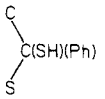
same concentration. With delocalization of the negative charge in the organic persulfide anion, the disulfide bond can acquire multiple-bond character as in the supersulfide ion where the bond order is formally 1.5. Thus, ν(S–S) frequencies should be similar.

As an alternative to the persulfide assignment, we associate the 545-nm absorbing species with the cis isomer of the dithio anion **5**. This may be the preferred form on initial cleavage of the dithiolylium ring, although a mechanism that postulates formation of an intermediate adduct can produce either cis or trans isomers upon collapse of the tetrahedral carbon center,



In dilute solutions the cis isomer is expected to be unstable and, thus, rapidly rearrange to give a trans form such as **9**. The very similar RR spectra that were obtained with excitation into the 545-nm band of the parent chromophore, Figure 1, spectrum C, and into the 473-nm band of the daughter, Figure 1, spectrum D, attest to the conclusion that the two species possess very similar structures. Geometrical isomerism is anticipated to have a minimum effect on the positions of most vibrational modes, stretching and bending, in the dithio anion, except, perhaps, on the energies of bending modes in the immediate vicinity of the geometrical change. In the low-symmetry molecules (C_{2v} for cis isomer, C_s for trans), local bonding properties dominate in their influence on vibrational spectra. The 600-cm^{-1} RR band that is noticeably affected lies in the region of CCS and CCC angle bending mode frequencies.

Conclusions

The present RR study shows the high potential of this technique in obtaining information on the mechanisms of disulfide bond cleavage reactions. When parity-allowed bands of the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ type are present in the chromophoric molecule, such as the cyclic disulfides of the 1,2-dithiolylium cation and its reaction products, excited states and chromophore-linked vibrations and therefore intermediate reaction species can be identified. In nucleophilic reactions of this cation, intermediates and products that retain at least one sulfur atom absorb either in the 340–400-nm range or to longer wavelengths and thus serve as resonance Raman probes of the reaction pathway.

In the present study of the reaction between 3,5-diphenyl-1,2-dithiolylium perchlorate and excess sodium sulfide in ethanol, we prefer to assign the shorter lived transient that absorbs maximally at 545 nm to the open-chain disulfide anion. Therefore, the open-chain aliphatic disulfides and the cyclic disulfide cation appear to have a common persulfide intermediate in their nucleophilic reaction with hydrosulfide ion. The possible existence of a shorter lived cation–hydrosulfide adduct species remains to be proved. The presence of a fleeting perthiolate ligand suggests that it may be trapped in chelate form with an appropriate metal ion. Perthiolate functional groups have reportedly been obtained by addition of elemental sulfur to a copper(I) cluster complex, $Cu_8L_6^{4-}$, where L = 1,1-dicarbobutoxyethylenedithiolate,[17] and in nickel(II) dithiocarboxylate complexes.[18] The longer lived red species, λ_{max} 473 nm, has been assigned to the trans isomer of the dithioacetylacetonate anion, which results from reaction of the open-chain disulfide anion with another mole of hydrosulfide. Again, this is similar to the reaction mechanism that was suggested for the reaction of open-chain organic disulfides with hydrosulfide ion.

Acknowledgment. We thank Dr. Paul Carey of the National Research Council of Canada for use of the Raman spectrometer in the ultraviolet region and Dr. G. Edwin Wilson for helpful discussions.

Registry No. 1 perchlorate, 1270-66-2; bis(1,3-diphenyl-1,3-propanedithionato-*S*,*S*′)nickel, 21609-14-3; sodium sulfide, 1313-82-2.

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Natural-Abundance One-Bond ^{13}C–^{13}C Coupling Constants in Monosaccharide Derivatives and in Sucrose

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Abstract: Natural-abundance one-bond ^{13}C–^{13}C coupling constants have been measured (at 25.16 MHz) for monosaccharide derivatives and for sucrose in the presence of the strong signals due to species containing only one ^{13}C isotope. In the case of strong AB systems the measurement of the carbon–carbon couplings was carried out also at 50.31 MHz via double quantum coherence. Equations are established for the calculation of coupling constants for situations where all four lines of an AB or AX system cannot be observed. The measured one-bond coupling constants have been correlated with the stereochemical changes in the carbohydrates studied.

