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ASPECTS OF THE CHEMISTRY OF GLYCOSIDES

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Abstract - Observations dealing with the synthesis and properties of glycosides are reported. A description is given of the use of 1-O-sulfonyl derivatives, prepared from aldoses with sulfonic anhydrides, as intermediates for the synthesis of glycosides and glycosyl halides; the synthesis of disaccharides containing D-mannopyranosyl residues receives particular attention. Glycosyl esters are formed by reactions of carboxylic acids with 1,2-alkyl orthoacetates. Measurements of $^{13}C-^{1}H$ coupling are discussed in relation to studies on the orientation of glycosidic bonds in di- and oligosaccharides, and to anomalous spectral characteristics exhibited by glycosides of 5-thio-D-galactopyranose.

INTRODUCTION

Several topics of current interest in the author's laboratory are dealt with here. Each of these is concerned with some aspect of the chemistry of simple glycosides, or of di- and oligosaccharides. Unpublished data reported here were obtained in collaboration with F. Balza, N. Cyr, G.K. Hamer, R. Helleur, J. Leroux, J.E.N. Shin, R.G.S. Ritchie and G.J. Williams.

SYNTHESIS OF GLYCOSIDES OF D-MANNOPYRANOSE

Most glycoside syntheses, aside from those of the simple 1-O-alkyl type, involve the reaction of a glycosyl halide with an appropriate alcohol in the presence of an acid acceptor. The Koenigs-Knorr reaction (Refs. 1,2) is perhaps the best known of these. Disaccharides containing α-D-mannopyranosyl residues (1) may be synthesized (Refs. 3,4) using Koenigs-Knorr conditions through the reaction of 2,3,4,6-tetra-O-acetyl (or -benzoyl)-α-D-mannopyranosyl bromide (2) with a suitable monosaccharide derivative (3) in the presence of silver oxide. That is, the reaction proceeds with virtually complete retention of configuration. In an analogous manner, disaccharides in the α-L-rhamnopyranosyl series may be obtained (Ref. 3). The stereochemical outcome of these syntheses has been ascribed (Ref. 4) to neighbouring group participation (Refs. 5-7) by the AcO-2 group of 2. Indeed, a 1,2-orthoacetate form (4) of disaccharide 1 has been reported (Refs. 8,9) as a minor by-product, and the yield of 4 [preferentially the OR-exo disastereomer (Refs. 10,11) shown] is enhanced markedly in the presence of a hindered base (Ref. 11) (Note a).
Access to synthetic disaccharides (5) containing β-D-mannopyranosyl residues, has been gained (Ref. 4) by use of a halide in which position-2 is constrained from playing a participating role at the anomeric centre, i.e., the 2,3-cyclic carbonate derivative, 6. Another approach (Ref. 16), in which a suitably protected β-D-gluco analog is oxidized at position-2 and the ketone formed is then reduced to the manno epimer (Ref. 17) also has been successfully developed (Refs. 18,19) for syntheses of β-D-mannopyranosyl disaccharides and oligosaccharides. Although an O-benzyl group is likely to be a poorly participating substituent (Ref. 20), the use of 3,4,6-tri-O-acetyl-2-O-benzyl-α-D-mannopyranosyl bromide (7) in disaccharide synthesis afforded not a β-anomer, but the α-linked product, 8 (Ref. 4). It has been recognized more recently in work with derivatives of 2-O-benzyl-D-glucose (Refs. 21,22) that O-acyl substituents at other positions [e.g., O-6 (Ref. 22)] may play a prominent participating role in glycoside formation. Consequently, since 7 could have given rise to 8 for this

