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## Note

# N.m.r. assignments of acetyl and trityl groups in derivatized carbohydrates via proton–carbon long-range couplings*

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A two-dimensional, heteronuclear shift-correlated n.m.r. technique known as H,C-COLOC ($^1$H–$^{13}$C *co*rrelation spectroscopy via *lo*ng-range *co*uplings) has been developed to detect specifically $^1$H–$^{13}$C spin–spin coupling through two and three bonds[2]. Other n.m.r. techniques are also capable of detecting $^1$H–$^{13}$C long-range couplings, for instance selective INEPT (selective *i*nsensitive *n*uclei *e*nhanced by *p*olarization *t*ransfer)[3], DEPT (*d*istortionless *e*nhancement by *p*olarization *t*ransfer)[4], FUCOUP (*fu*lly *coup*led)[5], LR HETCOSY (*l*ong-*r*ange $^1$H–$^{13}$C *het*eteronuclear *co*rrelation *spectroscopy*)[6], C-relayed H,C-COSY ($^{13}$C-relayed $^1$H–$^{13}$C *co*rrelation *sp*ectroscopy)[7], and a modified version of the $^1$H-detected heteronuclear multiple quantum experiment[8].

We applied the COLOC technique first to methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (**1**), as this molecule has already had its acetyl methyl-proton peaks assigned in several solvents by chemical techniques[9]. We then examined 3,4,6-tri-*O*-acetyl-D-glucal (**2**), methyl 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronate (**3**), and 2,3,4,3′,4′-penta-*O*-acetyl-6,1′,6′-tri-*O*-tritylsucrose (**4**), in order to assign each of the individual acetyl- and trityl-group signals in the $^1$H- and $^{13}$C n.m.r. spectra to a specific position in each molecule.

Assignment methods for the n.m.r. signals of individual substituents in derivatized carbohydrates are useful for determining both position and degree of substitution. Previous methods for assigning individual acetyl- and methyl-group resonances involved unambiguous synthesis of derivatives containing a trideuterioacetyl or trideuteriomethyl group at one position. A summary of such work has been given[10] and several subsequent papers have appeared[11]. Another method[12] utilizes lanthanide shift-reagents for acetyl-proton assignments.

For each individual acetyl group in **1**–**4**, the methyl $^1$H signal and carbonyl $^{13}$C signal are assigned based on the COLOC spectrum (Fig. 1). This is accomplished by taking advantage of two long-range couplings, one between a sugar-

*See ref. 1 for a preliminary report of this work.

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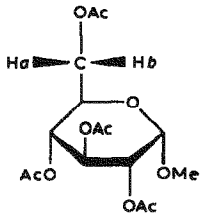
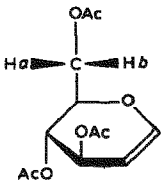



1

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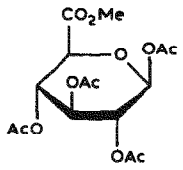


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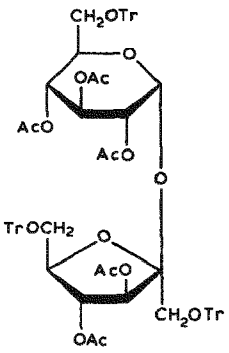
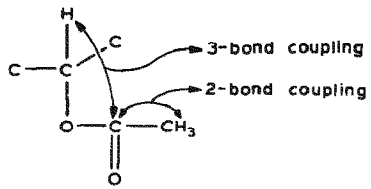



4

Scheme 1




Scheme 2

ring proton and the carbonyl carbon of its respective acetyl group (three-bond coupling) and the other between this same carbonyl carbon and the acetyl protons (two-bond coupling). The methyl $^{13}C$ signal of each group is then assigned from $^{1}H$–$^{13}C$ one-bond couplings in a conventional, H,C-COSY ($^{1}H$–$^{13}C$ *co*rrelation *s*pectroscop*y*) experiment. In order for such assignments to be made, the sugar-ring proton assignments must be known from previous experiments.