Introduction

Since the advent of carbon-13 nuclear magnetic resonance spectroscopy in the late 1960's, a vast amount of research has been directed with this technique toward the structural elucidation and conformational analysis of complex molecules.[2] Application of ^{13}C NMR spectroscopy has been focused on the chemical shift of this nucleus or on ^{13}C–^{1}H coupling constants. However, recent advances in instrumentation and the availability of high-field spectrometers have increased greatly the scope and utility of ^{13}C–^{13}C coupling constants at natural abundance in structural and

(1) (a) Central Research Institute for Chemistry, Hungary; (b) Institut de Chimie des Substances Naturelles, France.

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conformational studies of medium molecular weight substances.

The interest in carbon–carbon coupling has increased substantially during the last few years in connection with their use in biosynthetic studies.[3] The potential of using one-bond carbon–carbon coupling constants for unequivocal spectral analysis of compounds of known constitution or for structural investigations of new substances has been recognized a long time ago. However, as a result of problems related to sensitivity, carbon–carbon couplings at natural abundance have been reported mostly[4] on compounds of low molecular weight.

The importance of one-bond or long-range ^{13}C–^{13}C coupling constants in the conformational analysis of carbohydrate derivatives has been demonstrated previously.[5] Some unambiguous determinations of carbon resonance assignments in monosaccharides were also based on carbon–carbon coupling constants.[5b,c] However, in earlier investigations these informations were limited by the available specific labeling techniques with ^{13}C at C-1 and at C-6.[5b,c,e] Specifically labeled carbohydrates at C-2, C-3, C-4, or C-5 were not at the disposal of the spectroscopists. Studies aimed at obtaining carbon–carbon coupling data have also been undertaken on carbohydrates uniformly enriched to high levels of ^{13}C by biosynthetic methods.[5a,d,6,7] Unfortunately, the complexity of the nuclear magnetic resonance spectra of these compounds precluded an evaluation even of certain one-bond coupling constants. In a recent study on a uniformly labeled material the spectral interpretation could be achieved with the help of ^{13}C homonuclear decoupling experiments.[5d] In the light of these results the importance of obtaining informations about ^{13}C–^{13}C coupling constants at natural abundance on carbohydrates became obvious.

The observation of carbon–carbon couplings requires the presence of two carbon-13 isotopes. At natural abundance there is approximately one such molecule out of 10000. In proton-decoupled carbon-13 spectra the resonances due to these species appear as weak doublet-type satellites superimposed on the signals of molecules containing only one ^{13}C isotope. As a consequence of the very low natural abundance of species with three ^{13}C spins (1 in 10^6 molecules) the spectra of interest are always of the AX or AB type. A prerequisite for the determination of carbon–carbon couplings at natural abundance is an extremely high signal-to-noise ratio and sharp resonance lines. Furthermore, the importance of very good line shapes cannot be overemphasized. The latter is necessary in order to prevent the satellites being partially or completely hidden by the very strong central lines due to species containing only one ^{13}C isotope. Problems originating from the central line spinning side bands overlapping with the satellite lines can be eliminated by using variable spinning speeds determined according to the value of the expected carbon–carbon coupling constants.

In the presence of the strong central lines due to molecules with a single ^{13}C nucleus, the observation of long-range ^{13}C–^{13}C coupling constants in most cases is impossible.[8] The corresponding satellites are on the steeply rising flanks of the central lines and couplings <6 Hz are generally obscured in molecules of biological interest.

In the present investigation, the width of the central lines at 0.55% height in the case of proton bearing carbons was about 6–7 Hz as a result of the relatively short spin–spin relaxation times associated with substances whose molecular weight is in the 150–250 range.[9] For the quaternary carbon of sucrose (**6**) the corresponding line width at 0.55% height was only 3.5 Hz.

An important drawback in the detection of carbon–carbon couplings by this method may arise from the presence of impurities in concentrations comparable to the rare double-labeled species of interest. In such cases the spectroscopic investigation at two different spectrometer frequencies should be advocated.

