A Carbon-13 Nuclear Magnetic Resonance Study of Chlorinated and Polyol Analogs of Glucose and Related Oligomers[1]

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Complete assignments of the carbon-13 n.m.r. spectra of the following compounds in aqueous solution are presented: 6-chloro-6-deoxy-D-glucose, 6-*O*-methyl-D-glucose, ribitol, glucitol, 4-*O*-methyl-glucitol, maltose, maltitol, 6,6′-dichloro-6,6′-dideoxymaltose, 6′-chloro-6′-deoxymaltose, isomaltose, isomaltitol, and 6′-chloro-6′-deoxyisomaltose. Some earlier assignments for maltose are reversed. Chlorination on the exocyclic carbon of the glucopyranose ring usually results in a substantial decrease in the chemical shift of the substituted carbon (−17 p.p.m.) and the next-nearest carbon (−1.2 p.p.m.); methylation leads to an increased chemical shift for the contiguous carbon (+10 p.p.m.) and only small changes for other carbons in the molecule. The response to 4-*O*-methylation in glucitol is opposite for C-3 (+0.7 p.p.m.) and C-5 (−0.8 p.p.m.) demonstrating that response of a particular carbon to substitution at a neighboring carbon depends upon the configuration of the particular carbon. Dissolution of these compounds in pyridine results in a bunching together of resonances which makes unambiguous assignments very difficult. The data for this series of compounds are useful in assigning the more complex spectra of microbial polysaccharides.

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Nous présentons l'attribution complète des spectres de résonance magnétique nucléaire en carbone-13 des composés suivants étudiés en solution aqueuse: 6-chloro-6-désoxy-D-glucose, 6-*O*-methyl-D-glucose, ribitol, glucitol, maltose, maltitol, 6,6′-dichloro-6,6′-didésoxymaltose, 6′-chloro-6′-désoxymaltose, isomaltose, isomaltitol et 6′-chloro-6′-désoxyisomaltose. Certaines attributions antérieures du maltose sont inversées. La chloruration du carbone exocyclique de l'anneau glucopyranose conduit généralement à une diminution importante du déplacement chimique du carbone substitué (−17 p.p.m.) et de son voisin le plus proche (−1.2 p.p.m.); par contre, la méthylation provoque une augmentation importante du déplacement chimique du carbone substitué (+10 p.p.m.) sans influencer de façon notoire les autres carbones de la molécule. La méthylation en position 4 du glucitol est différemment ressentie par les carbones adjacents (C-3, +0.7 p.p.m.; C-5, −0.8 p.p.m.). Ceci démontre que la stéréochimie des carbones adjacents à un carbone substitué peut différencier leur comportement lors d'une substitution. La mise en solution de ces composés dans la pyridine conduit à un resserrement des résonances et l'attribution de certaines d'entre elles reste ambiguë. Les données de cette série de composés sont utiles pour attribuer les spectres plus complexes de polysaccharides microbiens.

Introduction

Simple carbohydrates have been studied extensively by ^{13}C n.m.r. (1). Numerous investigations have been devoted to glucose and related compounds (2–14) and to complex carbohydrates containing these residues (15–20). Nearly all the resonances of glucose have been resolved and assigned, particularly by the study of the influence of *O*-methylation (5–7, 10–12), *O*-acetylation (6, 10), and deuterium incorporation (2, 12, 13). Cyclic and acylic polyol spectra have also been assigned (14, 21–22). Recently, the influence of methylation on the ^{13}C chemical shifts of galactose derivatives and galactitols has been reported (23–24).

We describe here the usefulness of chlorinated and polyol derivatives of glucose and related disaccharides in the assignment process. The correlations deduced here can be used to resolve difficult assignments and related problems of other carbohydrates, such as sialic acid, which is composed of a cyclic sugar and an acyclic

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polyol (20) and polymers containing glycerol side chains.

