Registry No.—Ethyl *tert*-butoxycarbonyl-L-leucylglycinate, 51220-76-9; benzyloxycarbonyl-L-prolyl-L-alanine hydrazide, 52895-37-1; ethyl benzyloxycarbonyl-L-asparaginyl-L-alaninate, 52928-60-6; ethyl *tert*-butoxycarbonyl-L-leucyl-L-alaninate, 52895-38-2; ethyl benzyloxycarbonyl-L-alanyl-L-valinate, 52895-36-0.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Branched-Chain Sugars. Configurational Assignment of the Branching Carbon Atom of Methyl Branched-Chain Sugars[1]

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Carbon-13 nmr spectra of α and β anomers of branched-chain sugars, having the branched-chain group (methyl) at the 2 and 4 carbons and epimeric at the branching carbon atom, are reported and discussed.

The identification of a relatively large number of branched-chain sugars as the glycoside component of antibiotics,[2] the discovery that cell walls of some aquatic plants contain a high percentage of the branched-chain sugar apiose,[3] the isolation of branched-chain sugar nucleotides from the microorganism *Azobacter vinelandi*,[4] and the observed cytostatic and virostatic activity of nucleosides with branched-chain sugars[5-7] are all responsible for the rapid development of the synthetic chemistry of branched-chain sugars in recent years.

However, the determination of the configuration of a branching carbon atom in branched-chain sugars was notoriously difficult, since a simple and reliable method was not available.[8]

In late 1972 carbon-13 nmr spectroscopy was applied, for the first time, to the configurational assignment of quaternary carbon atoms in branched-chain sugars having the 1,3-dithian-2-yl and 2-methyl-1,3-dithian-2-yl residues as the branched chains.[20-23]

Using the observation on methylcyclohexanes[24,25] that the carbon-13 chemical shift of an axial methyl group is ~6 ppm upfield relative to that of an equatorial methyl group, we have unequivocally determined the configuration of the branching-carbon atom in a number of branched-chain sugars having the branched chain (methyl group) at the 4-carbon atom.[26] Since the influence of the configuration of the branching-carbon atom and the anomeric configuration upon the carbon-13 resonances of other carbon atoms of a branched-chain sugar was not thus far studied and since the methyl group is the most frequent branched chain in naturally occurring branched-chain sugars, a detailed analysis of carbon-13 nmr spectra of α and β forms of branched-chain sugars epimeric at the branching carbon atom seemed appropriate. The following branched-chain sugars were studied by carbon-13 nmr spectroscopy: methyl 4-*C*-methyl-3-*O*-methyl-6-*O*-triphenylmethyl-α-D-galactopyranoside (**1**), methyl 4-*C*-methyl-3-*O*-methyl-2-*O*-methylsulfonyl-6-*O*-triphenylmethyl-α-D-galactopyranoside (**2**), methyl 4-*C*-methyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-galactopyranoside (**3**), methyl 4-*C*-methyl-3-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**4**), methyl 4-*C*-methyl-3-*O*-methyl-2-*O*-methylsulfonyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**5**), methyl 4-*C*-methyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-α-D-glucopyranoside (**6**), methyl 4-*C*-methyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-β-D-galactopyranoside (**7**), methyl 4-*C*-methyl-2,3-di-*O*-methyl-6-*O*-triphenylmethyl-β-D-glucopyranoside (**8**), methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-methyl-α-D-glucopyranoside (**9**), methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-meth-