In order to improve the technique of observation of ^{13}C–^{13}C coupling constants at natural abundance, recently Freeman proposed a new method.[10] The latter enables the spectroscopist to investigate one-bond and long-range carbon–carbon couplings by suppressing the strong signals from molecules with a single carbon-13 nucleus. Spinning side bands and signals due to small impurities are also eliminated. Excellent suppression ratios were achieved by momentary conversion of the magnetization from coupled spins into double quantum coherence and phase cycling. It has been shown that the main restriction on the generality of this technique arises from the condition for optimum transfer into double quantum coherence:

$$\tau = (2n + 1)/(4J_{cc}) \qquad n = 0, 1, 2, \ldots$$

where τ is the delay in the pulse sequence

$$90° (X)\text{–}\tau\text{–}180° (\pm Y)\text{–}\tau\text{–}90° (X)\text{–}\Delta\text{–}90° (\phi)\text{–acquisition } (\psi)$$

This paper describes the results of an investigation on the measurement of the one-bond carbon–carbon coupling constants at natural abundance of monosaccharide derivatives (from **1a** to **5b**) and of a disaccharide sucrose (**6**). A similar study on the long-range carbon–carbon coupling constants of carbohydrates with Freeman's technique[10] is in progress in our laboratories. The work was undertaken in order to deepen our knowledge about these simple compounds of fundamental importance and also to demonstrate the utility of this diagnostically powerful research tool for carbon signal assignments and for structural studies on carbohydrates of unknown constitution.

Materials and Methods

Published procedures were used[11,12] for the preparation and purification of the methyl glycosides used in this study. L-Rhamnose and sucrose were obtained from Fluka and used without purification. The proton-decoupled natural-abundance ^{13}C Fourier transform (FT) NMR spectra of the carbohydrates were recorded at 25.16 MHz with a Varian XL-100-15 spectrometer equipped with a Varian 620/L-100 computer operated with the MOS-E disk system (no quadrature detection was available); 12-mm o.d. tubes were used containing 1.5 g of the sugars and 2–3 mL of D_2O at a temperature of 90 °C. For the measurement of the ^{13}C–^{13}C couplings the spectrum was accumulated for 6–10 h in the case of the monosaccharide derivatives and for 16 h for sucrose (**6**). The number of data points was 32K with a frequency range of 2000 Hz giving a digital resolution of 0.12 Hz/point. The sample tubes were rotated slowly (10 Hz). Resolution enhancement was applied using the Gaussian multiplication technique.[13]

The proton-decoupled FT NMR spectra of **2a**, **3a**, **3b**, and **4a** were also recorded at the same concentration at 50.31 MHz on a Varian XL-200 or on a Bruker WP-200 spectrometer using Freeman's INADEQUATE technique.[10] Optimization was set to J = 40 Hz ($J\tau$ = 3/4); 10-mm o.d. tubes were used. The spectra were accumulated for 10 h. The number of data points was 32K with a frequency range of 5000 Hz giving a digital resolution of 0.32 Hz/point. Resolution enhancement was also applied.[13]

Results

Natural-abundance ^{13}C–^{13}C coupling constants for the monosaccharides studied and for sucrose (Figure 1) are given in Tables I and II, respectively. Chemical shift assignments were already

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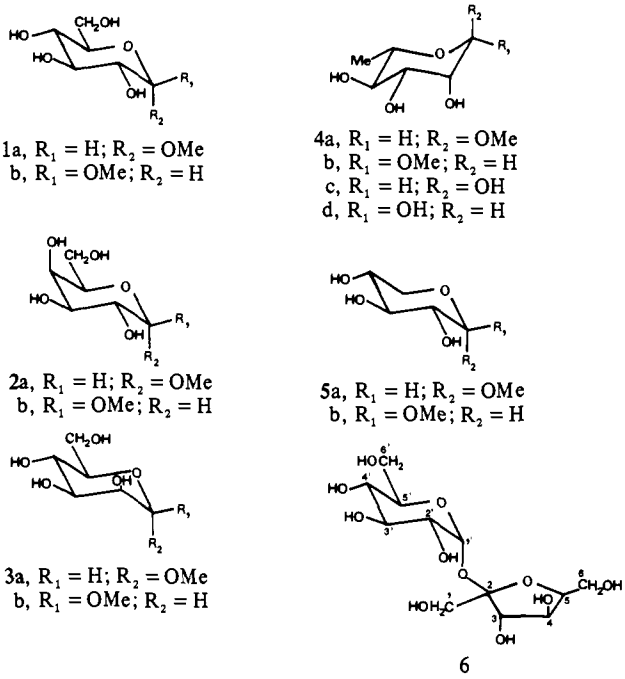

Figure 1.