Experimental

Nuclear magnetic resonance spectra were obtained on a Varian XL-100-15 (sample tubes of outside diameter 12-mm, 32°) or a Varian CFT-20 (10-mm tubes, 30°) spectrometer with complete proton decoupling. Chemical shifts were measured relative to tetramethylsilane in a sealed concentric tube of outside diameter 5 mm and are expressed as increasingly positive with increasing frequency (decreasing field) from the resonance of Me_4Si. Differences in susceptibility correction between the 12- and 10-mm tubes were less than the experimental accuracy of 0.1 p.p.m. and were neglected. Carbohydrate samples were 100 mg/ml in neutral deuterium oxide.

Paper chromatographic analysis was carried out on Whatman No. 1 filter paper using the following solvent system: butan-1-ol, pyridine, water (6:4:3, v/v) and the mobilities of the components are given relative to that of D-glucose (R_{Glc} 1.0).

4-*O*-Methyl-D-glucose was prepared by the method of Kenner and Richards (25) and 6-*O*-methyl-D-glucose by the hydrolysis of 6-*O*-methyl-α-D-glucopyranoside (26). 4-*O*-Methyl-D-glucitol was prepared by the sodium borohydride reduction of 4-*O*-methyl-D-glucose.

Maltose and isomaltose were commercial samples used without further purification and maltitol and isomaltitol were obtained by the sodium borohydride reduction of the respective reducing disaccharides using standard procedures.

6,6′-Dichloro-6,6′-dideoxy maltose was prepared in the following way. Maltose (5 g) was treated with sulfuryl chloride and pyridine by a procedure previously described for the synthesis of fully chlorosulfated pentapyranosyl chlorides (27). In the case of maltose due to the presence of exocyclic primary hydroxyl groups specific chloro substitution of these groups occurred to yield syrupy 6′,6-dichloro-6′,6-dideoxymaltosyl chloride 2′,2,3′,3,4′-pentachlorosulfate (10.2 g, 80%). Additional 4′-chloro substitution, which normally occurs when the product of this reaction is isolated at ambient temperature (28), was avoided by the low-temperature isolation (−10 to 0°) of the product. The syrupy pentachlorosulfate (5 g) was treated with sodium iodide in aqueous acetone (29) and the resultant solution was deionized and concentrated to yield a syrup (1.5 g; 69.4%) which was shown to be homogeneous by paper chromatographic analysis (R_{Glc} 2.6) and had $[\alpha]_D$ +99.6° (*c*, 2.0 in water). Hydrolysis of the syrupy product (*N* sulfuric acid at 100° for 16 h) gave only 6-chloro-6-deoxy-D-glucose (R_{Glc} 2.5), which was characterized as its known crystalline peracetate derivative (30).

6′-Chloro-6′-deoxyisomaltose was prepared by an identical procedure to that described above. From isomaltose (0.5 g), syrupy 6′-chloro-6′-deoxyisomaltose was obtained in an overall yield of 58% (0.29 g). The product was homogeneous by paper chromatographic analysis (R_{Glc} 1.1) and hydrolysis (*N* sulfuric acid at 100° for 16 h) yielded both glucose and 6-chloro-6-deoxyglucose (paper chromatographic analysis). Recently, 6-chloro-6-deoxy-D-glucose has also been synthesized by this procedure and this preparation will be reported in detail in a subsequent communication (31).

6′-Chloro-6′-deoxymaltose was prepared according to the method of Melton and Slessor (32).