In previous synthetic work[9] with **1**, the individual acetyl-methyl $^{1}H$ signals were assigned to specific positions in the molecule by the unambiguous synthesis of derivatives specifically substituted at one position by a trideuterioacetyl group. During this work it was also found that the acetyl-methyl $^{1}H$ shifts of **1** were solvent dependent. The agreement of the COLOC acetyl-methyl proton assignments with those from this synthetic work (Table I) proves COLOC's ability to make such assignments and allows it to be extended with some confidence.

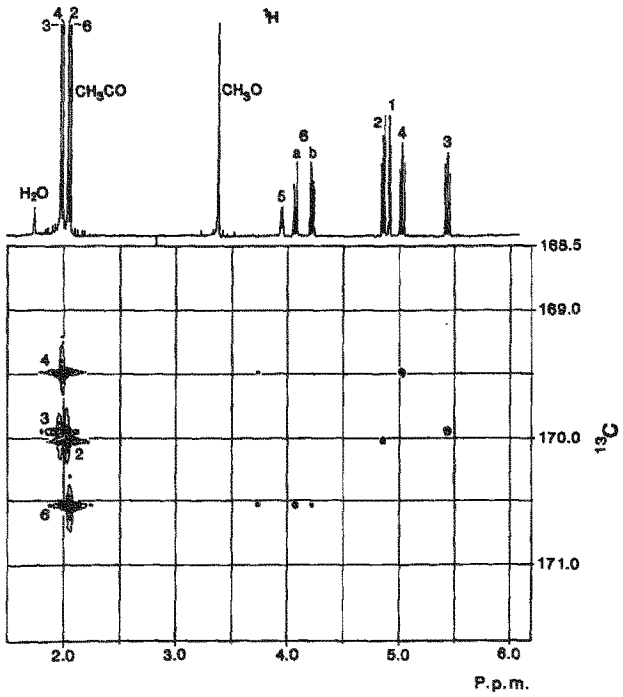



Fig. 1. COLOC spectrum of 1 in $CDCl_3$. The complete $^1H$ spectrum is along the horizontal axis, whereas only the carbonyl region of the $^{13}C$ spectrum is along the vertical axis. Two artifacts appear along the vertical at ~3.75 p.p.m. (for measuring conditions, see Experimental Section).

Our initial COLOC experiments were hampered by the presence of a large number of harmonic artifacts along the $F_1$ axis, apparently arising from the acetyl-methyl groups. These artifacts were eliminated after the installation of a digital phase-shifter capable of more accurately controlling the radiofrequency (r.f.) phases. Precise control of the r.f. phase appears to be very important for this application of COLOC.

We also attempted to assign the acetyl-methyl proton peaks of **1** by using the DEPT technique adjusted for long-range couplings. This experiment succeeded, but was not as sensitive as the COLOC experiment because of the additional refocussing delays in the DEPT technique.

The ring protons of **1** have been assigned previously in chloroform-*d*, benzene-$d_6$, and pyridine-$d_5$ (Table II)[9]. The ring- and acetyl-group carbon assignments of **1** in each of these solvents, along with previous ring-carbon assignments in chloroform-*d*, are recorded in Tables III and IV, respectively. The 3-OAc and 6-OAc methyl $^1H$ signals of **1** in benzene-$d_6$, which were unresolved at 100 MHz in the previous synthetic work[9], were distinguishable at 500 MHz and were assigned (Table I). We found that water (~15 mol% relative to the solvent) in the sample of **1** dissolved in pyridine-$d_5$ reversed the relative positions of the 4-OAc and 6-OAc