Table I. Natural-Abundance One-Bond ^{13}C–^{13}C Coupling Constants (Hz) in the Monosaccharide Derivatives Studied[a,b]

	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
methyl α-D-glucopyranoside (**1a**)	46.3	38.3	38.6	39.3	43.3
methyl β-D-glucopyranoside (1b)	46.9	38.6	39.3	40.3	43.2
methyl α-D-galactopyranoside (2a)	46.3	39.0	37.5*	38.4	44.6
methyl β-D-galactopyranoside (2b)	46.6	39.7	38.2	38.6	44.6
methyl α-D-mannopyranoside (3a)	47.4	37.5*	39.9	40.1	43.8
methyl β-D-mannopyranoside (3b)	43.6	38.4*	40.2	41.0	43.0
methyl α-L-rhamnopyranoside (4a)	47.2	37.4*	39.3	40.2	41.2
methyl β-L-rhamnopyranoside (4b)	43.6	38.2	39.9	*c*	41.0
α-L-rhamnose (4c)	46.5				40.5
β-L-rhamnose (4d)	42.5				40.5
methyl α-D-xylopyranoside (5a)	46.4	38.0	38.4	39.4	
methyl β-D-xylopyranoside (5b)	46.8	38.8	39.1	39.9	

[a] Asterisks denote values obtained in strong coupling cases by Freeman's 'INADEQUATE' technique.[10] Optimization at $J = 40$ Hz ($J\tau = 3/4$).[10c] [b] For L-rhamnose only $J_{1,2}$ and $J_{5,6}$ were measured. [c] The very strong AB system [$J/\Delta\nu$ (100.61 MHz) ~4] precluded the measurement of this coupling constant. However, with the help of the satellites unambiguous signal assignments were achieved for the two very closely spaced resonances of 4b: δ (C-1)102.2, (C-2)71.5, (C-3)74.1, (C-4)73.35, (C-5)73.25, (C-6)17.9, and (OMe)57.8 ppm.

Table II. Natural-Abundance One-Bond ^{13}C–^{13}C Coupling Constants (Hz) in Sucrose (6)

$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$
52.0	45.7	40.3	39.8	42.2	46.8	38.0	38.6	39.6	42.9

known[5b,14,15] and agree perfectly with the connectivity deduced from carbon–carbon coupling constants and satellite distributions. In Figure 2 the spectral section of C-3 and C-5 of methyl β-D-glucopyranoside (**1b**) is represented. The satellite signals were attributed as described previously[16] on the basis of their unsymmetrical distribution with respect to the strong central lines. All