Results and Discussion

Glucose and Related Derivatives

In order to study derivatives of maltose and isomaltose chlorinated at C-6, it was first necessary to assign the resonances of the analogous monomer, 6-chloro-6-deoxy-D-glucose. In Table 1, its resonances are compared to those of glucose and 6-*O*-methyl-D-glucose. We are in agreement with the published assignments for these compounds (4, 10, 11). However, we could resolve two resonances due to C-6 in each of D-glucose and 6-chloro-6-deoxy-D-glucose and assign them to the α- and β-anomer species by taking into account the relative populations of the two anomers, as manifest in the C-1 resonances. We also distinguished between the C-2 and C-5 resonances in 6-*O*-methyl-β-D-glucose because no chemical shift effect is expected on C-2 due to methylation of C-6. Thus, the peaks at 75.9 and 75.5 p.p.m. are assigned to C-5 and C-2, respectively. The chlorination effect on the contiguous carbon occurs in the sense opposite to that of methylation and is considerably larger (*ca.* −17 and +10 p.p.m. displacements for chlorination and methylation, respectively). Qualitatively, these effects can be foreseen taking into account that the replacement of a substituent by a more polar group causes an upfield shift of the carbon bearing this substituent (33). In fact, we substitute an —OH group by an $—OCH_3$ or —Cl group and the order of polarity is —Cl > —OH > $—OCH_3$. If we refer to the ^{13}C chemical shifts observed in the alkanes (34), a −17 p.p.m. displacement is expected when a chlorine is substituted for a hydroxyl group. This comparison with alkanes is reasonable as the substitution is done on the exocyclic carbon. Chlorination at C-6 of glucose results in better resolution of the resonances due to this carbon in the two anomers (0.1 and 0.5 p.p.m. in D-glucose and 6-chloro-6-deoxy-D-glucose, respectively). The effect on the nearest neighbor carbon, a so-called β-effect, of the two substituents is nearly equivalent, −1.2 p.p.m., in the two anomers. As previously observed (4, 5), methylation usually produces negligible effects beyond the nearest neighbor carbon. However, a chemical shift change of +0.6 p.p.m. is observed on C-4 of the two anomers.

The spectra of ribitol, glucitol, and 4-*O*-

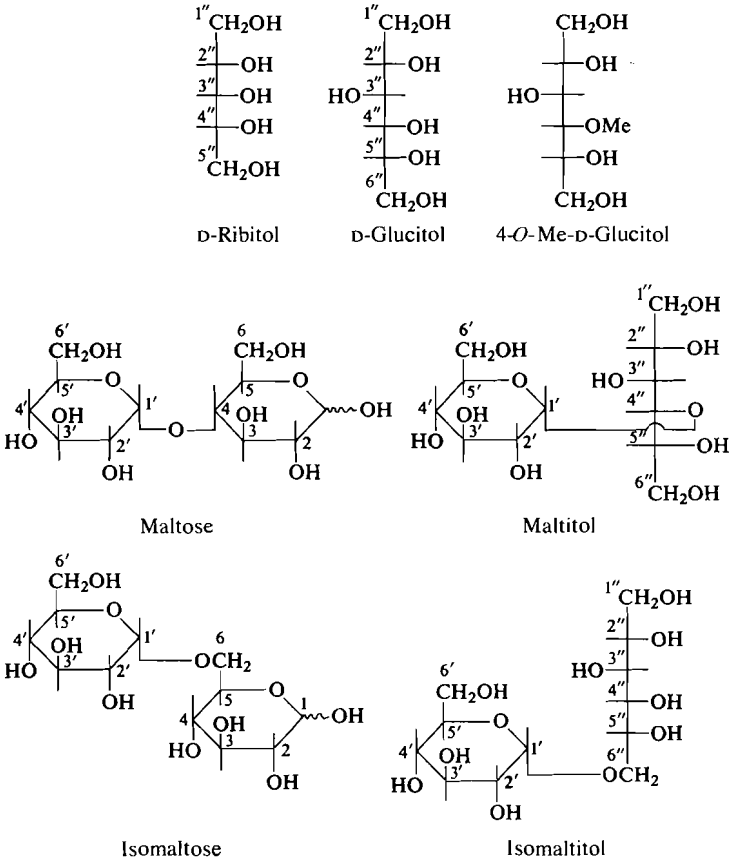

FIG. 1. Formulae of maltose, isomaltose, and some polyol derivatives related to them and to glucose.