TABLE I

METHOXYL AND ACETYL METHYL $^1H$ CHEMICAL SHIFTS

| *Compd.* | *Solvent* | *MeO* | *Me-1* | *Me-2* | *Me-3* | *Me-4* | *Me-6* | *Ref.* |
|---|---|---|---|---|---|---|---|---|
| **1** | $CDCl_3$ | 3.42 | | 2.071 | 2.005 | 2.025 | 2.093 | 9 |
| | | 3.417 | | 2.074 | 2.006 | 2.027 | 2.095 | [a] |
| | $C_5D_5N$ | 3.35 | | 1.971 | 2.021 | 2.032 | 2.035 | 9 |
| | | 3.368 | | 1.989 | 2.042 | 2.053 | 2.054 | [a,b] |
| | $C_6D_6$ | 3.00 | | 1.641 | 1.743 | 1.719 | 1.743 | 9 |
| | | 2.971 | | 1.635 | 1.738 | 1.713 | 1.734 | [a] |
| **2** | $CDCl_3$ | | | | 2.047 | 2.078 | 2.094 | [a] |
| **3** | $CDCl_3$ | 3.747 | 2.119 | 2.041 | 2.031 | 2.041 | | [a] |
| **4** (G)[c] | $CDCl_3$ | | | 1.911 | 1.956 | 1.591 | | [a] |
| (F)[d] | | | | | 1.931 | 1.972 | | [a] |

[a]The present paper. [b]The systematic difference between these values and those of ref. 9 may be due to a difference in referencing. [c]Glucopyranosyl residue. [d]Fructofuranosyl residue.

TABLE II

$^1H$-N.M.R. CHEMICAL SHIFTS

| *Comp.* | *Solvent* | *H-1* | *H-2* | *H-3* | *H-4* | *H-5* | *H-6a* | *H-6b* | *Ref.* |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $CDCl_3$ | 4.96 | 4.89 | 5.49 | 5.07 | 3.92 | 4.09 | 4.29 | 9 |
| | | 4.953 | 4.896 | 5.473 | 5.063 | 3.989 | 4.113 | 4.263 | [a] |
| | $C_5D_5N$ | 5.17 | 5.26 | 5.90 | 5.42 | 4.13 | 4.30 | 4.43 | 9 |
| | | 5.200 | 5.292 | 5.917 | 5.462 | 4.155 | 4.346 | 4.490 | [a] |
| | $C_6D_6$ | 4.89 | 5.04 | 5.80 | 5.27 | 3.83 | 4.06 | 4.29 | 9,13 |
| | | 4.892 | 5.047 | 5.826 | 5.298 | 3.828 | 4.082 | 4.267 | [a] |
| **2** | $CD_3COCD_3$ | 6.543 | 4.842 | 5.311 | 5.174 | 4.334 | 4.182 | 4.398 | 14 |
| | $CDCl_3$ | 6.53 | 4.81 | 5.34 | 5.20 | 4.19 | 4.09 | 4.29 | 15 |
| | | 6.472 | 4.849 | 5.348 | 5.223 | 4.260 | 4.203 | 4.404 | [a] |
| **3** | $CDCl_3$ | 5.80 | | 4.90–5.40 | | 4.18 | | | 16 |
| | | 5.777 | 5.142 | 5.316 | 5.247 | 4.193 | | | [a] |
| **4** (G)[b] | $CDCl_3$ | 5.32 | 4.81 | 5.16 | 5.21 | 3.96 | 3.32 | 3.26 | 17 |
| | | 5.30 | 4.79 | 5.22 or 5.17 | | ~4.15 | ~3.18 | ~2.77 | 18[c] |
| | | 5.322 | 4.809 | 5.190 | 5.229 | 3.975 | 3.172 | 2.767 | [a] |
| | | H-1′*a* | H-1′*b* | | | | | | |
| **4** (F)[d] | | 3.32 | 3.26 | 5.83 | 5.36 | 4.14 | 3.37 | 3.30 | 17 |
| | | ~3.35 | ~3.25 | 5.82 | 5.35 | ~4.30 | [e] | [e] | 18[c] |
| | | 3.333 | 3.268 | 5.839 | 5.364 | 4.142 | 3.380 | 3.307 | [a] |

[a]The present paper. [b]Glucopyranosyl residue. [c]Approximate values estimated from a published spectrum. [d]Fructofuranosyl residue. [e]Not assigned.

methyl $^1H$ signals and also caused shifts in other signals. The nonequivalent methylene protons of **1** have previously been assigned in benzene-$d_6$ by synthesis of 6-monodeuterio derivatives[13] (Table II). Based on the values for $J_{5,6a}$ and $J_{5,6b}$, these assignments can be extended to other acetylated glucose derivatives, including **1** in other solvents and **2** (Tables II and V).

