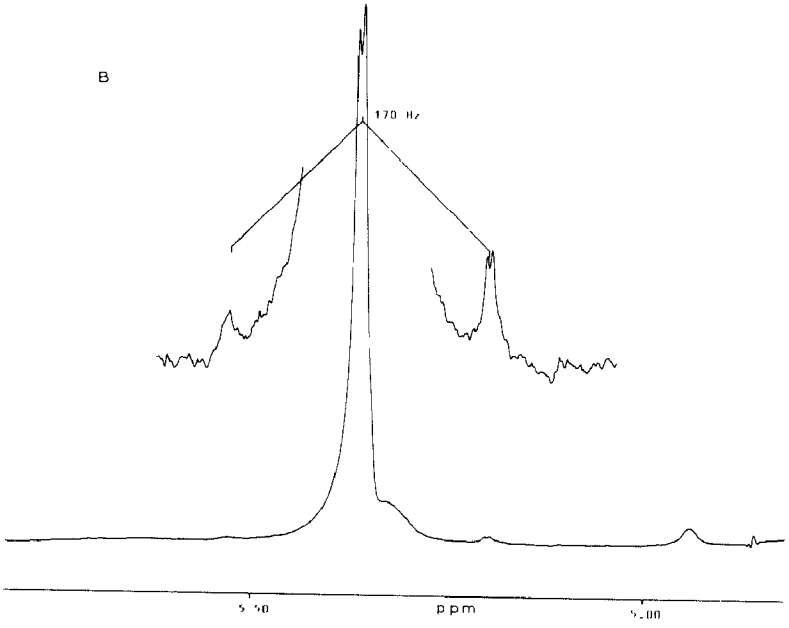
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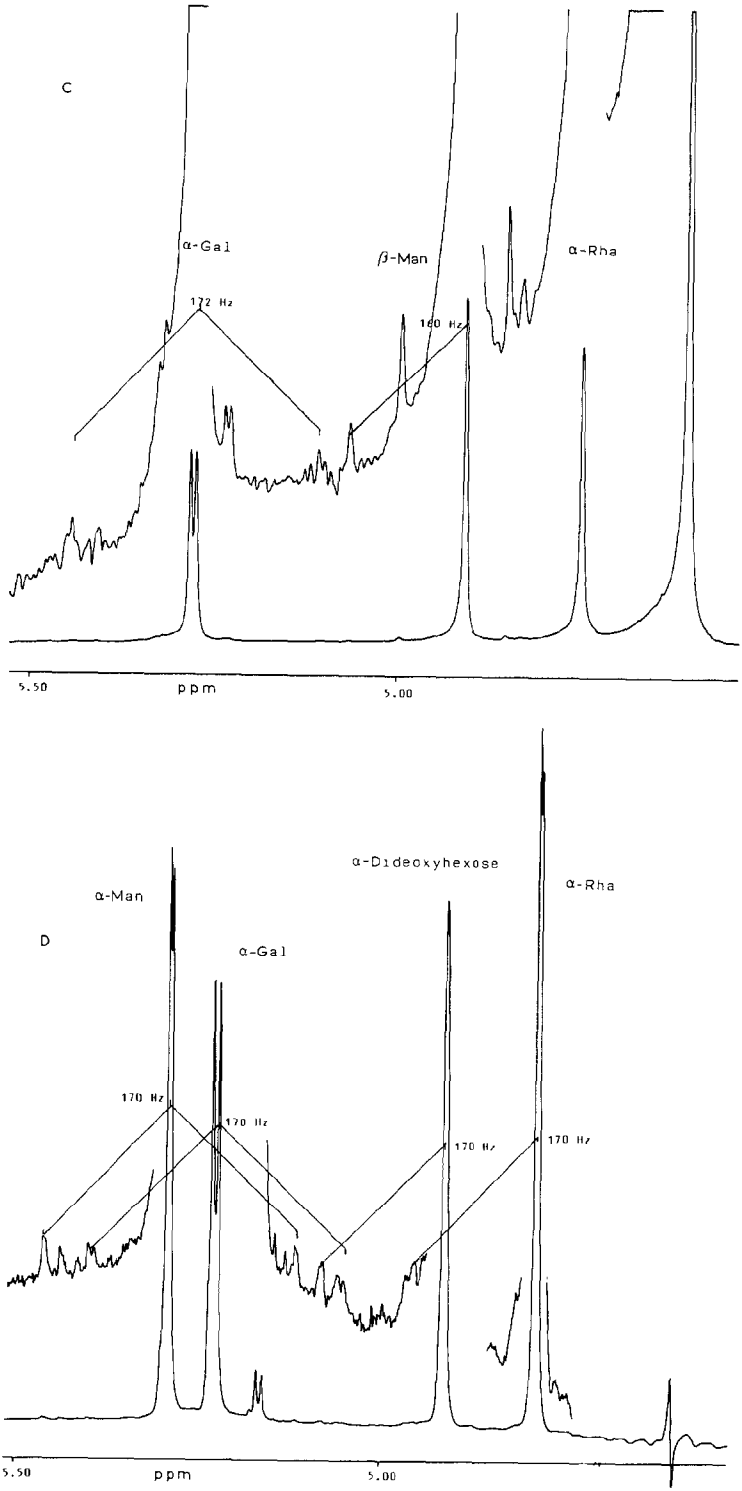