Table I

Line	Branched-chain sugar, chemical shifts[a] 1	2	3	4	5	6	7	8	9	10	11	Assignment
1	99.5	98.1 DQ[b]	97.7 DQ	98.9	97.6	97.4 DQ	104.9 DQ	105.2 DQ	102.6	104.2	103.8 DQ	C-1
2	70.7	79.1 DQ	80.0 DQ	71.1	78.9	80.9 DQ	82.9 DQ	83.1 DQ	41.3	37.6	38.1 DQ	C-2
3	84.3	81.0 DQ	83.0 DQ	86.0	82.4	85.1 DQ	86.8 DQ	88.4 DQ	80.1	76.6	79.5 DQ	C-3
4	73.8	74.9 ST[b]	74.2 ST	74.7	75.9	74.4 ST	73.6 ST	74.7 ST	84.4	79.1	78.9 DQ	C-4
5	73.2	72.5 DQ	72.9 DQ	71.5	70.7	71.2 DQ	77.7 DQ	75.6 DQ	63.0	63.8	67.6 DQ	C-5
6	63.1	63.1 ST	63.4 ST	63.1	63.0	63.1 ST	63.4 ST	63.2 ST	69.4	69.1	68.9 ST	C-6
7	55.1	55.4 DQ	55.3 DQ	55.2	55.4	55.1 DQ	56.7 DQ	57.1 DQ	55.0	54.7	56.9 DQ	C-1 CH_3O
8			58.9 DQ			58.9 DQ	60.7 DQ	60.6 DQ				C-2 CH_3O
9		37.7 DQ			38.2							C-2 CH_3SO_3
10									12.4	11.0	5.7 DQ	C-2 CH_3
11	62.2	62.2 DQ	62.1 DQ	61.9	61.7	61.9 DQ	62.2 DQ	61.9 DQ	60.8	57.7	57.6 DQ	C-3 CH_3O
12	21.9	21.7 DQ	21.8 DQ	15.4	15.3	15.6 DQ	21.3 DQ	16.0 DQ				C-4 CH_3
13	87.2	87.5 ST	87.4 ST	87.8	88.1	87.7 ST	87.5 ST	87.9 ST	101.4	101.8	101.7 DQ	C-O Ph
14	144.0	143.7 ST	144.2 ST	143.6	143.4	143.7 ST	144.2 ST	143.6 ST	137.8	137.8	137.7 ST	C-substituted Ph
15	127.8	127.9 DQ	128.0 DQ	128.0	128.1	128.0 DQ	128.1 DQ	128.2 DQ	128.2	128.1	128.1 DQ	C-ortho Ph
16	128.7	128.7 DQ	128.9 DQ	128.6	128.6	128.7 DQ	129.0 DQ	128.8 DQ	128.8	128.8	128.8 DQ	C-meta Ph
17	127.0	127.2 DQ	127.2 DQ	127.3	127.4	127.2 DQ	127.4 DQ	127.4 DQ	126.1	126.3	126.2 DQ	C-para Ph

[a] δ_C using internal tetramethylsilane as reference. [b] ST = singlet or triplet, DQ = doublet or quartet.[23]

yl-α-D-mannopyranoside (**10**), and methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-3-*O*-methyl-β-D-mannopyranoside (**11**).

The synthesis of branched-chain sugars **1–8** is already described,[26] whereas the preparation of branched-chain sugars **9–11** will be reported elsewhere.[27]

Table I summarizes the chemical shifts, assignments, and line multiplicities (in some examples) from the proton noise decoupled and off resonance spectra.

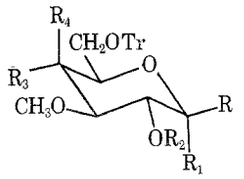
Lines 14–17 are assigned to aromatic carbon atoms of triphenylmethyl (branched-chain sugars **1–8**) and benzylidene (branched-chain sugars **9–11**) groups. The carbon-13 resonances of the C-substituted carbon of the benzene ring in branched-chain sugars **1–8** are low-field singlets at 143.6–144.2 ppm, whereas the carbon-13 resonances of the C-substituted carbon in branched-chain sugars **9–11** are the low-field singlets at ~137.8 ppm (line 14). The carbon-13 resonances of the *para* carbon of the benzene ring (line 17) are high-field doublets at 127.0–127.4 (for branched-chain sugars **1–8**) and at 126.1–126.3 (for branched-chain sugars **9–11**). Lines 15 and 16 are assigned to carbons in the ortho and meta position; these assignments can be, however, reversed.

The chemical shifts of the quaternary carbon atom of the triphenylmethyl group in branched-chain sugars **1–8**, and of the methine carbon of the benzylidene group in branched-chain sugars **9–11**, were determined on the basis of their position, consistency, and multiplicity (line 13). The carbon-13 resonances of the methine carbon in branched-chain sugars **9–11** (101.4–101.8 ppm) are in a very good agreement with the reported values in similar systems (100.9–101.6 ppm).[22] The carbon-13 resonances of the quaternary carbon of the triphenylmethyl group in branched-chain sugars **1–8** seem to be slightly influenced by the configuration of the 4-carbon atom. Thus, when the C-4 methyl group is equatorial (branched-chain sugars **1–3** and **7**) the carbon-13 resonances are 87.2–87.5 ppm, whereas in the corresponding C-4 epimers where the methyl group is axially oriented (branched-chain sugars **4–6** and **8**) the chemical shifts are 87.7–88.1 ppm.