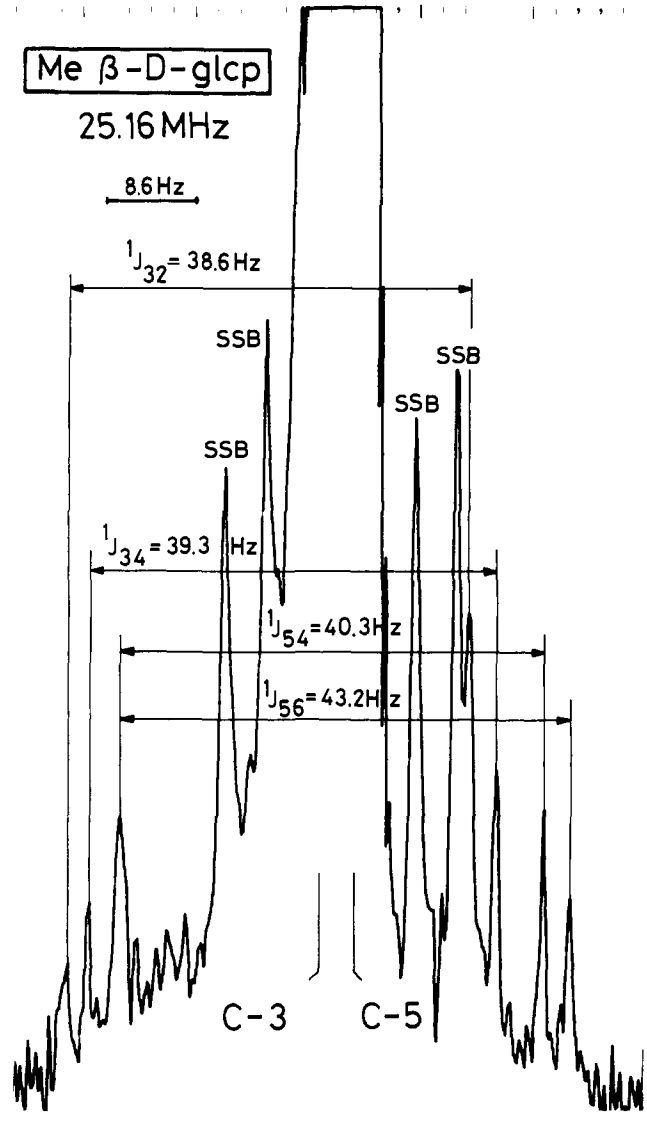

Figure 2. ^{13}–^{13}C coupling constants (spectral region of C-3 and C-5) in methyl β-D-glucopyranoside (**1b**) observed at 25.16 MHz in the presence of the strong signals due to species containing only one ^{13}C isotope (SSB = spinning side bands). Total acquisition time: 7 h.

the satellite assignments were calculated with the recently developed computer program CABSA for the determination of matching satellite pairs[17] and evaluating the isotope shifts.[18]

In the measurement of ^{13}C–^{13}C coupling constants the strong central lines or spinning side bands may preclude the observation of all the four satellites of AB or AX systems. The detection of all the satellite signals may be difficult also in situations when they are not hidden by other signals, but the chemical shift difference between the interacting nuclei is small. As a result of strongly coupled AB systems the weak outer satellites may be buried in the noise of the spectrum. In studying the carbohydrate derivatives we encountered some strong coupling situations [$J/\Delta\nu$ (25.16 MHz): (**2a**) $J_{2,3} = 1.22$, $J_{3,4} = 4.3$; (**3a**) $J_{2,3} = 2.0$] where the detection of the outer satellites was not easy. The obvious solution to such problems is to carry out the measurement of the ^{13}C–^{13}C coupling constant at higher magnetic field. However, on the one hand, a number of research laboratories do not have superconducting NMR facilities; on the other, for instance, $J/\Delta\nu$ for **2a** $J_{3,4}$, would be still too high even at 100.6 MHz for the outer satellites to be readily detected at reasonable concentrations. In

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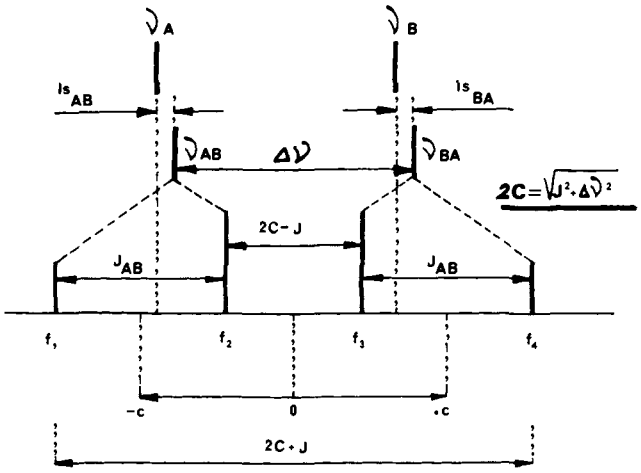

Figure 3. ν_A chemical shift of carbon A; ν_{AB} chemical shift of carbon A in molecules with a neighboring ^{13}C nucleus B; f_1 and f_2 resonance frequencies of the outer and inner satellites respectively of carbon A in the doubly labeled isotopomer; Is_{AB} isotope shift of carbon A induced by the neighboring ^{13}C nucleus B; J_{AB} coupling constant.

this connection a fundamental question has arisen. Knowing the positions of the two central lines due to molecules with a single ^{13}C nucleus, would it be possible to determine with good accuracy the one-bond carbon–carbon coupling constants in strongly coupled AB systems only from the positions of the two strong inner satellites? Also, as an extension of this problem, knowing the positions of the two central lines, would it be possible to determine the one-bond carbon–carbon coupling constant in AX systems only from the positions of the two outer satellites or from one outer and one inner satellites? A solution of these problems is proposed by eq 1–3.