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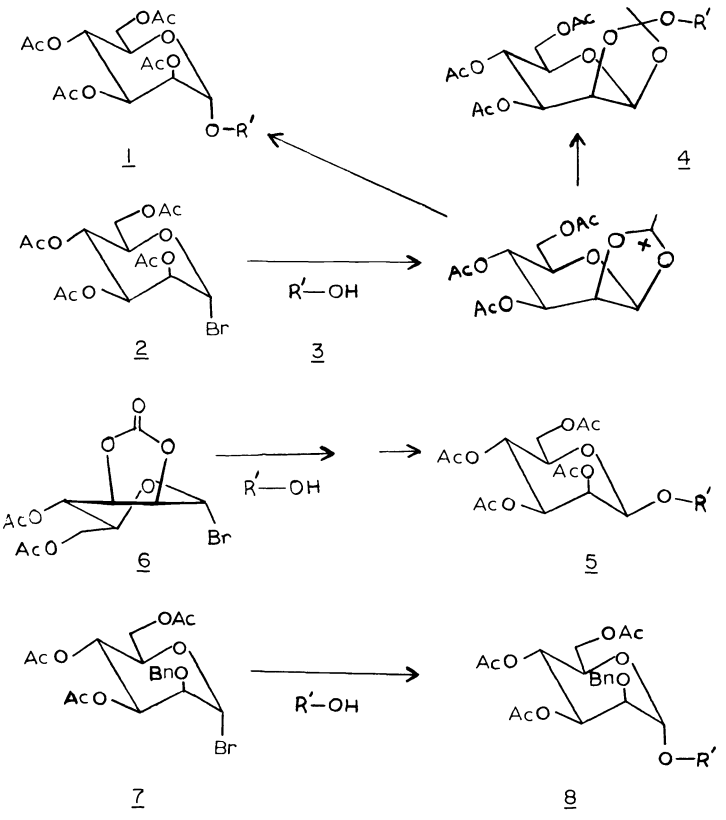
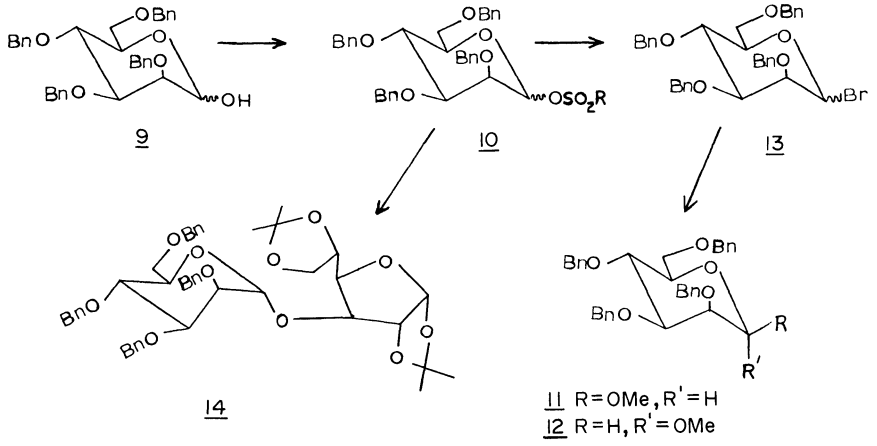
Note a. As is well known, substituted pyridines [quinoline (Ref. 12), 2,6-lutidine or 2,4,6-collidine (Refs. 11,13)] facilitate orthoester formation in the gluco, as well as manno series, and strongly favour the OR-exo diastereomeric product (Refs. 10,13). Other orthoacetates are formed in side-reactions due to decomposition of halide 2 in the presence of silver oxide (Ref. 14), including a unique trisaccharide linked together as an orthoester-ketal of acetoacetic acid (Ref. 15).



latter reason, we have now turned to reactions based on 2,3,4,6-tetra-O-benzyl-D-mannose (9), i.e., a glycosylating moeity bearing no O-acyl substituent.
In a variety of reactions in which 1-O-sulfonyl derivatives (e.g. 10) play an intermediate role (see following section), it was found (Refs. 23,24) that the use of 9 with simple alkanols leads to mixtures of α and β glycosides (in 85-90% overall yield). Thus, a 1:1 mixture of the anomeric methyl glycosides (11,12) was obtained from the reaction of methanol with the 1-bromide (13) generated in situ (Ref. 23) with trifluoromethanesulfonic (triflic) anhydride and bromide ion in the presence of collidine; similarly, the reaction of aldose 9 with methanesulfonic (mesic) anhydride in collidine (Ref. 24) and then 2-propanol, gave a 1:1 mixture of the corresponding α,β-glycosides. In disaccharide synthesis, by contrast, only α-anomers have been obtained (Ref. 24); e.g., disaccharide 14 was synthesized (∿50% yield) by treating 9 with methanesulfonic anhydride in collidine-methylene chloride at room temperature followed by addition of 1,2:5,6-di-isopropylidene-α-D-glucofuranose.