Assignment of the acetyl-group resonances in the $^1H$ and $^{13}C$ spectra of **2** and

TABLE III

$^{13}C$ CHEMICAL SHIFTS

| *Compd.* | *Solvent* | *MeO* | *C-1* | *C-2* | *C-3* | *C-4* | *C-5* | *C-6* | *Ref.* |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $CDCl_3$ | 55.6 | 96.3 | 70.4 | 69.7 | 68.2 | 66.8 | 61.5 | 19 |
| | | 55.4 | 98.9 | 70.9 | 70.2 | 68.7 | 67.3 | 62.1 | 20 |
| | | 55.46 | 96.82 | 70.83 | 70.15 | 68.61 | 67.19 | 61.97 | [a] |
| | $C_5D_5N$ | 55.27 | 97.29 | 71.31 | 70.68 | 69.30 | 67.83 | 62.47 | [a] |
| | $C_6D_6$ | 54.99 | 97.17 | 71.43 | 70.73 | 69.15 | 67.73 | 62.07 | [a] |
| **2** | $CDCl_3$ | | 145.5 | 99.3 | 67.5 | 67.3 | 74.0 | 61.3 | 21 |
| | | | 145.67 | 99.05 | 67.47 | 67.27 | 74.01 | 61.42 | [a] |
| **3** | $CDCl_3$ | 52.99 | 91.41 | 70.23 | 71.87 | 68.97 | 73.04 | 166.83 | [a] |
| **4** (G)[b] | $CDCl_3$ | | 90.14 | 70.03 | 70.81 | 68.45 | 69.21 | 60.70 | [a] |
| (F)[c] | | | 63.11 | 105.42 | 76.26 | 76.21 | 80.07 | 63.92 | [a] |

[a]The present paper, assignments were made by using H,C-COSY. [b]Glucopyranosyl residue. [c]Fructofuranosyl residue.

TABLE IV

ACETYL-GROUP CARBONYL AND METHYL $^{13}C$ CHEMICAL SHIFTS

| *Compd.* | *Solvent* | *C=O-1* | *C=O-2* | *C=O-3* | *C=O-4* | *C=O-6* | *Me-1* | *Me-2* | *Me-3* | *Me-4* | *Me-6* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | $CDCl_3$ | | 170.10 | 170.01 | 169.56 | 170.59 | | 20.68 | 20.65 | 20.59 | 20.69 |
| | $C_5D_5N$ | | 170.19 | 170.25 | 169.83 | 170.48 | | 20.44 | 20.50 | 20.45 | 20.56 |
| | $C_6D_6$ | | 169.72 | 169.69 | 169.30 | 169.99 | | 20.17 | 20.35 | 20.19 | 20.27 |
| **2** | $CDCl_3$ | | | 170.37 | 169.55 | 170.55 | | | 20.98 | 20.79 | 20.71 |
| **3** | $CDCl_3$ | 168.80 | 169.16 | 169.87 | 169.38 | | 20.75 | 20.52[a] | 20.55 | 20.46[a] | |
| **4** (G)[b] | $CDCl_3$ | | 169.86 | 170.14 | 168.83 | | | 20.54 | 20.76 | 20.39 | |
| (F)[c] | | | | 169.46 | 169.49 | | | | 20.62 | 20.87 | |

[a]Assignments may be reversed. [b]Glucopyranosyl residue. [c]Fructofuranosyl residue.

