ASSIGNMENT TECHNIQUES FOR ^{29}Si NMR SPECTRA OF PERTRIMETHYLSILYLATED PRODUCTS. ^{29}Si SATELLITES IN ^{13}C NMR SPECTRA MEASURED WITH SELECTIVE ^{29}Si DECOUPLING

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It is shown that measurement of ^{29}Si satellites in proton decoupled ^{13}C NMR spectra with selective ^{29}Si decoupling allows correct assignment of lines in ^{29}Si NMR spectra of pertrimethylsilylated products. The experimental scheme, where selective decoupling and FID phase alternation are used (difference spectroscopy), has sufficient sensitivity and selectivity, provided the ^{29}Si lines are well separated. The main advantage of the method is that it can be applied to compounds with unresolved ^{1}H NMR spectra or with no protons in γ position to the silicon atom.

The main obstacle for a wider application of ^{29}Si NMR to analysis of pertrimethylsilylated products is the lack of suitable assignment techniques. Empirical assignment rules are difficult to formulate for ^{29}Si NMR since, in general, the silicon chemical shifts are not an additive property of the substituents. Exact experimental techniques for ^{29}Si line assignment can utilize only couplings of the silicon with the rest of the molecule because of all the NMR parameters of the trimethylsilyl group only the silicon-29 chemical shift is sufficiently sensitive to structural changes (the so-called isolating effect of the silicon atom).

In compounds with functional groups XH bonded to hydrogen bearing carbon atoms (CH_n) the trimethylsilylation yields moieties of the type $(CH_3)_3SiXCH_n$ in which spin–spin coupling between silicon and CH_n protons can be, at least in principle, used for the assignment purposes. Selective deuteration[1], off-resonance selective decoupling[2] and ^{29}Si INDOR (ref.[3]) on these protons have been used to demonstrate feasibility of this approach. No method, however, has been suggested for groups bonded to carbon atoms that bear no hydrogen atom. Such functional groups are frequently encountered in lignin fractions (carboxyl and phenol groups), enols, and other materials. In the search for an assignment technique which would be adequate in such cases we have tried two, both based on $^2J(^{13}C-O-^{29}Si)$ spin–spin coupling: heteronuclear $(^{29}Si-^{13}C)$ INADEQUATE (ref.[4]) and measurements of ^{29}Si satellites

in ^{13}C NMR spectra with selective ^{29}Si decoupling. In the present paper we will describe the latter method as its implementation on different spectrometer systems is easier.

RESULTS AND DISCUSSION

Measurement of ^{29}Si satellites in the ^{13}C NMR spectra is a more sensitive alternative to the complementary measurement of ^{13}C satellites in the ^{29}Si spectra and the intensity of the central line relative to satellites in the ^{13}C spectra is approximately 5 times lower than in ^{29}Si spectra.

Since the two-bond couplings $^2J(^{13}\text{C}\text{---O---}^{29}\text{Si})$ are small, even the stronger ^{29}Si satellites in the ^{13}C NMR spectrum may be obscured by the strong central peak. Therefore, partial suppression of the main central line is necessary. In our selective decoupling experiments the following scheme to suppress the central line is used.

^{13}C NMR FIDs are recorded with proton broad-band decoupling and with selective ^{29}Si decoupling. The silicon decoupler frequency alternates between two values in the two consecutive FIDs which are summed with opposite signs, *i.e.* all the added FIDs are recorded with one decoupler frequency and all the subtracted ones with the other frequency. The appearance of the resulting spectrum depends on the ^{29}Si NMR frequency and decoupling frequencies. If both decoupling frequencies are far away from the silicon resonance frequency, the subtracted FIDs completely cancel the added FIDs and there is no signal in the spectrum. When the decoupling frequencies are near the ^{29}Si resonance, the coupling is reduced and, as a result, the center line is
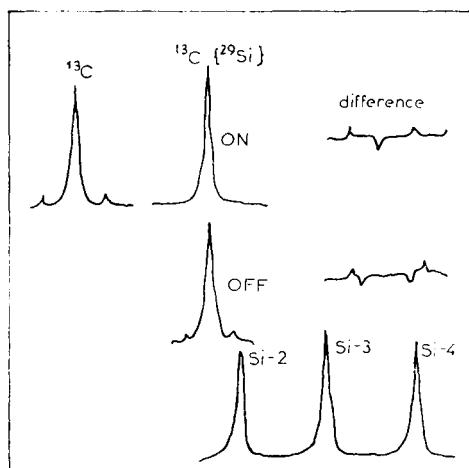