According to the analysis of the AB spin system,[19,20] two fundamental equations must be considered here:

$$f_2 - f_3 = \sqrt{J^2 - \Delta\nu^2} - J \qquad \text{(a)}$$

$$\Delta\nu = \sqrt{(f_1 - f_4)(f_2 - f_3)} \qquad \text{(b)}$$

Inspection of Figure 3 reveals that

$$f_1 - f_4 = 2J + f_2 - f_3$$

Consequently, eq b′ can be written:

$$\Delta\nu = \sqrt{(2J + f_2 - f_3)(f_2 - f_3)} \qquad \text{(b′)}$$

It follows that

$$\frac{\text{(b′)}}{\text{(a)}} = \frac{\Delta\nu}{|f_2 - f_3|} = \frac{\sqrt{(2J + f_2 - f_3)(f_2 - f_3)}}{|f_2 - f_3|} = \sqrt{1 + 2\frac{J}{|f_2 - f_3|}}$$

from where the important eq 1 can be easily deduced, allowing the determination of the coupling constant from the two linear satellites only:

$$J = \frac{1}{2}\left(\frac{\Delta\nu^2}{|f_2 - f_3|} - |f_2 - f_3|\right) \qquad (1)$$

The same procedure affords eq 2 permitting the calculation of the coupling constant from one inner and one outer satellite:

$$J = \sqrt{(f_2 - f_4)^2 - \Delta\nu^2} \text{ or } J = \sqrt{(f_1 - f_3)^2 - \Delta\nu^2} \qquad (2)$$

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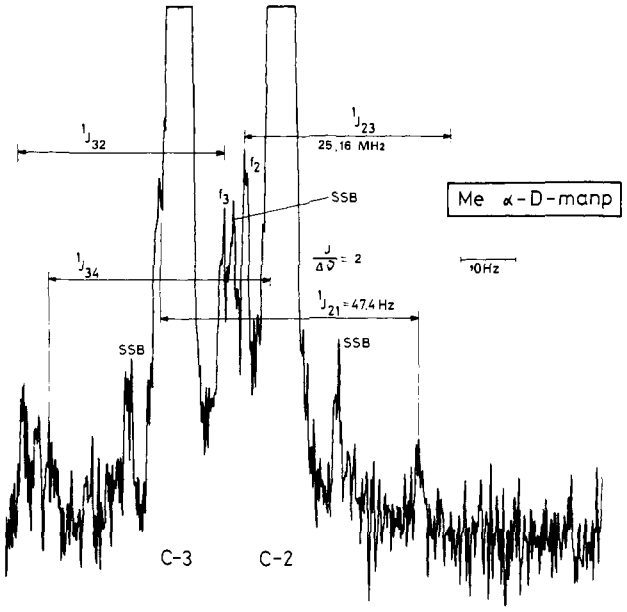

Figure 4. ^{13}C–^{13}C coupling constants (spectral region of C-2 and C-3) in methyl α-D-mannopyranoside (**3a**) observed at 25.16 MHz in the presence of the strong signals due to species containing only one ^{13}C isotope (SSB = spinning side bands). In view of the strong AB system, the weak outer satellites f_1 and f_4 cannot be detected. The resonance frequency of f_2 and f_3 cannot be determined accurately. Total acquisition time: 9.5 h.

and eq 3 allowing the determination of the coupling constant by knowing the resonance frequencies of the two outer satellites only.

$$J = \frac{1}{2}\left(|f_1 - f_4| - \frac{\Delta\nu^2}{|f_1 - f_4|}\right) \qquad (3)$$

In our investigation on the determination of one-bond ^{13}C–^{13}C coupling constants of carbohydrates we had to use eq 1 several times in situations where the resonance frequencies of the inner satellites were only available. However, before doing this operation we evaluated the accuracy of eq 1 by considering its sources of errors. They are of two types from the point of view of $\Delta\nu$: one originating from an insufficient digital resolution and one from a difference in the isotope shifts[18] induced by the interacting nuclei on each other. In the present investigation, for the sp^3-hybridized carbons of the carbohydrates the measured isotope shifts were between 0 and −0.03 ppm. On the other hand, in our experimental conditions the error originating from the digital resolution should be about 0.12 Hz. Thus the total error of $\Delta\nu$ should be less than 0.9 Hz. The source of error as far as $|f_2 - f_3|$ is concerned depends mainly on the digital resolution. The error ΔJ can be expressed by:

$$\Delta J = \frac{\Delta\nu}{|f_2 - f_3|}\Delta(\Delta\nu) + \frac{1}{2}\left[1 + \left(\frac{\Delta\nu}{f_2 - f_3}\right)^2\right]\Delta(|f_2 - f_3|) \qquad (4)$$

ΔJ can be of the order of 1.5–2.0 Hz in the case of strong AB systems ($J/\Delta\nu \simeq 1$), and, in fact, this limits the use of (1).