TABLE 1. Comparison of the effects of methylation and chlorination at carbon 6 on the ^{13}C chemical shifts of glucose

	α-Anomer			β-Anomer		
	Unsubstituted	6-Cl	6-*O*-Me	Unsubstituted	6-Cl	6-*O*-Me
C-1	93.1	93.4	93.5	97.0	97.1	97.4
C-2	72.5*	72.5	72.9	75.2	75.2	75.5
C-3	73.8	73.6	74.2	77.0†	76.5	77.2
C-4	70.7	71.3	71.3	70.7	71.2	71.3
C-5	72.5*	71.4	71.3	76.8†	75.6	75.9
C-6	61.7	45.6	72.7	61.8	45.1	72.7
CH_3	—	—	60.1	—	—	60.1

*No differentiation in chemical shift observed with a resolution of 0.03 p.p.m.
†Two resonances distinguishable but no reliable method available for assigning resonances differing by so little.

methyl-D-glucitol (see Fig. 1 and Table 2) were also assigned to be used as references for polyol derivatives of disaccharides with possible extension to polysaccharides. In the following, unprimed and primed carbons will correspond to the reducing and nonreducing units of the disaccharides, respectively. Double primed carbons will represent those of polyol chains. Two resonance regions can be distinguished for secondary (70–75 p.p.m.) and primary (63–64 p.p.m.) alcohol carbon atoms. The two secondary alcohol resonances found by Voelter *et al.* (21) for ribitol could not be resolved under resolution conditions of 0.05 p.p.m. In glucitol, no un-

TABLE 2. Assignments of the ^{13}C resonances of maltose and its chlorinated and polyol derivatives

	Ribitol	Glucitol	4-*O*-Me-Glucitol	Maltose	Maltitol	6′-Chloro-6′-deoxymaltose	6,6′-Dichloro-6,6′-dideoxymaltose
C-1α				93.1		93.0	93.2
C-1β				97.1		96.9	97.0
C-1′				100.8	101.6	100.8	101.0
C-1″	63.7	64.0	63.9		64.0		
C-2α				72.5		72.4	72.4
C-2β				75.2		75.1	75.1
C-2′				73.8	73.8	73.4	72.9
C-2″	73.4*	72.4†	72.4‡		72.7		
C-3α				74.4		74.4	74.2
C-3β				77.3		77.3	77.1
C-3′				74.1	74.1	73.6	73.6
C-3″	73.4*	70.9	71.6‡		71.6		
C-4α				78.3		78.3	78.9
C-4β			61.0§	78.1		78.1	78.6
C-4′				70.5	70.6	71.2	71.2
C-4″	73.4*	72.2†	82.6		83.0		
C-5α				71.2		71.0	69.7
C-5β				75.7		75.6	74.0
C-5′				72.8	72.7	72.8	72.8
C-5″	63.7	74.1	73.3		73.6		
C-6α				62.0		62.1	46.1
C-6β				61.8		61.9	45.6
C-6′	—			61.7	61.6	45.4	45.6
C-6″		63.7	63.5		64.5		

*No resolution of these resonances observed.
†Uncertainty concerning relative assignments.
‡Differentiation based on the more important influence of 4-*O*-methylation on the resonance of C-3 than on that of C-2.
§Resonance of methyl group at C-4.

equivocal distinction between the C-2″ and C-4″ resonances can be made at present because they differ in chemical shift by so little (0.2 p.p.m.). However, regardless of the assignment, comparison of the chemical shifts of C-2″ of glucitol (72.2 or 72.4 p.p.m.) with that of ribitol (73.4 p.p.m.) demonstrates a *ca.* 1 p.p.m. influence of reversing the configuration of a neighboring carbon atom in a polyol. The peak at 63.7 p.p.m. can be attributed to C-6″ of glucitol, the conformational environment of which is more similar to those of C-1″ and C-5″ of ribitol than to that of C-1″ of glucitol (64.0 p.p.m.). Of the two possible assignments for C-3″ and C-5″ of glucitol (70.9 and 74.1 p.p.m.), that in Table 2 is chosen because it minimizes the difference in chemical shift between C-5″ of glucitol and C-2″ of ribitol which it closely resembles. In 4-*O*-methyl-D-glucitol, the methylation effect is greatest on C-4″, +10.4 p.p.m. It is of considerable interest to note that the effects of methylation at C-4″ are approximatly equal in magnitude but opposite in sign for C-3″ (+0.7 p.p.m.) and C-5″ (−0.8 p.p.m.) due to the different relative positions of the hydroxyl groups of C-3″ and C-5″ with respect to the substituent on C-4″. As no significant geminal effect, a so-called γ-effect, is foreseen, the resonance at 72.4 p.p.m. for 4-*O*-methyl-D-glucitol must be due to C-2″, whereas those at 63.9 and 63.5 p.p.m. are unambiguously attributable to C-1″ and C-6″ carbons, respectively. The resonance at 61.0 p.p.m. is assigned to the *O*-methyl group by reference to the derivatives of glucose methylated on the ring (5, 11, 19).