Fig. 1

Scheme of resultant spectrum formation from two subtracted spectra with different selective decoupling frequencies

suppressed and two pairs of satellites with opposite phases appear in the spectrum. Whether the inner or outer pair of satellites has positive intensity depends on which of the two frequencies is closer to the resonance. (Fig. 1). When one of the decoupler frequencies is in exact resonance, the pair of satellites collapses into the central line which is thus enhanced and cannot be fully cancelled by the alternating scans. Similarly the satellites in the alternating scans are not compensated either and, as a result, we obtain a $(\pm 1):(\pm-2):(\pm 1)$ triplet, the sign combination depending on whether the added or subtracted FIDs are in exact resonance. A series of such experiments with different decoupling frequencies can yield an assignment of multi-line ^{29}Si NMR spectrum, provided that the ^{13}C NMR spectrum of the compound is well resolved and assigned.

For a test of the method we have chosen 2,3,4-O-tris(trimethylsilyl)-1,6-anhydro--β-D-glucopyranose (*I*) and methyl 2,3,4-O-tris(trimethylsilyl)-β-D-xylopyranoside (*II*) because the ^{29}Si NMR spectra of these compounds can be assigned also by other method[3] as the siloxy groups are bonded to carbon atoms of CH groups.
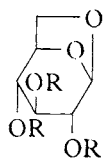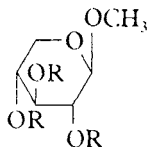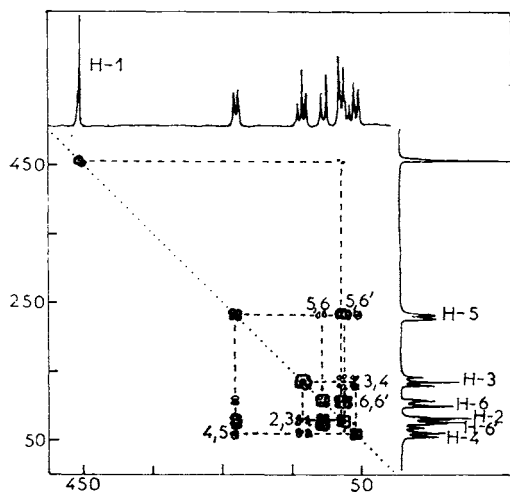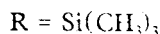

$$I \qquad\qquad II$$

$$R = Si(CH_3)_3$$

FIG. 2

Partial ^1H NMR spectra of *I* in hexadeuteriobenzene. Upper spectrum is standard one-dimensional spectrum, lower spectrum is a contour plot of 2D homonuclear shift correlated spectrum. The assignments refer to 1D spectrum and to dia-peaks in 2D spectrum. Protons are labeled by the numbers of their skeletal carbon atoms (200 MHz)

For sensitivity reasons, the satellites of *I* had to be measured in hexadeuterio-benzene solutions, the ^{13}C NMR spectra in this solvent were assigned by a combination of homonuclear and heteronuclear chemical shift correlated two-dimensional spectra[5] shown in Figs 2 and 3. The assignment derived here (δ(Si-2) = 17·54, δ(Si-3) = 17·30, and δ(Si-4) = 16·30) is in disagreement with that determined by the INDOR method[3] and that found empirically[6] on the basis of Hammett type dependence of the chemical shifts. Since the latter two assignments were found for deuteriochloroform solutions we have measured concentration dependence of the ^{29}Si chemical shifts in *I* in a ternary mixture with chloroform and hexadeuterio-benzene. As it is obvious from Fig. 4, the shielding changes with the solvent. The two experimental assignments for the two solutions are in agreement. The empirical assignment is at variance already discussed in ref.[3].