Accurate values for the one-bond carbon–carbon coupling constants could not be obtained in four cases [(**2a**) $J_{3,4}$, (**3a**) $J_{2,3}$, (**3b**) $J_{2,3}$, and (**4a**) $J_{2,3}$] because of the presence of strong AB systems and also because of satellite overlapping with other signals (Figure 4). For these situations, therefore, the measurement of the ^{13}C–^{13}C coupling constants was repeated at 50.31 MHz by using Freeman's INADEQUATE technique[10] (Figure 5). This enabled us to determine carbon–carbon coupling constants at natural abundance by suppressing the strong signals from molecules with a single carbon-13 nucleus. It has been shown recently that in order to obtain the optimum intensity for the satellites of the strongly coupled nuclei, the condition $J\tau = 3/4$ should be used instead of $J\tau = 1/4$ as is usual for weak coupling situations.[10c] Optimization of the spectrum was set choosing $J = 40$ Hz. Under

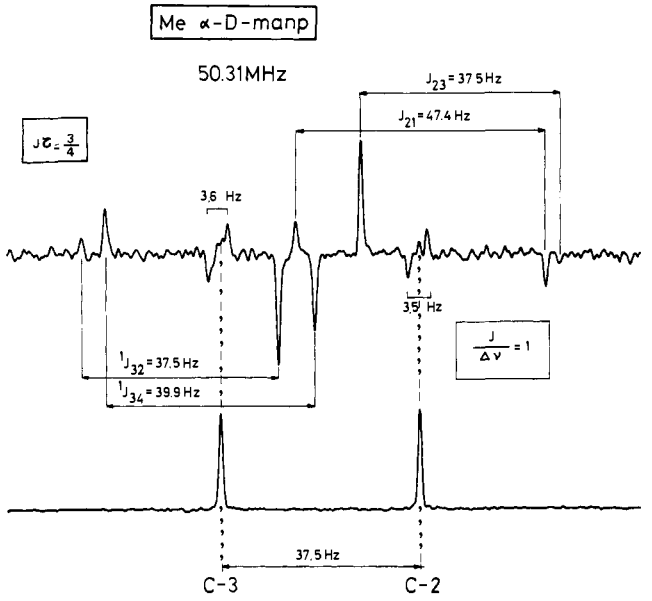

Figure 5. ^{13}C–^{13}C coupling constants (spectral region of C-2 and C-3) in methyl α-D-mannopyranoside (**3a**) observed at 50.31 MHz via double quantum coherence.[10c] Optimization at J = 40 Hz ($J\tau$ = 3/4). The inner satellites of the strong AB system ($J/\Delta\nu$ = 1) show relatively high intensity. Satellites due to ^{13}C–^{13}C couplings higher or much smaller (long-range coupling 3.6 and 3.5 Hz) than the optimization value appear with considerably reduced intensity. Total acquisition time: 8 h.

these conditions the satellite lines of the strong AB systems exhibited nearly maximum intensity. In Figure 5 the spectral section of C-2 and C-3 in methyl α-D-mannopyranoside (**3a**) is represented. A remarkable suppression ratio of 1000:1 for the central line has been achieved during this experiment carried out in Professor Freeman's laboratory. Satellite lines due to ^{13}C–^{13}C coupling higher ($J_{2,1}$ = 47.4 Hz) or much smaller (long-range couplings, 3.6 and 3.5 Hz) than the optimization value appeared as expected with reduced intensity. Half-line width of the satellite lines was the same as for the experiments performed on the XL-100 spectrometer. The application of this extremely important new technique permitted the accurate determination of the one-bond ^{13}C–^{13}C coupling constants for the four coupled systems mentioned above (Table I) where the measurement with the "old" central band + satellite method was not successful.