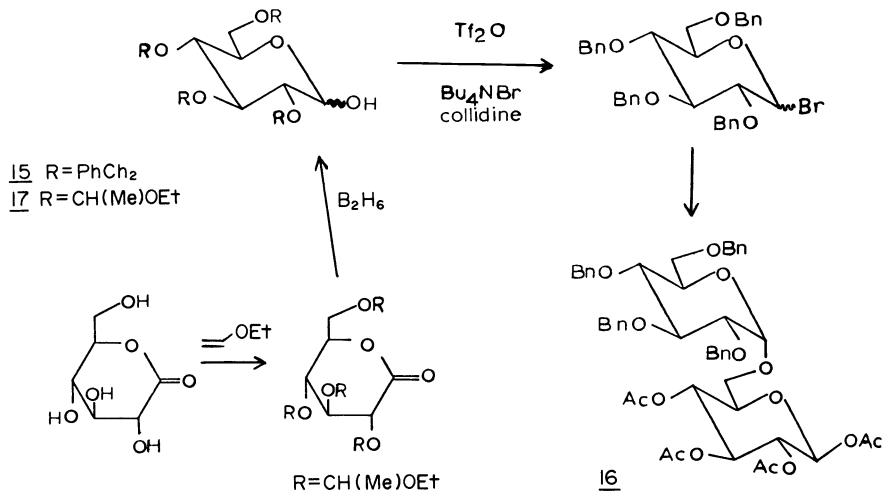
Although the preponderant formation of α-anomers observed earlier with 7 may well have involved participation of the O-acyl substituents, the experimental conditions employed with 9 likely favor formation of α-anomers through kinetic control, as in reactions of the gluco epimer (following section). In any event, the present procedure offers a good synthetic route to α-D-mannopyranosyl disaccharides, which avoids the formation of orthoester side-products, and gives higher yields, than the use of O-acylated halides.

^{13}C N.m.r. spectroscopy has been valuable for characterization of these glycosides of D-mannose. Although α- and β-anomers in this series may exhibit chemical shifts that are too similar for easy differentiation (Refs. 25,26), their configuration may be assigned confidently on the basis of $^{1}J_{C\text{-}1,H\text{-}1}$ measurements. That is, in common with various diastereomers (Refs. 27-29), α-mannosides exhibit ^{1}J values of ∿170 Hz, whereas values for their β-anomers are closer to 160 Hz. Accordingly, the methyl and isopropyl α-glycosides cited above gave $^{1}J_{C\text{-}1,H\text{-}1}$ = 168 Hz (^{1}J for the β-glycosides was 154-155 Hz) and disaccharides, including 14, gave values of 170-172 Hz. In addition, the ^{13}C spectra afford an excellent means for determining the anomeric composition of non-crystalline products.

SYNTHESIS OF GLYCOSYL HALIDES AND GLYCOSIDES VIA 1-O-SULFONYL DERIVATIVES

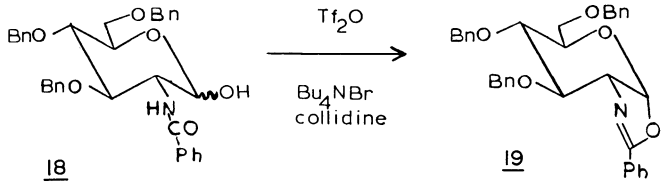
One of the objectives of this study has been to circumvent the use of acidic conditions that are customarily employed in the preparation of glycosyl halides (e.g., of a glycosyl bromide by the action of hydrogen bromide on a related 1-O-acyl derivative) so that acid-labile blocking groups might be used more readily in glycoside synthesis. Another source of concern has been the problem of side reactions of glycosyl halides (Note a) in syntheses moderated by metal salts, although much improvement has been achieved in this direction recently (Refs. 30-33) through the introduction of more efficient acid acceptors.

Both of these objectives are met in substantial measure by the use of 1-O-sulfonyl derivatives. Some reactions in this category have already been cited (preceding section). The base-catalysed reaction of aldose 9 with triflic anhydride in the presence of bromide ion led to formation of bromide 13, via a 1-triflate intermediate. With the introduction of an alcohol, a convenient glycoside synthesis (Refs. 24,34) was effected. The steric outcome of the reaction should be influenced by the fact that halide exchange (Refs. 2,21,32) may occur under these conditions. This is consistent with what has been observed (Refs. 34,35) in the analogous reaction between 2,3,4,6-tetra-O-benzyl-D-glucose (15) and suitable monosaccharide derivatives, which affords α-linked disaccharides (e.g. 16) selectively. That is, once the glycosyl halide has been formed in situ, the outcome of glycoside synthesis conforms to well-known principles (Note b). However, the present modification requires fewer steps, and thus is conducive to higher yields. Furthermore, it has permitted successful glycoside syntheses to be carried out with compounds bearing such acid-labile substituents as acyclic acetal (e.g., 17) cyclic acetal, or O-trityl (Refs. 23,34,35).