**3** was straightforward (Tables I and IV). Previous assignments of the ring $^1H$ and $^{13}C$ resonances and $^1H$–$^1H$ coupling-constants of **2** and **3** have been substantiated and expanded, as shown in Tables II, III, and V. Previous ring-proton assignments and $^1H$–$^1H$ coupling-constants of **4** have been expanded and corrected as shown in Tables II and V. The ring-carbon assignments of **4** are recorded in Table III.

The initial COLOC spectrum of **4** (102 ms evolution period and 40 ms refocussing period) revealed only couplings to the acetyl groups on the glucose residue. Measurement of appropriate long-range coupling-constants showed that all of the ring-proton to carbonyl-carbon couplings were ~3 Hz and that the carbonyl-carbon to methyl-proton couplings were ~7 Hz. These values were similar to those found for **1**–**3**. A second experiment using slightly different delay-times (125 ms evolution period and 42 ms refocussing period) revealed the couplings of the acetyl groups on the fructose residue. However, the coupling of glucose H-2 to its carbonyl group disappeared. In a COLOC experiment covering the entire $^{13}C$

TABLE V

$^1H$–$^1H$ COUPLING CONSTANTS (Hz)

| *Comp.* | *Solvent* | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6a}$ | $J_{5,6b}$ | $J_{6a,6b}$ | *Ref.* |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $CDCl_3$ | 3.5 | 9.5 | 9.5 | 10.0 | 2.5 | 4.6 | 12.2 | 9 |
| | | 3.7 | 10.2 | 9.5 | 10.2 | 2.3 | 4.7 | 12.3 | [a] |
| | $C_5D_5N$ | 4.0 | 9.5 | 9.5 | 10.0 | 2.5 | 5.0 | 12.5 | 9 |
| | | 3.6 | 10.3 | 9.6 | 10.1 | 2.5 | 4.9 | 12.2 | [a] |
| | $C_6D_6$ | 3.5 | 9.5 | 9.5 | 10.0 | 2.5 | 4.5 | 12.2 | 9 |
| | | 3.6 | 10.2 | 9.5 | 10.0 | 2.4 | 4.6 | 12.3 | [a] |
| **2** | $CD_3COCD_3$ | 6.15 | 3.25 | 5.79 | 7.75 | 3.16 | 5.99 | −12.35 | 14 |
| | | $J_{1,3}$ = − 1.39 | | | | | | | |
| | $CDCl_3$ | 6.4 | 3.2 | 6.4 | 6.8 | 2.4 | 6.3 | 14.0 | 15 |
| | | $J_{1,3}$ = 1.3 | | | | | | | |
| | | 6.2 | 3.3 | 5.7 | 7.6 | 3.1 | 5.8 | 12.1 | [a] |
| | | $J_{1,3}$ = 1.2 | | | | | | | |
| **3** | $CDCl_3$ | 7.0 | [b] | [b] | [b] | | | | 16 |
| | | 7.7 | 9.0 | 9.6 | 9.6 | | | | [a] |
| **4** (G)[c] | $CDCl_3$ | 3.8 | 10.0 | 10.0 | 10.0 | 1.75 | 3.25 | 10.25 | 17 |
| | | 3.8 | 9.9 | 9.9 | 9.9 | 1.8 | 3.1 | 10.4 | [a] |
| (F)[d] | | $J_{1a,1b}$ = 10.25 | 5.2 | 5.2 | 5.7 | 5.2 | 10.0 | | 17 |
| | | $J_{1a,1b}$ = 10.3 | 5.2 | 5.2 | 6.0 | 5.4 | 10.0 | | [a] |

[a]The present paper. [b]Not assigned. [c]Glucopyranosyl residue. [d]Fructofuranosyl residue.

spectrum of **4** (rather than just the carbonyl region), the interglycosidic coupling between glucose H-1 and fructose C-2′ was observed.

