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Note

The application of ^{13}C-n.m.r. spectroscopy to products derived from sucrose*

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Earlier parts of this series[1] have described chemical transformations of sucrose into products whose structures were arrived at largely by extensive use of high-resolution ^{1}H-n.m.r. and mass spectrometry. The ^{13}C-n.m.r. spectra of several disaccharides have been described[2]; for sucrose, most of the twelve signals observed have been assigned to specific carbon atoms[2,3]. More recently, the ^{13}C-n.m.r. spectra of several chlorodeoxymonosaccharide glycosides were interpreted[4], and this has prompted us to report on the related application to sucrose derivatives. Information concerning the position of substitution and the stereochemistry may be readily obtained[5] from ^{13}C-n.m.r. spectra, and the technique should greatly facilitate studies of di- and higher-saccharides.

Table I lists the ^{13}C-chemical shifts (in p.p.m. downfield from Me_4Si) of sucrose (**1**), *galacto*-sucrose[6] (**2**), 6,6′-dichloro-6,6′-dideoxysucrose[7] (**3**), 6,1′,6′-trichloro-6,1′,6′-trideoxysucrose[8] (**4**), and 4,6,6′-trichloro-4,6,6′-trideoxy-*galacto*-sucrose[1] (**5**). The lowest-field resonance in all cases was that due to C-2′, the chemical shift of which remained fairly constant throughout the series since, with the exception of **4**, it is well-removed from sites undergoing modification. It is well-known that substituents have the greatest effect on the chemical shift of the α carbon atom, the effect being much less for β and γ carbon atoms[5]. For **4**, where C-2′ is β to a primary chlorine atom, the small effect is consistent with previous observations[4]. Likewise, there is little variation in chemical shift of C-1 for the series, although it is noteworthy that the introduction of chlorine at C-1′ (in **4**) had a slight deshielding effect, probably due to the close proximity of C-1 to the C-1′ substituent. The signal for C-3′ was also virtually unaffected regardless of substituent changes, whereas a small shielding of C-4′ was observed in **3**, **4**, and **5** relative to sucrose and *galacto*-sucrose, due to the

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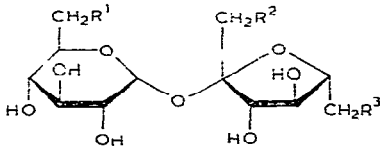
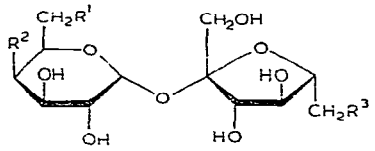
substitution of chlorine in the D-fructofuranosyl ring. A downfield shift (1–2 p.p.m.) was found for C-5′ in **3**, **4**, and **5** where it is β to a chlorine atom (at C-6′), in contrast to the small shift for C-2′ in **4**. However, the β carbon atoms may experience shifts of this order, *e.g.*, the C-5 resonances in methyl α-D-galactopyranoside and methyl 4-chloro-4-deoxy-α-D-galactopyranoside differ by 1.6 p.p.m. For the latter compound, however, the shift is to *higher* field in the chloro compound. It is noteworthy that in **4**, where there is also a chlorine atom present at C-1′, the shift in the C-5′ resonance is not so pronounced.



1 $R^1 = R^2 = R^3 = OH$
3 $R^1 = R^3 = Cl$, $R^2 = OH$
4 $R^1 = R^2 = R^3 = Cl$



2 $R^1 = R^2 = R^3 = OH$
5 $R^1 = R^2 = R^3 = Cl$

TABLE I

^{13}C-CHEMICAL SHIFTS IN P.P.M. DOWNFIELD FROM Me_4Si

Compound	**1**	**2**	**3**	**4**	**5**
C-2′	104.5	104.4	104.8	104.9	104.6
C-1	92.9	93.1	93.0	93.5	93.1
C-4′	82.2	82.2	81.6	81.8	81.6
C-3′	77.6	77.7	77.7	77.4	77.6
C-5′	75.0	75.1	76.9	76.1	76.6
C-2	73.5	72.2	73.2	73.0	71.5
C-3	73.2	70.2	72.6	72.6	68.8
C-5	71.9	70.1	72.0	71.7	68.5
C-4	70.2	68.9	71.4	71.1	64.4
C-6′	63.1	63.2	46.2	44.5	46.1
C-1′	62.5	62.6	62.4	45.3	62.6
C-6	61.2	61.8	45.4	45.7	44.4