The described method of selective decoupling did not produce unambiguous assignment for the second compound (*II*) as the silicon chemical shifts did not differ sufficiently. For such cases selective heteronuclear INADEQUATE assignment experiments are more appropriate as they permit higher selectivity[7].

CONCLUSION

The proposed method for ^{29}Si NMR line assignment based on measurements of ^{29}Si satellites in ^{13}C NMR spectra with selective silicon decoupling has been
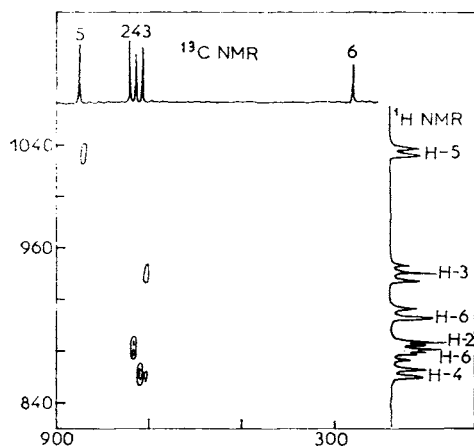

FIG. 3

Partial ^{1}H and ^{13}C NMR spectra and their correlation map obtained as a contour plot of heteronuclear shift correlated 2D NMR spectrum of *I* (in hexadeuteriobenzene)
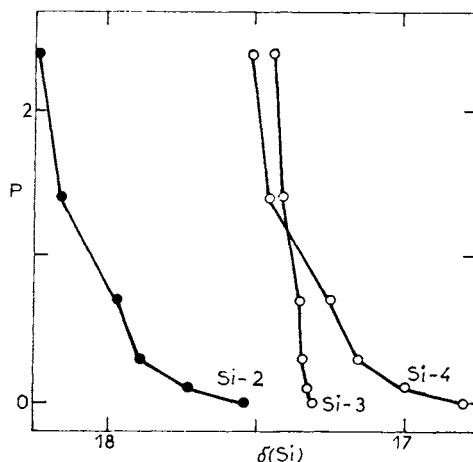
FIG. 4

Concentration dependence of ^{29}Si chemical shifts of *I* in ternary mixture with hexadeuteriobenzene and chloroform. (*P* is the molar ratio of chloroform to benzene)

shown to give correct results. The method is especially useful for assigning the spectra of compounds with trimethylsiloxy groups bonded to tertiary carbon atoms or in cases when proton spectra are not sufficiently resolved.

EXPERIMENTAL

Pertrimethylsilylation of the parent monosaccharides was reported earlier[6,8]. In order to obtain sufficient signal-to-noise ratio in a reasonable time, the samples were measured as approximately 90% solutions in hexadeuteriobenzene.

^{1}H, ^{13}C, and ^{29}Si NMR spectra shown in Figs 1—3 were measured on a Varian XL-200 spectrometer operating at 200, 50·3, and 39·7 MHz for these nuclei, respectively. Standard software provided by the manufacturer (H-1Z version) was employed for the measurements, calculation and plotting of 1D and 2D NMR spectra (HOMCOR and HETCOR pulse sequences, 1 024 × 1 024 data matrices, pseudo-echo FID shaping in both dimensions with data symmetrization for HOMCOR experiments and exponential smoothing and no symmetrization for HETCOR spectra). ^{29}Si NMR chemical shifts were measured by the routine INEPT technique[9].

The selective decoupling experiments were carried out on a Bruker CXP-360 spectrometer operating at 90·6 MHz for ^{13}C, and at 71·5 MHz for ^{29}Si resonances. For irradiation of ^{29}Si nuclei another decoupling channel was added by mixing the pulsed 60 MHz frequency (available in the spectrometer console) with the 11·5 MHz output from a Wavetek Model 178 synthesizer. As the needed *r.f.* field strength was only about 4 Hz, a small power preamplifier was used. Its output was fed into the double tuned^{13}C coil of Bruker 10 mm probe. To produce small shifts in the decoupling frequency according to the procedure described above, output frequency of the Wavetek synthesizer was alternatively derived from two 10 MHz quartz oscillators with a 2 Hz frequency difference.

For the samples in 8 mm (o.d.) NMR tubes, sealed in order to protect the compounds from moisture, about 3 000 scans provided sufficient S/N ratio for each experiment.

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