The acetyl-group assignments of **4** are shown in Tables I and IV. Interestingly, the 4-OAc resonances in the glucose residue are shifted significantly upfield. A similar effect has been seen for the 4-OAc methyl protons in methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-$\alpha$-[9] and -$\beta$-[10] D-glucopyranoside. This upfield shift was attributed to shielding of the 4-OAc by the 6-OTr group, the effect being similar to that observed on almost all proton resonances in aromatic solvents. A similar, although much smaller, shielding-effect occurs for the remaining acetyl-methyl protons of **4**. Shielding and deshielding effects on ring protons in acetyltritylsucrose derivatives have been studied[18].

Assignment of the trityl-group $^1H$ and $^{13}C$ resonances of **4** (Table VI) was accomplished by using COLOC, FUCOUP, and $^1H$–$^1H$ decoupling experiments. A COLOC experiment allowed the methane carbon atoms in each trityl group to be assigned from their coupling to the methylene protons at positions 1′,6′, and 6. Coupling of the methane carbons to the aromatic *ortho* protons allowed assignment of these protons, which were downfield of both the *meta* and *para* protons (Fig. 2a). Decoupling of the *ortho* protons at each position allowed assignment of the *meta* protons on the trityl group at position 1′, while the remaining *meta* and *para* protons were not sufficiently resolved for exact assignment (Fig. 2a). A second COLOC experiment showed coupling of *ortho* protons to the *ortho* (one-bond couplings sometimes appear), *meta*, and *para* carbons, but did not allow unambiguous

TABLE VI

$^1H$ AND $^{13}C$ CHEMICAL SHIFTS AND $^1H$–$^1H$ COUPLING CONSTANTS (Hz) FOR THE TRITYL GROUPS OF 4 IN $CDCl_3$

| *Position* | *Protons* | | | | | *Carbon atoms* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ortho | meta | $J_{o,m}$ | $J_{m,p}$ | $J_{o,p}$ | ipso | ortho | meta | para | *Methane* |
| 1′ | 7.458 | 7.267 | 8.1 | 8.1 | 1.2 | 143.31 | 128.83 | 127.87 | 127.15 | 87.14 |
| 6′ | 7.398 | [a] | 8.1 | [a] | 1.4 | 143.72 | 128.65 | 127.80 | 127.02 | 86.99 |
| 6 | 7.352 | [a] | 8.1 | [a] | 1.4 | 143.72 | 128.78 | 127.70 | 126.81 | 86.17 |

[a] *meta* Protons at these positions and *para* protons from all three positions formed a broad multiplet extending from 7.139–7.227 (Fig. 2a).

distinction between these three groups (Fig. 2b). The *ortho* carbon atoms at each position were identified from one-bond couplings in the H,C-COSY spectrum. Intensity differences in the carbon spectrum were used to distinguish the *meta* and *para* carbon atoms (Fig. 2b). Individual assignment of the *meta* and *para* carbons then followed from the COLOC experiment. Coupling of the *meta* protons to the *ortho* and *meta* carbons at the 1′ position supported the foregoing assignments, as did previous carbon assignments for triphenylmethanol and chlorotriphenylmethane[22]. Finally, a FUCOUP experiment (which, because of its fully coupled nature, works best for quaternary carbon atoms) identified individual *ipso* carbons