Note b. Another analogy to reactions involving glycosyl halides is seen in the fact (Ref. 23) that the use of tetra-O-acetyl-D-glucose in place of the O-benzyl derivative (15) affords a 1,2-orthoacetate, rather than a glycoside.

It appears (Refs. 34,35) that a 1-triflate is insufficiently stable for satisfactory use in a direct reaction with an alcohol and, as indicated above, functions better as an intermediate in the formation of a glycosyl halide. By contrast, a 1-mesylate formed in a base-catalysed reaction of methanesulfonic anhydride with an aldose, functions smoothly in a direct glycosylation step. An example of this in the D-mannose series has already been given above, and successful reactions in the D-gluco series also have been carried out (Ref. 35).
One facet of these studies bears emphasis: i.e., 1-O-sulfonyl derivatives may be used in the preparation of glycosyl halides, such as bromides 13 and 17, from aldoses. Through a related reaction, glycosyl chlorides may be obtained more directly: e.g., treatment of 2,3:5,6-di-O-isopropylidene-α-D-mannofuranose with mesyl chloride in collidine--dichloromethane affords the α-glycosyl chloride (Ref. 35). Hence these procedures supplement the general chemistry of glycosyl halides. In addition, as illustrated by the use of methanesulfonic anhydride, glycosylation reactions are feasible without the intervention of halides (Note c), although it is not known how closely the mechanistic aspects of this experimentally simpler route resemble the reactions of glycosyl halides. Also to be assessed, is the general relationship between the reactions described here and those devised by Schuerch and colleagues (Refs. 22, 30), in which the reaction of a glycosyl halide and an alcohol is mediated by using a silver sulfonate to generate a 1-O-sulfonyl intermediate from the halide in situ.
Related reactions being studied (Ref. 37) involve derivatives of 2-amino-2-deoxy-aldoses. For example, benzamido derivative 18 affords a 1,2-oxazoline derivative (19), a type of transformation that might find application in a synthesis of the corresponding β-glycoside. The reaction characteristics of derivatives in which the N-substituent plays less of a participatory role, is yet to be clarified.



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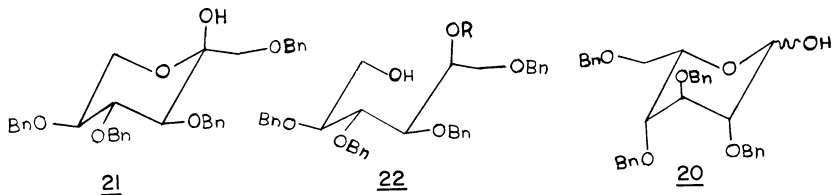
For analogous syntheses directed towards oligosaccharides in the α-L-ido series, a route to 2,3,4,6-tetra-O-benzyl-L-idopyranose (20) has been devised (Ref. 38); it also constitutes a new synthesis of L-idose. That is, 1,3,4,6-tetra-O-benzyl-L-sorbopyranose (21) is converted by reduction and substitution into polyol 22 (R = t-butyl-dimethylsilyl) which, through oxidation and desilylation, leads to the aldose (20, readily separated from the admixed, gluco, epimer).

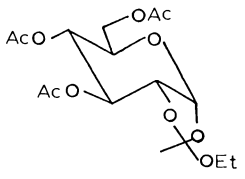


21 22 20

SYNTHESIS OF GLYCOSYL ESTERS

The marked acid-lability of cyclic 1,2-orthoesters is well-known, and the acid-catalysed reaction of an orthoester with an alcohol (Refs. 9,39) has been developed (Refs. 40,41) into an important method for synthesis of glycosides, including higher saccharides. Analogously, the reaction of a carboxylic acid with a 1,2-orthoester affords (Ref. 42) a glycosyl ester. For example (Ref. 23), 3,4,6-tri-O-(1-ethoxyethylidene)-α-D-glucopyranose (23), when heated under reflux in chloroform with acetylsalicylic acid, affords the corresponding 1-O-acyl-β-aldose (24). Similarly, the reaction of 3,4,6-tri-O-acetyl-1,2-O-(1-methoxyethylidene)-β-D-mannopyranose with cyclohexylmethanoic acid in dioxan, yields the corresponding 1-O-acyl-α-aldose (25). These reactions are highly stereoeselective, since in neither series has the second anomeric product been detected. It is reasonable to assume that mechanisms of orthoester ring-opening in these reactions are closely analogous to those associated (Ref. 39) with the acid-catalysed conversion of 1,2-orthoesters into glycosides.