The signals for C-2,3,5 have not so far been assigned unequivocally, and even in monosaccharides these assignments are only tentative. However, in general terms, we can say that the chemical shifts of all three carbon atoms are virtually unaffected by the introduction of chlorine at C-6, *i.e.*, in **3** and **4**, which is in agreement with other data[4]. Epimerisation at C-4 in sucrose gives *galacto*-sucrose (**2**), and this results in upfield shifts of C-2,3,5 by values ≤ 3.4 p.p.m. Prior studies on $\alpha\beta$-D-glucose and $\alpha\beta$-D-galactose[9], maltose, cellobiose, and lactose[2] have shown that upfield shifts of this order are experienced by C-2, C-3, and C-5 in galactopyranosyl rings relative to the signals for glucopyranosyl rings. The effect of epimerisation at one centre on the chemical shifts of β and γ carbon atoms is of general applicability, and was initially studied for cyclohexanols[10] and inositols[11]. For **5**, which possesses a 4,6-dichloro-

4,6-dideoxy-D-galactopyranosyl ring, C-2, C-3, and C-5 are shifted to a higher field relative to the corresponding signals for **2**, by values which appear to be similar to those recorded for methyl 4,6-dichloro-4,6-dideoxy-α-D-galactopyranoside in relation to methyl-α-D-galactopyranoside[4]. The H-4 resonance in *galacto*-sucrose (**2**) was shifted upfield by 1.3 p.p.m. relative to the corresponding signal for sucrose, as was expected by analogy with related systems[9–11], and the presence of chlorine at C-6 (in **3** and **4**) caused the H-4 signals to shift to lower field by 0.9–1.2 p.p.m. For **5**, the signal was shifted upfield by 4.5 p.p.m. relative to *galacto*-sucrose (**2**), which is of magnitude similar to that reported for related monosaccharides[4]. For each compound in Table I, the primary carbons (C-6′, C-1′, and C-6) were readily distinguished by the high-field location of their signals. Furthermore, the replacement of a hydroxyl group by chlorine had the expected effect of shifting the signal of the α carbon atom by ~16 p.p.m. to higher field[4]. Previous assignments of the ^{13}C-resonances in sucrose have not differentiated between C-6′, C-1′, and C-6, although C-6 was tentatively assigned to the signal at highest field, by comparison with the spectrum of maltose[2,9c]. Our results with *galacto*-sucrose (**2**) are in agreement with this assignment. Thus, epimerisation at C-4 in sucrose results in a shift (to lower field) of 0.6 p.p.m. (61.2 to 61.8 p.p.m.) for the signal at highest field in sucrose; the other two signals remain at virtually the same value in both **1** and **2**. It seems logical to assume that only C-6 would be affected significantly by a stereochemical change at C-4, and therefore C-6 can be assigned to the resonance at 61.2 p.p.m. in sucrose (**1**) and 61.8 p.p.m. in *galacto*-sucrose (**2**). The remaining two signals may be differentiated as follows. Inspection of the resonances in **3** and **5**, in which two of the three primary carbon atoms are substituted with chlorine, *viz.*, C-6 and C-6′, shows that they are shifted by the expected amount (~16 p.p.m.) to higher field. The remaining high-field resonance (62.4 p.p.m.) in **3** and in **5** (62.6 p.p.m.) can be assigned to C-1′, and these values correspond very closely with one of the resonances (62.5 p.p.m.) that appears in the spectrum of sucrose. Therefore, a complete assignment of the resonances of the primary carbon atoms in sucrose is possible.

Finally, the trichloro compound **4**, in which all three primary groups are substituted, showed three resonances for the primary carbon atoms at ~45 p.p.m., as expected.

EXPERIMENTAL

^{13}C-n.m.r. spectra were recorded on a Bruker WH-90 spectrometer for compounds **1**, **3**, **4**, and **5**, and on a Bruker WP-60/DS spectrometer for compound **2**. Solutions of concentration 75–150 mg/cm^3 were made up in D_2O, with 2–3 drops of *p*-dioxane added as internal reference. The tabulated chemical shifts relative to Me_4Si were obtained by adding 67.4 p.p.m. (the chemical shift of *p*-dioxane relative to Me_4Si) to the experimentally obtained values. In each case, the sample temperature was 34 ±2°.

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