Fig. 2. Partial ^{1}H-n.m.r. spectra (500 MHz) of anomeric protons measured in 5-mm sample tubes at 310 K: A, sucrose (3 mg in 0.5 mL of D_2O) after 300 transients (12 min); B, starch (2 mg in 0.5 mL of D_2O) after 1000 transients (30 min); C, α-D-Gal*p*-(1→2)-β-D-Man*p*-(1→4)-α-L-Rha*p*-OR[4] (**1**, R = 8-methoxycarbonyloct-1-yl) (3 mg in 0.5 mL of D_2O) after 1000 transients (30 min); D, α-D-Gal*p*-(1→2)-3,6-dideoxy-α-D-*arabino*-Hex*p*-(1→3)-α-D-Man*p*-(1→4)-α-L-Rha*p*-OR[5] (**2**, R = 8-methoxycarbonyloct-1-yl) (3 mg in 0.5 mL of D_2O) after 1000 transients (30 min).

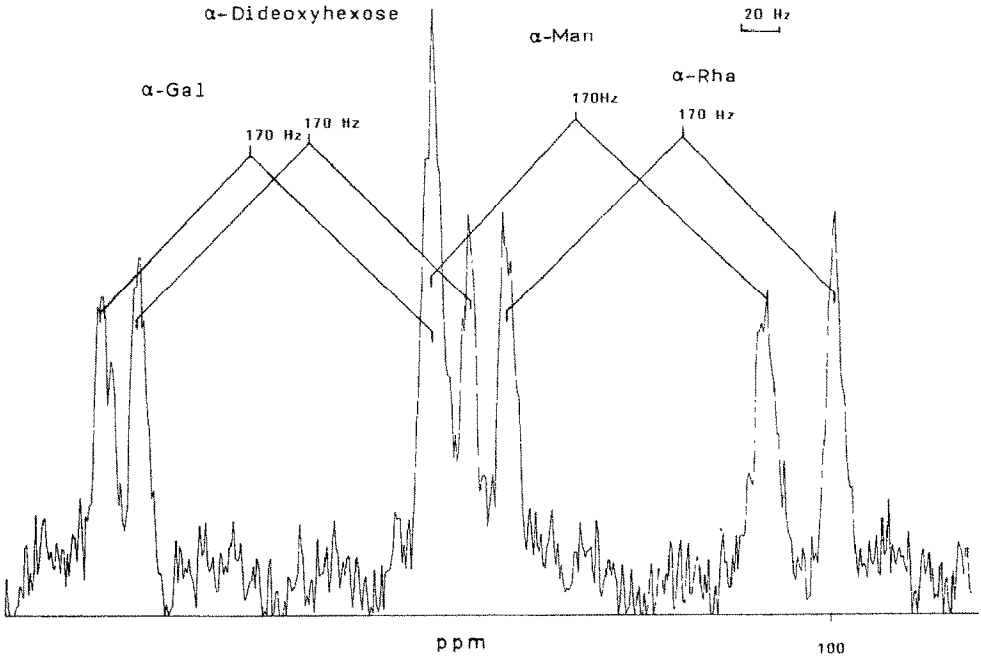

Fig. 3. Proton-coupled ^{13}C-n.m.r. spectrum (125.7 MHz) of **2** (see Fig. 2) obtained in the gated mode, showing the anomeric carbon signals. The spectrum was obtained for 3 mg of sample in 0.5 mL of D_2O in a 5-mm insert with 30,000 accumulations (18 h).

Fig. 3 shows a coupled ^{13}C-n.m.r. spectrum of the tetrasaccharide derivative α-D-Gal*p*-(1→2)-3,6-dideoxy-α-D-*arabino*-Hex*p*-(1→3)-α-D-Man*p*-(1→4)-α-L-Rha*p*-OR (R = 8-methoxycarbonyloct-1-yl) (**2**), the ^{1}H spectrum of which is presented in Fig. 2d. Whereas the latter was recorded within ~30 min, the former involves 30,000 scans over 18 h on 3 mg of sample. It is clear that the signal intensity is reduced due to long-range couplings.

Thus, for many compounds, the determination of anomeric configuration from $^1J_{C,H}$ values can be achieved easily and rapidly by measurement of the ^{13}C-satellites in the high-field ^{1}H-n.m.r. spectra.

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