Note c. A related type of reaction is the preparation of glycosyl alkoxyphosphonium salts from aldoses, for use in glycoside synthesis (Ref. 36).



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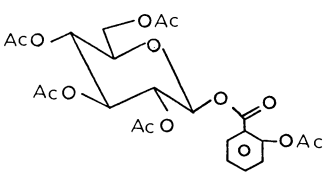

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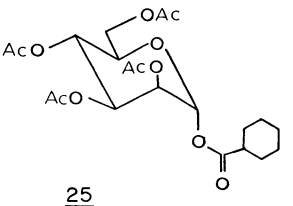

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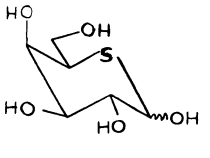
GLYCOSIDES OF 5-THIO-D-GALACTOPYRANOSE. ANOMALOUS ^{13}C-^{1}H COUPLING

In order to examine the effect of a sulfur heteroatom on the susceptibility of D-galactose and derivatives towards various enzymes, 5-thio-D-galactose (26) has been synthesized (Ref. 43). This sugar yielded the α-glycoside (27) almost exclusively when treated with acidified methanol; i.e., it appears that the anomeric effect is expressed more strongly in 27 than in its oxygen analog (Note d). Furthermore, a 4:1 mixture of α- and β-glycosides (28,29) was obtained in the reaction of 2,3,4,6-tetra-O-acetyl-(5-thio)-D-galactopyranosyl bromide and methanol in the presence of silver carbonate; again, in comparison to the oxygen analog, there is a notable tendency for the α-anomer to be formed, although probably under kinetic control in this instance.



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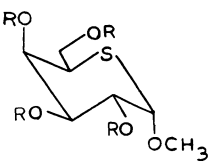
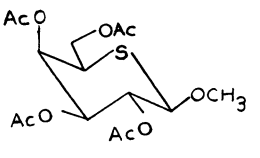
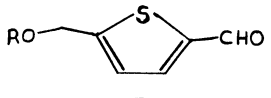


27 R=H
28 R=Ac ($^{1}J_{C\text{-}1,H\text{-}1}$ 157 Hz)



29 ($^{1}J_{C\text{-}1,H\text{-}1}$ 157 Hz)

It was noted above, in dealing with mannosides, that $^{1}J_{C,H}$ values help to define configuration because a substantial difference (~10 Hz) is regularly found between anomeric pairs of glycosides. The 5-thioaldosides appear to be exceptional in this regard. Thus, a difference of only 3 Hz is found between methyl 5-thio-α-D-glucopyranoside tetraacetate (^{1}J 160 Hz) and its β-anomer (^{1}J 157 Hz); the same values are obtained for the corresponding gluco isomers. It has been proposed (Refs. 44,45) that the difference in $^{1}J_{C\text{-}1,H\text{-}1}$ of about 10 Hz between the anomers of the conventional aldosides (noted above) may be attributed to differences in the influence of the ring oxygen atom upon the neighboring C-1,H-1 bond. That is, electron donation to this bond by the oxygen lone pairs is greater in the α-anomer, leading to an increase in the s character of C-1_{α} relative to C-1_{β} (Ref. 45), and a corresponding increase in $^{1}J_{C,H}$. Since the lone pairs on sulphur are expected to be less strongly electron donating than those on oxygen, the small difference found between 28 and 29 (and their gluco epimers) may be ascribed, therefore, to an anomalously small $^{1}J_{C,H}$ value for the α-anomer of the pair. Also to be considered (Ref. 46) are the relative sizes of bond angles associated with the anomeric centres of these compounds.
Of general interest also (Refs. 47,48) is the fact that in this series the use of acidic conditions for glycoside formation is accompanied by prominent side-products, such as thiophene derivatives (e.g. 30) and anhydrides (e.g. 31)(Ref. 43).



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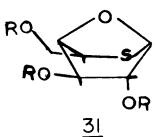

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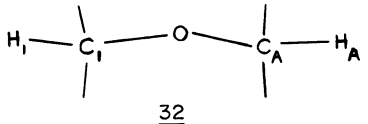
Note d. The glycoside (27) was not hydrolysed by an α-galactosidase from A. fumigatus that readily hydrolysed the corresponding oxygen analog; however, it was oxidized by galactose oxidase (Ref. 43).