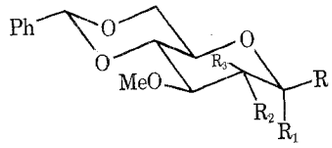
Line 7 is assigned to the C-1 methoxy group based on a previous finding[29] that the carbon-13 resonances of the C-1 methoxy group of α and β anomers are 55.12 and 56.70, respectively. The observed deshielding of the C-1 methoxy group in β anomers **7**, **8**, and **11** with respect to the corresponding α anomers **3**, **6**, and **10** (1.4–2.2 ppm) is in a good agreement with the reported value (1.5 ppm).[29]

The chemical shifts of the C-6 methylene carbons were determined on the basis of their position, multiplicity, and consistency (line 6). The carbon-13 resonances of the C-6 carbon of branched-chain sugars **1–8** (63.0–63.4 ppm) are in a good agreement with reported values (63.0–63.5 ppm),[30] whereas the chemical shifts of the C-6 carbon of branched-chain sugars **9–11** (68.9–69.4 ppm) are in a good agreement with values reported for 4,6-*O*-benzylidene derivatives of C-3 branched-chain sugars (68.8–69.0 ppm).[22] The chemical shifts of the C-6 carbon of branched-chain sugars **1–11** are independent of the anomeric configuration and seem to be not affected by the configuration of the branching-carbon atom and by the nature of substituents at other carbon atoms of the pyranoside ring.

Lines 8 and 11 are assigned to the C-2 and C-3 methoxy groups, respectively. The anomeric configuration should have larger effect upon the chemical shift of the C-2 methoxy group than upon the carbon-13 resonance of the C-3 methoxy group. The deshielding of the C-2 methoxy group in β anomers of branched-chain sugars **3**, **6**, **7**, and **8** is 1.8 ppm relative to the α anomers whereas it is insignificant for



1, R = R_2 = H; R_1 = CH_3O; R_3 = CH_3; R_4 = OH
2, R = H; R_1 = CH_3O; R_2 = CH_3SO_2; R_3 = CH_3; R_4 = OH
3, R = H; R_1 = CH_3O; R_2 = R_3 = CH_3; R_4 = OH
4, R = R_2 = H; R_1 = CH_3O; R_3 = OH; R_4 = CH_3
5, R = H; R_1 = CH_3O; R_2 = CH_3SO_2; R_3 = OH; R_4 = CH_3
6, R = H; R_1 = CH_3O; R_2 = R_4 = CH_3; R_3 = OH
7, R = CH_3O; R_1 = H; R_2 = R_3 = CH_3; R_4 = OH
8, R = CH_3O; R_1 = H; R_2 = R_4 = CH_3; R_3 = OH



9, R = R_3 = H; R_1 = CH_3O; R_2 = CH_3
10, R = R_2 = H; R_1 = CH_3O; R_3 = CH_3
11, R = CH_3O; R_1 = R_2 = H; R_3 = CH_3

the C-3 methoxy group. The C-4 methyl group orientation has, however, a small but definite influence upon the carbon-13 resonances of the C-3 methoxy group; *i.e.*, whenever the C-4 methyl group is axially oxiented the C-3 methoxy group is shielded by 0.2–0.3 ppm.

The carbon-13 resonances at 37.7 and 38.2 ppm in branched-chain sugars **2** and **5** are assigned to the methyl carbon of the C-2 methylsulfonyl group on the basis of their position and multiplicity (line 9).

Line 1 is assigned to the C-1 carbon since it is to the lowest field, excluding the aromatic carbons. The C-1 carbon of the β form of branched-chain sugars with the branching group at the C-4 carbon (branched-chain sugars **1–8**) is deshielded by 7.2 and 7.8 ppm with respect to the corresponding α anomer (**7** vs. **3** and **8** vs. **6**). The methylation or mesylation of the C-2 hydroxyl group causes an upfield shift of the carbon-13 resonance of the C-1 carbon atom. This shielding is larger when the C-2 hydroxyl group is methylated (1.3–1.8 ppm for **3** and **6**) rather than mesylated (1.3–1.4 ppm for **2** and **4**). The carbon-13 resonance of the anomeric carbon of branched-chain sugar **9**, where the C-2 methyl group is equatorially oriented, is shifted downfield by ~2 ppm with respect to methyl α-D-glucopyranoside,[30-32] whereas the C-1 carbon in branched-chain sugars **10** and **11**, where the C-2 methyl group is axially oriented, is deshielded by ~3 ppm with respect to methyl α- and β-D-mannopyranosides.[32] It has been reported[30,32] that the anomeric carbon of methyl α-D-mannopyranoside is deshielded by 1.0–1.4 ppm with respect to the anomeric carbon of methyl α-D-glucopyranoside. The similar amount of dishielding (1.6 ppm) is observed in branched-chain sugars **9** and **10**, which are 2-deoxy-2-methyl analogs of methyl α-D-gluco- and mannopyranosides. Furthermore, it has been reported[32] that the carbon-13 resonance of the anomeric carbon of methyl β-D-mannopyranoside is *shifted upfield* by 0.3 ppm with respect to the α anomer. The similar upfield shift (0.4 ppm) of the carbon-13 resonance of the C-1 carbon is observed in the β anomer (**11**) of branched-chain sugars **10** and **11**, which are 2-deoxy-2-methyl analogs of methyl α- and β-D-mannopyranosides.