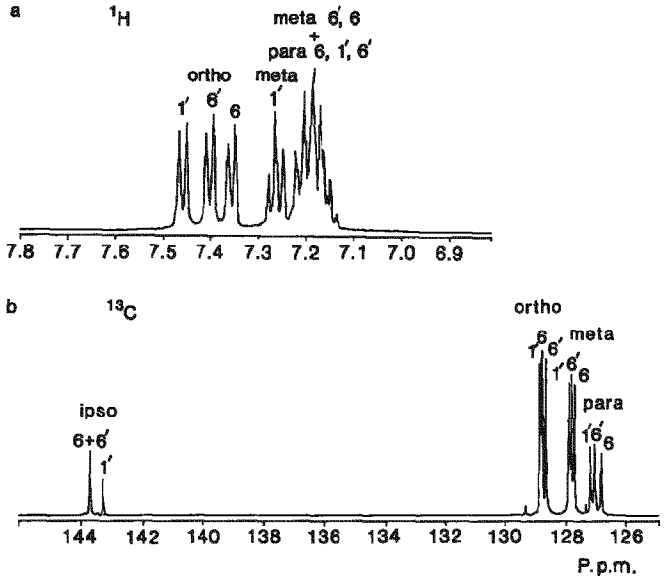



Fig. 2. Aromatic region of the $^1H$ (a) and $^{13}C$ (b) spectra of 4 in $CDCl_3$, showing the trityl-group assignments at each position.

from their coupling to *ortho* protons. This specific two-bond coupling did not appear in any of the COLOC experiments.

## EXPERIMENTAL

All n.m.r. experiments were performed with a Bruker 500 MHz spectrometer equipped with a digital phase-shifter. Wilmad 528-PP or 535-PP sample-tubes were used. Generally, spectra were recorded at a probe temperature of ~27°. The $^1H$ spectra of **1** in $C_6D_6$ were recorded at 24°. The $^{13}C$ spectra of **3** and **4** were recorded at 30°. All solvents were dried (multistage technique) with 3Å molecular sieves (10–20% w/v) which had been activated[23] by heating for 24 h at 300°. Compounds were dried *in vacuo* in the presence of $P_4O_{10}$. Generally, solutions were ~10% (w/v); compound **3** was 8% (w/v). A 10% solution of **1** in $C_6D_6$ appeared to be supersaturated, as crystals appeared after some time; measurements were therefore made on a saturated solution. Compounds **2** and **3** were purchased from the Sigma Chemical Co.; **1** was synthesized according to the literature procedure[9], as was **4** (ref. 24). All spectra were analyzed on a first-order basis, with chemical shifts in p.p.m. ($\delta$) downfield from internal $Me_4Si$ (1% v/v). Coupling constants (Hz) are the measured peak spacings and are accurate to ±0.5 Hz.

H,C-COLOC and H,C-COSY experiments were performed with the microprograms supplied by Bruker (COLOC.AU and X,H CORRD.AU respectively). The delays in the H,C-COSY and H,C-COLOC experiments were typically 3.5 and 102 ms respectively, for the evolution period and 2 and 40 ms respectively, for the refocussing period. A typical COLOC experiment required 12–14 h for data acquisition.

## NOTE ADDED IN PROOF

Several papers have just appeared in which acyl group assignments have been made by n.m.r. techniques[25].

## ACKNOWLEDGMENTS

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## REFERENCES

1 M. L. Appleton, C. E. Cottrell, and E. J. Behrman, *Abstr. Pap. Am. Chem. Soc., Meet.*, 190 (1985) BIOL-39; *Biochemistry*, 24 (1985) 3362.

2 H. Kessler, C. Griesinger, J. Zarbock, and H. R. Loosli, *J. Magn. Reson.*, 57 (1984) 331–336; H. Kessler, C. Griesinger, and J. Lautz, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 444–445; H. Kessler, W. Bermel, and C. Griesinger, *J. Am. Chem. Soc.*, 107 (1985) 1083–1084.