ORIENTATION OF GLYCOSIDIC BONDS OF DISACCHARIDES. INTER-RESIDUE ^{13}C-^{1}H COUPLING

Also of current interest in our laboratory is an attempt to define the geometry of glycosidic linkages of disaccharides and oligosaccharides in solution. These studies have taken the form of measurements of inter-residue ^{13}C-^{1}H coupling between nuclei of adjacent residues, i.e., three-bond coupling (^{3}J) between C-1 and H-A or C-A and H-1 of the linkage region represented by 32. The available data (Refs. 49-51) indicate that for some compounds the conformation of this region corresponds closely to that in the crystalline modification,



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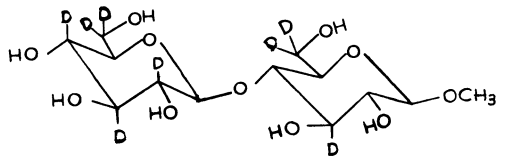
whereas for others the difference is substantial. For instance, the 1→4-β-linkage of β-cellobiose is characterized both in solution (Ref. 51) and the solid state (Ref. 52) by small values of torsion angles ϕ and ψ (25-30°), whereas it appears that the corresponding α-linkage of β-maltose in solution (Ref. 50) is considerably more staggered than in the crystalline form (Ref. 53) (torsion angles of ∿45° vs angles of ∿20°). In these ^{13}C n.m.r. studies, the inter-residue coupling is measured from ^{1}H-coupled ^{13}C spectra (Note e), which frequently suffer seriously from signal overlap and contain second order splitting patterns (Ref. 57). For example, in the spectrum of methyl β-cellobioside the C-1 and C-1' signals overlap, and the possibility of coupling between C-1 and H-4' is obscured by spin interactions of C-1 with H-1,2,3,5. However, substantial simplification of this spectrum (and others) has been accomplished (Refs. 51,58) through the use of a facile procedure for C-deuteration (Ref. 59) involving ^{1}H-^{2}H exchange with D_2O catalysed by Raney nickel. Being far less complex than that of the original glycoside, the spectrum of the octa-C-deutero product (33) is more amenable to analysis and, by employing computer simulation of spectra, has readily afforded values for coupling between C-1 and H-4' (4.0 Hz) and between C-4' and H-1 (4.2 Hz). These ^{13}C-^{1}H coupling values reflect the magnitudes of ψ and ϕ of the ^{13}C-O-C-^{1}H linkages, inasmuch as $^{3}J_{C,H}$ varies with the size of dihedral angles (Refs. 27,28,60).



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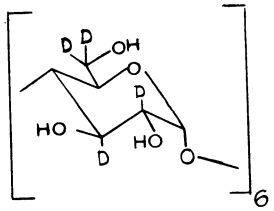

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An important model compound in this context proved to be cyclohexaamylose; a good deal is known about its conformation in solution as well as in the solid state (Ref. 61), and the $^{3}J_{C,H}$ vs dihedral angle information it afforded served as a reference standard in evaluating the disaccharide conformations mentioned above. Here, also, analysis of the ^{13}C spectrum to obtain the inter-residue ^{13}C-^{1}H couplings (C-1,H-4' 4.8 Hz, (C-4',H-1 5.2 Hz) was greatly facilitated through preparation (Refs. 51,58) of the tetra-C-deutero analog of the oligosaccharide (34).

It is worth noting that the retention of H-2' in 33 reflects (Ref. 62) the relatively slow rate of ^{1}H-^{2}H exchange of H-2 in methyl β-glucoside. Presumably, the cis,gauche arrangement of H-2 and OMe allows for poor contact with the surface of the nickel catalyst. This possibility is emphasized by the fact that H-2 of isopropyl β-glucopyranoside is even less prone to exchange, whereas H-2 of methyl β-mannopyranoside (trans,gauche H-2/OMe) is readily replaced. Similarly, hindrance to exchange is found with H-3 of the α-anomers, in which that proton and the 1-O-alkyl group are syn-periplanar, an effect that is reinforced by increasing the bulk of the aglycon substituent (Ref. 62).

Note e. That is, at the natural ^{13}C abundance level. Observations on ^{13}C-^{1}H coupling between nuclei of the anomeric centre and those of appended substituents also have been made from ^{1}H n.m.r. spectra using ^{13}C-enriched compounds (Refs. 27,54,55). Such observations have contributed to the concept of an "exo-anomeric effect" (Ref. 54), and to information about angle ψ in several disaccharides (Refs. 55,56).

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