The chemical shift of the C-2 carbon was determined on the basis of its position and multiplicity (line 2). For branched-chain sugars **1–8** there is a moderate downfield shift (~9 ppm) with methylation of the C-2 hydroxyl group which is in good agreement with the previous observation[31,33] that the methylation of a hydroxyl group causes an 8–11 ppm downfield shift in the position of the resonance of the directly attached carbon. The upfield position of the carbon-13 resonances of the C-2 carbon of branched-chain sugars **9–11** are due to the absence of a directly attached electronegative substituent, *i.e.*, hydroxyl group. From studies on methylated cyclohexanes[24] it is known[34] that an equatorially oriented methyl group deshields the carbon to which it is attached by 5.6 ppm whereas the carbon atom bearing an axially oriented methyl group is deshielded by 1.1 ppm. Subtracting the first value from the observed carbon-13 resonance of the C-2 carbon of branched-chain sugar **9** (41.3 ppm) and the second value from the observed carbon-13 resonances of the C-2 carbon of branched-chain sugars **10** and **11** (37.6 and 38.1 ppm), it can be calculated that the chemical shift of the C-2 carbon of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside would by 36.1–37.0 ppm. This calculated chemical shift is in a good agreement with reported values (35.8–36.4) for carbon-13 resonances of the C-2 carbon of 4,6-*O*-benzylidene-2-deoxy branched-chain sugars with a branching at the C-3 carbon atom.[22]

Lines 10 and 12 are assigned to C-2 and C-4 methyl carbons. In branched-chain sugars **1–6** (α anomers) the chemical shift difference between the equatorially and axially oriented C-4 methyl group is 6.4 ppm, whereas in branched-chain sugars **7** and **8** (β anomers) the chemical shift difference is 5.3 ppm. In both α and β anomers, the carbon-13 resonance of the axial C-4 methyl group is shifted upfield which is in an agreement with the observation made on methylcyclohexanes.[24,25] The carbon-13 resonances of the C-2 methyl carbon of C-2 branched-chain sugars **9–11** are shifted upfield by ~4 ppm (branched-chain sugar **10**) and by ~10 ppm (branched-chain sugars **9** and **11**), with respect to the corresponding C-4 branched-chain sugars (**1–3** and **4–6** and **8**). This upfield shift can be accounted for by the absence of an electronegative substituent, *i.e.*, hydroxyl group, at the C-2 carbon (*e.g.*, carbon-13 resonances of the methyl group in *cis*- and *trans*-4-tert-butyl-1-methylcyclohexan-1-ol[23,26] are deshielded by 6–8 ppm, with respect to the chemical shift of the methyl group in the corresponding methylcyclohexanes[24] depending upon the orientation of the methyl group). The proposed configurational assignments of the C-2 carbon of branched-chain sugars **9–11**, made on the basis of previous findings[23-26] that an equatorially oriented methyl group is deshielded with respect to an axially oriented methyl group, is strongly supported by the chemical shift difference of the C-2 carbon of **9** *vs.* **10** and **11** (*vide supra*) and by the pmr spectra of branched-chain sugars **9–11**. The C-2 hydrogen of **9** appears in the pmr spectrum as a broad multiplet, centered at *ca.* δ 1.8, whereas broad multiplets corresponding to the C-2 hydrogen of branched-chain sugars **10** and **11** are centered at δ 2.4 ppm. The upfield shift (0.6 ppm) of the C-2 hydrogen in **9** with respect to chemical shifts of C-2 hydrogens in **10** and **11** indicates the axial orientation of the C-2 hydrogen and, hence, the equatorial orientation of the C-2 methyl group in **9**. The chemical shift difference between the axially and equatorially oriented methyl group in C-2 epimers **9** and **10** is only 1.4 ppm, instead of being 6 ppm as it was observed for methylcyclohexanes[24,25] and for branched-chain sugars **1–8**.[26] The downfield shift (*ca.* 5 ppm) of the carbon-13 resonance of the axially oriented C-2 methyl group in **10** could be accounted for in the following way. Comparing **9** and **11**, in each instance the C-2 methyl is gauche with respect to the C-1 methoxy group. However, in **11**, the C-2 methyl group

is axially oriented and, therefore, it should exhibit the greater shielding by about 6 ppm (as in **1–8**) which is actually observed. By contrast, although the C-2 methyl group of **10** is axially oriented, it should not be as strongly shielded as in **11** because the adjacent C-1 methoxy group is anti to this C-2 methyl group. It is interesting to note the very high field position of the carbon-13 resonance of the axially oriented C-2 methyl group in **11** (5.7 ppm).