Glucobioses and Related Compounds

Maltose (O-α-D-Glucopyranosyl-(1 → 4)-O-α-D-glucopyranose)

Assignment of the ^{13}C n.m.r. spectrum of maltose (Fig. 2) has been previously attempted (9–11). Numerous uncertainties remain in the data of Voelter *et al.* (9) and a significant difference in chemical shift is present for all the resonances with respect to those given by other authors, due to the choice of an indirect chemical

shift reference. The assignments of C-3α and C-3β made by Dorman and Roberts (10) have to be interchanged with those of C-5α and C-5β to be consistent with the assignment of 4-*O*-methyl-D-glucose and methyl 4-*O*-methyl-α-D-glucopyranoside previously given (11, 19). As seen in Table 2, our assignment of the maltose resonances agrees very well with those of Usui *et al.* (11). In some cases, we were able to obtain better resolution for some resonances. Taking into account the relative intensities of these resonances, the peaks at 78.3 and 78.1 p.p.m. can be assigned to C-4α and C-4β, respectively, and the C-6 peaks at 62.0, 61.8, and 61.7 p.p.m. to C-6α, C-6β, and C-6′, respectively. Finally, the two peaks at 74.4 and 74.1 p.p.m. are due to C-3α and C-3′, respectively.

The maltitol assignment (Fig. 2) can be facilitated by considering that the reducing glucose unit of maltose is replaced by 4-*O*-methyl-D-glucitol. This direct comparison shows that only C-1′ differs by more than 0.5 p.p.m. with respect to the additive spectra of the constituents. This change of chemical shift by +0.8 p.p.m. demonstrates the relative effects of substitution of a glucopyranose ring by a polyol aliphatic chain or by another glucose residue. Turning to the glucitol moiety, C-4″ is displaced by +0.4 p.p.m. more on substitution with a glucosyl residue than with a methyl group. A corresponding difference of 0.3 p.p.m. exists for C-2″ and C-5″, whereas the influences of methyl and glycosyl substitution on C-3″ are equal. This underlines again the observation that the response on neighboring carbon chemical shifts to substitution depends on the orientation of their substituents relative to those of the carbon being substituted. All other resonances in the comparison correspond. Thus, the C-6′ resonance situated at 61.6 p.p.m. confirms our previous assignment of this carbon in maltose.

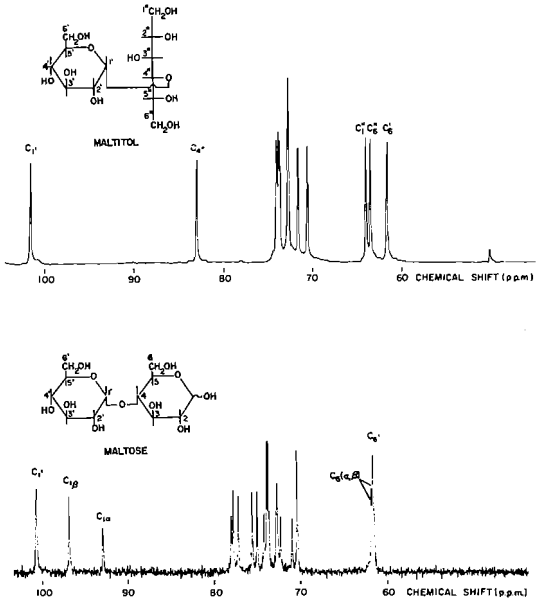

FIG. 2. ^{13}C n.m.r. spectra of maltitol and maltose, 100 mg/ml in D_2O, 32°, p*D* 7.0, spectral width 2.5 KHz, 6K data points, cycle time 1.2 s, pulse angle 45°, 21 900 and 7700 transients for maltitol and maltose, respectively.