Discussion

Influence of the Configuration of the Anomeric Substituent on the One-Bond ^{13}C–^{13}C Coupling Constants in the Carbohydrates Studied. (a) If the carbohydrate has an equatorial hydroxyl group at C-2, $J_{1,2}$ is a little larger [$\Delta J_{1,2}$(**1b**–**1a**, 0.6 Hz; **2b**–**2a**, 0.3 Hz; **5b**–**5a**, 0.4 Hz)] in the corresponding methyl glycosides when the anomeric substituent is equatorially oriented.

(b) If the carbohydrate has an axial hydroxyl group at C-2, as reported previously,[5b] $J_{1,2}$ is considerably larger [$\Delta J_{1,2}$(**3a**–**3b**, 3.8 Hz; **4a**–**4b**; 3.6 Hz; **4c**–**4d**, 4.0 Hz)] in the corresponding methyl glycosides or free sugars when the anomeric substituent is axially oriented [$J_{1,2}$ is smaller in the free sugars than in the methyl glycosides: $\Delta J_{1,2}$(**4a**–**4c**, 0.7 Hz; **4b**–**4d**, 1.1 Hz)].

(c) The coupling constants ($J_{2,3}$, $J_{3,4}$, and $J_{4,5}$) in the methyl glycoside pairs are slightly larger (0.2≃1.0 Hz) when the anomeric substituent is equatorially oriented.

Influence of the Configurational Change of a Hydroxyl Group on the One-Bond ^{13}C–^{13}C Coupling Constants. Replacement of an equatorial hydroxyl group at C-4 or at C-2 by an axial hydroxyl group is reflected in two ways by the alteration of the ^1J coupling constants.

(a) A carbon atom to which an axial hydroxyl group is attached exhibits a coupling constant with the adjacent carbon atoms which is smaller (0.2–1.7 Hz) than in the case of the corresponding methyl D-glucopyranosides (this observation is not related to $J_{1,2}$ where other effects predominate[5b,e]).

(b) The α,β-carbon bonds with respect to the axially substituted sites show larger coupling constants [$\Delta J_{2,3}$(**2a**–**1a**, 0.7 Hz; **2b**–**1b**, 1.1 Hz), $\Delta J_{5,6}$(**2a**–**1a**, 1.3 Hz; **2b**–**1b**, 1.4 Hz), $\Delta J_{3,4}$(**3a**–**1a**, 1.3 Hz; **3b**–**1b**, 0.9 Hz)] than in the case of the corresponding methyl D-glucopyranosides.[21]

In addition to these observations the following results are of interest. (a) As reported previously,[5b] $J_{5,6}$ in the hexopyranosides is smaller than $J_{1,2}$ but is significantly larger than $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$. The latter observation can be related to the well-known fact that methyl carbons exhibit larger coupling constants than methylene or methine carbons in cyclohexane systems.[4]

(b) In the 6-deoxy sugars, as a result of the absence of an oxygen atom, $J_{5,6}$ is smaller than in the other hexopyranosides (this value is smaller in the free sugars than in the corresponding methyl glycosides).

(c) In the two pentopyranosides studied (**5a** and **5b**), $J_{4,5}$ is almost identical with the value in the corresponding hexopyranosides **1a** and **1b**.

(d) As far as sucrose (**6**) is concerned coupling constants for the pyranose ring are very similar to those of methyl α-D-glucopyranoside (**1a**). For the furanose ring $J_{1,2}$ appears to be a little larger than expected.[4] (The carbon connectivity pattern of sucrose has recently been determined by a two-dimensional experiment although the one-bond ^{13}C–^{13}C coupling constants have not been reported[22]).

Conclusion

In the study presented here one-bond carbon–carbon coupling constants were measured at 25.15 and 50.3 MHz at natural abundance for some biologically important carbohydrates. It is obvious that with high-field spectrometers these experiments would require only moderately concentrated solutions and much shorter acquisition time. However, isotopic labeling remains in the carbohydrate field an extremely important technique especially for the measurement and the interpretation of long-range carbon–carbon coupling constants.

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(21) Similar observations have been made in studying the ^{13}C–^{13}C coupling constant variations in substituted cyclohexanol derivatives: G. Lukacs and A. Neszmelyi, unpublished results.

(22) A. Bax, R. Freeman, T. A. Frenkiel, and M. H. Levitt, *J. Magn. Reson.*, **43**, 478 (1981).