Line 5 is assigned to the C-5 carbon. The chemical shift positions of the C-5 carbon of branched-chain sugars **1–8** are approximately the same as the C-5 carbon resonance in methyl α- and β-D-glucopyranosides[30–32] and in β anomers the C-5 carbon is deshielded by a similar amount (4.8 ppm for **3** and **7**, and 4.4 ppm for **6** and **8**). It should be noted that an axial C-4 methyl group shields the C-5 carbon unlike the remainder of the ring carbons (1.7 ppm for **3** and **6**, and 2.1 ppm for **7** and **8**). It has been reported[23] that the carbon-13 resonance of the C-5 carbon of methyl 4,6-*O*-benzylidine-2-deoxy-3-*C*-(1′,3′-dithian-2′-yl)-α-D-*ribo*-hexopyranoside is 59.25 ppm. Using this value, we can calculate, by adding 5 ppm, which is approximately the shielding of the C-5 carbon atom in this branched-chain sugar due to the presence of the axially oriented C-3 hydroxyl group (γ effect), that the carbon-13 resonance of the C-5 carbon atom of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside analog should be ~64.2 ppm, which is in a good agreement with the observed values for chemical shift of the C-5 carbon of branched-chain sugars **9** and **10**, (63.0 and 63.8 ppm). The downfield shift of the carbon-13 resonance of the C-5 carbon of branched-chain sugar **11**, with respect to the C-5 carbon of **10**, can be accounted for by the fact that in the β-anomer the C-5 carbon should be deshielded, in this case by 3.8 ppm.

Taking into account the previous finding[32] that the chemical shifts of the C-3 carbon of methyl α- and β-D-gluco- and -mannopyranosides are 74.8, 76.8, 70.1, and 73.3 ppm and that the methylation of a hydroxyl group causes a downfield shift of 8–11 ppm,[31,33] the chemical shifts given in line 3 must then be assigned to the carbon-13 resonances of the C-3 carbon of branched-chain sugars **1–11**. Furthermore, in β anomers the C-3 carbon is deshielded with respect to the corresponding α anomers by 3.8 ppm (**7** *vs.* **3**), 3.3 ppm (**8** *vs.* **6**), and 2.9 ppm (**11** *vs.* **10**).

Line 4 is assigned to the C-4 carbon. It is the remaining unassigned peak (singlet carbon for branched-chain sugars **1–8**), and the chemical shift position is not significantly different for α and β anomers. The carbon-13 resonances of the C-4 carbon of branched-chain sugars **9–11** are in a good agreement with the reported values for a similar glycopyranoside derivative.[22,23]

Experimental Section

The carbon-13 nmr spectra of branched-chain sugars **3**, **6**, **7**, and **8** were recorded in a $CDCl_3$ solution on a Bruker HFX-90 nmr spectrometer at 22.63 MHz, using a Nicolet FT-1083 computer, by the Fourier transform method. An 8K data table was used for data accumulation yielding 4K transformed spectra on the 5000-Hz sweep width. The spectrometer operates on a fluorine lock and a small amount of C_6F_6 was added to the sample solution for a lock. TMS was used as the internal reference.

The proton noise decoupled carbon-13 nmr spectra of branched-chain sugars **4–6** were recorded in a $CDCl_3$ solution with a Jeol TNM PS-100 FT spectrometer. The spectra were obtained using 5000-Hz sweep width 8K data points.

The carbon-13 nmr spectra of branched-chain sugars **1**, **2**, and **9–11** were recorded in a $CDCl_3$ solution on a Varian CFT-20 carbon-13 nmr spectrometer. The spectrometer operates on a deuterium lock. The spectra were obtained using 4000-Hz sweep width 8K data points.

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Registry No.—**1**, 51016-12-7; **2**, 51016-16-1; **3**, 51016-14-9; **4**, 51016-13-8; **5**, 51016-17-2; **6**, 51016-15-0; **7**, 51016-22-9; **8**, 51016-23-0; **9**, 53011-00-0; **10**, 53011-01-1; **11**, 53011-02-2.

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