Chlorination of C-6′ of the nonreducing unit of maltose is not expected to produce changes in the chemical shifts of reducing unit carbons, as seen in Table 2. This substitution could be expected to produce displacements of the chemical shifts of C-4′, C-5′, and C-6′, by comparison of 6-chloro-6-deoxy-α-D-glucose with α-D-glucose. However, account must be taken that the nonreducing unit is actually a glycoside. The increased shielding of C-6′ by 16.3 p.p.m. on chlorination is comparable to that observed in glucose (α, −16.1 p.p.m.; β, −16.7 p.p.m.) but a corresponding effect on C-5′ is not found. The glycosidic link at C-1′ must be responsible for this decreased sensitivity. The small displacements of C-2′ and C-3′ by −0.4 and −0.5 p.p.m., respectively, are mainly due to the chlorination effect, as well as the +0.7 p.p.m. change in chemical shift of C-4′ (Table 2).

In the dichlorinated derivative, we expect effects in the nonreducing moiety similar to those found for 6′-chloro-6′-deoxymaltose. This is generally true, including the absence of an effect of chlorination on the chemical shift of C-5′ and the decreased shielding of C-4′ (Table 2). The reducing end is comparable to glucose with the complication of a linkage at C-4. The changes in chemical shift of C-6 (α, −15.9 p.p.m.; β, −16.2 p.p.m.) are comparable to those found for 6-chloro-6-deoxy-D-glucose (Table 1). Similarly, an increased shielding is found for C-5 (α, −1.5 p.p.m.; β, −1.7 p.p.m.), in contrast to the anomalous behavior of the nonreducing end. This predicted behavior for the C-5 resonances confirms our proposed alteration of the assignments of Dorman and Roberts (10). The distinction between the C-6 resonances of the α- and β-anomers of the reducing end is enhanced relative to maltose as was found for glucose.

Isomaltose (O-α-D-Glucopyranosyl-(1 → 6)-α-D-glucopyranose)

We agree with the assignments of Usui *et al.* (11) for isomaltose itself, except that we were able to resolve more resonances, including those of C-2β and C-5β (75.3 and 75.5 p.p.m., respectively). However, the resonance region between 74.3 and 70.8 p.p.m. has to be discussed. Of the two signals at 70.8 and 71.3 p.p.m. (relative intensities 149 to 42, respectively), C-4′ must be assigned to the former, as this is the only signal of sufficient intensity to accommodate a complete carbon signal (based on an average relative intensity of 90 per carbon signal in the spectrum). The resonances of C-4α and C-4β must also be located at or in close proximity to the C-4′ signal as it has been demonstrated that C-4 of glucose derivatives exhibits little sensitivity to either anomeric change or C-6 substitution (Table 1). In addition the C-5α resonance must also be located in this region as model compounds indicate almost identical chemical shifts for C-4α, C-4β, and C-5α (Table 1). The resonance at 71.3 p.p.m. is too intense to accommodate C-5α alone which should have an approximate relative intensity of 30 based on the intensity of C-5β and the known ratio of the two anomers. Therefore two interpretations are consistent with the intensity data for the C-4α, C-4β, and C-5α signals. The signal at 71.3 p.p.m. can be assigned either to both C-4α and C-5α or to C-4β. This leaves the signal at 70.8 p.p.m. assignable to C-4β or to both C-4α and C-5α, respectively. Finally, by comparison with maltose, the C-3′ and C-3α resonances are positioned at 74.3 p.p.m. and the C-2α resonance at 73.0 p.p.m. The peaks at 73.25 and 72.7 p.p.m. are assigned to C-2′ and C-5′. As reported earlier (16, 19), the passage from the (α-1 → 4) to the (α-1 → 6) linkage has induced a change of −1.5 p.p.m. in the position of the C-1′ resonance, of −7 p.p.m. for the two C-4 resonances of the reducing moiety, and of +5 p.p.m. for the two resonances of the linked C-6 of the reducing moiety. This information is all necessary for the assignment of isomaltitol.