3 A. BAX, *J. Magn. Reson.*, 57 (1984) 314–318.
4 G. BATTA AND A. LIPTÁK, *J. Chem. Soc., Chem. Commun.*, (1985) 368–370.
5 R. L. HALTERMAN, N. H. NGUYEN, AND K. P. C. VOLLHARDT, *J. Am. Chem. Soc.*, 107 (1985) 1379–1387.
6 Y. SATO, R. KOHNERT, AND S. J. GOULD, *Tetrahedron Lett.*, (1986) 143–146.
7 H. KESSLER, W. BERMEL, AND C. GRIESINGER, *J. Org. Chem.*, 51 (1986) 596–601.
8 A. BAX AND M. F. SUMMERS, *J. Am. Chem. Soc.*, 108 (1986) 2093–2094.
9 D. HORTON AND J. H. LAUTERBACH, *J. Org. Chem.*, 34 (1969) 86–92.
10 D. HORTON AND J. H. LAUTERBACH, *Carbohydr. Res.*, 43 (1975) 9–33.
11 K. KOIZUMI AND T. UTAMURA, *Carbohydr. Res.*, 33 (1974) 127–134; D. HORTON AND J. LEHMANN, *ibid.*, 61 (1978) 553–556; K. KOIZUMI AND T. UTAMURA, *ibid.*, 63 (1978) 283–287; M. MANLEY-HARRIS AND G. N. RICHARDS, *ibid.*, 82 (1980) 356–361; J.-P. UTILLE, *ibid.*, 121 (1983) c1–c3; P DAIS AND A. S. PERLIN, *ibid.*, 146 (1986) 177–191, J.-P. UTILLE AND P. VOTTERO, *Bull. Soc. Chim. Fr.*, (1976) 387–394; J.-P. UTILLE AND P. VOTTERO, *ibid.*, (1976) 1101–1104; T. SUAMI, T. OTAKE, T. IKEDA, AND R. ADACHI, *Bull. Chem. Soc. Jpn.*, 50 (1977) 1612–1615; K. KOIZUMI, AND T. UTAMURA, *Chem. Pharm. Bull.*, 29 (1981) 2791–2798.
12 L. PONCINI, *Bull. Soc. Chim. Belg.*, 90 (1981) 57–62.
13 D. GAGNAIRE, D. HORTON, AND F. R. TARAVEL, *Carbohydr. Res.*, 27 (1973) 363–372.
14 M. RICO AND J. SANTORO, *Org. Magn. Reson.*, 8 (1976) 49–55.
15 L. D. HALL AND L. F. JOHNSON, *Tetrahedron*, 20 (1964) 883–889.
16 M. MATSUI AND M. OKADA, *Chem. Pharm. Bull.*, 18 (1970) 2129–2131.
17 C. W. HOLZAPFEL, J. M. KOEKEMOER, AND C. F. MARAIS, *S. Afr. J. Chem.*, 37 (1984) 57–61.
18 T. OTAKE, *Bull. Chem. Soc. Jpn.*, 47 (1974) 1938–1944.
19 K. BOCK AND C. PEDERSEN, *Adv. Carbohydr. Chem. Biochem.*, 41 (1983) 27–66.
20 A. I. KALINOVSKII AND E. V. EVTUSHENKO, *Khim. Prir. Soedin.*, (1979) 6–8.
21 R. D. GUTHRIE AND R. W. IRVINE, *Carbohydr. Res.*, 82 (1980) 207–224.
22 A. LYČKA, D. ŠNOBL, K. HANDLÍŘ, J. HOLEČEK, AND M. NÁDVORNÍK, *Collect. Czech. Chem. Commun.*, 46 (1981) 1383–1388.
23 D. R. BURFIELD, G.-H. GAN, AND R. H. SMITHERS, *J. Appl. Chem. Biotechnol.*, 28 (1978) 23–30.
24 G. G. MCKEOWN, R. S. E. SERENIUS, AND L. D. HAYWARD, *Can. J. Chem.*, 35 (1957) 28–36.
25 H. KESSLER, W. BERMEL, C. GRIESINGER, AND C. KOLAR, *Angew. Chem.*, 98 (1986) 352–353; T. NISHIDA, C. R. ENZELL, AND G. A. MORRIS, *Mag. Reson. Chem.*, 24 (1986) 179–182; T. NISHIDA, G. A. MORRIS, I. FORSBLOM, I. WAHLBERG, AND C. R. ENZELL, *J. Chem. Soc., Chem. Commun.*, (1986) 998–1000; Y. KURAMITSU, M. IKURA, AND K. HIKICHI, *Rep. Prog. Polym. Phys. Jpn.*, 28 (1985) 531–534.