The assignment of isomaltitol is achieved by comparison of its spectrum with that of maltitol and by taking into account the different kind of linkage in isomaltitol (α-1 → 6). Thus, in the cyclic unit, the C-1′ and C-2′ resonances must be displaced relative to their values in maltitol. They undergo displacements of −2.1 and −0.5 p.p.m., respectively (similar to the corresponding differences between maltose and isomaltose). In the polyol chain, the substitution at C-6″ of the glucitol entity results in displacement of C-6″ and C-5″ by +6.2 and −1.0 p.p.m., respectively, whereas the other resonances are essentially unchanged from the values in glucitol. These effects are responsible for the chemical shift differences between C-3″, C-5″, and especially C-4″ in isomaltitol and maltitol, and aid in confirming the assignments between 74.2 and 70.7 p.p.m. in Table 3. Finally, the C-6″ resonance of the polyol chain is logically positioned at 69.9 p.p.m. Indeed, a carbon resonance is less shielded if linked to a methyl group or to an aliphatic chain than if linked to another ring (19). Replacement of the glucose ring by an aliphatic chain modifies the C-1′ resonance less in the (α-1 → 6) than in the (α-1 → 4) linkage (0.2 and 0.8 p.p.m., respectively). This is suggestive of the conformational influence on chemical shifts detected when comparing the relatively rigid cyclodextrins with linear (α-1 → 4) homopolymers or oligomers of glucose (19), and is due mainly to the extra degree of freedom in the linked C-6 moiety of a disaccharide relative to a linked C-4, C-3, or C-2.

In 6-′chloro-6′-deoxyisomaltose, the positions of the C-1, C-6, C-2β, C-3β, and C-5β resonances are well defined. As expected, the C-6′ resonance is the only one to undergo a drastic change in chemical shift on chlorination, −16.3 p.p.m. with respect to isomaltose. The region between 74.3 and 70.6 p.p.m. must again be discussed in greater detail. By comparison with isomaltose and isomaltitol, the C-3α and C-3′ resonances are located at 74.3 and 74.0 p.p.m., respectively, taking into account their relative intensities, whereas the C-2′ and C-2α resonances must be at 72.6 p.p.m. because they are not expected to change on chlorination of C-6′. On the other hand, the resonance at 71.9 p.p.m. can be assigned to C-5′, which undergoes an expected high-field shift. The four resonances between 71.4 and 70.6 p.p.m. (C-4α, C-4β, C-4′, C-5α) are assigned according to their relative intensities: 71.4 p.p.m. to the nonreducing end, 71.1 and 70.7 p.p.m. to the α-carbons, and 70.6 p.p.m. to a β-carbon of the reducing end. An uncertainty remains in the relative assignments of 71.1 and 70.7 p.p.m. for C-4α and C-5α.

The Influence of Dissolution in Pyridine

All compounds described above were also

TABLE 3. Assignments of the ^{13}C resonances of isomaltose and its chlorinated and polyol derivatives

	Isomaltose	Isomaltitol	6′-Chloro-6′-deoxyisomaltose
C-1α	93.4		93.4
C-1β	97.3		97.3
C-1′	99.3	99.5	99.1
C-1″		63.8	
C-2α	73.0		72.6
C-2β	75.3		75.3
C-2′	73.25	73.3*	72.6
C-2″		72.8	
C-3α	74.3		74.3
C-3β	77.2		77.2
C-3′	74.3	74.2	74.0
C-3″		70.9	
C-4α	71.3*		71.1*
C-4β	70.8*		70.6
C-4′	70.8	70.7	71.4
C-4″		72.2	
C-5α	71.3*		70.7*
C-5β	75.5		75.4
C-5′	72.7	72.8	71.9
C-5″		73.1*	
C-6α	67.1		67.0
C-6β	67.1		67.0
C-6′	61.8	61.8	45.5
C-6″		69.9	

*Uncertainty concerning relative assignments.

studied in pyridine solution. Pyridine was chosen because some chlorinated carbohydrates are only sparsely soluble in water. In pyridine the resonances cluster closely together and unambiguous assignments cannot be made without parallel studies of specifically-deuterated compounds. Therefore the data are not reported in detail but are available upon request.

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