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Determination of the Absolute Configuration of a Secondary Hydroxy Group in a Chiral Secondary Alcohol Using Glycosidation Shifts in Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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Abstract: A new method is proposed for determining the absolute configuration of a secondary hydroxy group in a chiral secondary alcohol using glycosidation shifts in ^{13}C NMR spectroscopy. The ^{13}C FT NMR spectra of a number of secondary alcoholic glucopyranosides in pyridine-d_5 were compared with those of methyl glucosides and the corresponding parent alcohols to obtain the glucosidation shifts; $\Delta\delta_S = \delta$(alcoholic glucoside) $- \delta$(methyl glucoside) for sugar moieties and $\Delta\delta_A = \delta$(alcoholic glucoside) $- \delta$(alcohol) for aglycone moieties. Characteristic $\Delta\delta_S$(C-1′), $\Delta\delta_A$(C-α), and $\Delta\delta_A$(C-β) values were obtained for the various kinds of secondary alcohols. They are summarized as a few rules for determining the absolute configuration of the hydroxyl.

In a recent review dealing with the conformational properties of glycosidic linkages, Lemieux and Koto[1] reported that ^{13}C chemical shifts around glycosidic linkages depend upon conformations thereabout based on investigations of ^{13}C NMR spectra of cyclohexyl α- and β-D-glucopyranosides and their *C*-methyl derivatives in connection with conformational analyses. During studies of structural determinations and ^{13}C FT NMR spectral signal assignments of natural plant glycosides,[2] Tanaka and co-workers[3] and we[4] also found that ^{13}C NMR signal shifts in the change from aglycone alcohol and pyranose into glycopyranoside, that is, glycosidation shifts,[2] are characteristic of chemical and steric environments of the hydroxy group in which the glycosidation takes place. This discovery has become important and useful for determining the glycosidation position in an aglycone moiety and the kind(s) and sequence of sugar moiety present in a natural glycoside without chemical degradation as well as for assigning ^{13}C NMR signals of the glycoside.[5]

Among several glycosidation shifts, the shift difference between signals due to two β carbons (see Figure 1) in chiral secondary alcoholic glycosides appears to be the most practical to use for determining the absolute configuration of the secondary hydroxy group in a chiral secondary alcohol. As a result of further extension of our study, we propose here a new ^{13}C NMR method for determining the absolute configuration of the secondary hydroxy group mentioned above.

Experimental Section

Materials. All the D-glucopyranosides and tetra-*O*-acetyl-D-glucopyranosides used were prepared by the Koenigs–Knorr method,[6] and their properties are listed in Table I.

Measurements of NMR Spectra. Natural-abundance ^1H noise-decoupled ^{13}C FT NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz using 8-mm spinning tubes. Samples of all alcohols examined were dissolved in both pyridine-d_5 and chloroform-*d*, whereas those of glucopyranosides and their peracetates were measured in pyridine-d_5 and chloroform-*d*, respectively. Tetramethylsilane (Me_4Si) served as an internal reference (δ 0). Samples of small-sized molecules were measured at ambient probe temperature (30 °C), while those of large-sized molecules were examined at elevated temperatures (100 °C in pyridine-d_5 and 80 °C in chloroform-*d*) to avoid signal broadenings on the 15-MHz spectrometer. Concentrations were about 0.1–0.5 mmol/cm^3. FT NMR measurement conditions were as follows: spectral width, 3923 Hz; pulse flipping angle, 15–30° according to molecular size; acquisition time, 0.6 s; number of data points, 4820. Accuracies of δ values were thus about ±0.1. The calibration of the spectrometer was checked by using the δ value of the carbonyl carbon resonance (171.50) of methyl acetate (82% v/v) in benzene-d_6 (10% v/v) and Me_4Si (8% v/v) ac-

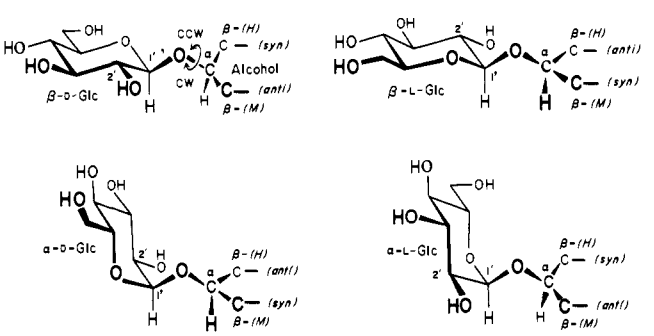

Figure 1. Conformations around glucosidic linkages.[1]

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Table I. Physical Properties of α- and β-D-Glucopyranosides of Secondary Alcohols and Their Tetra-*O*-acetyl Derivatives

Glc[a]	Alcohol	Mp,[b] °C	$[\alpha]_D$,[c] deg	Lit.
α-D-Glc	2-Propanol (**1**)	Syrup	+140.0	*d*
α-D-Glc-Ac_4		86	+143.9	
β-D-Glc	2-Propanol (**1**)	131	−54.9	*e*
β-D-Glc-Ac_4		140	−23.3	*e*
α-D-Glc	Cyclopentanol (**2**)	Syrup	+122.8	
α-D-Glc-Ac_4		Syrup	+108.7	
β-D-Glc	Cyclopentanol (**2**)	Syrup	−49.0	*f*
β-D-Glc-Ac_4		119	−34.2	*f*
α-D-Glc	5α-Cholestan-3α-ol (**5**)	220–221	+83.1	*g*
α-D-Glc-Ac_4		140	+91.6	*g,h*
β-D-Glc	5α-Cholestan-3α-ol (**5**)	225	−4.0	*g*
β-D-Glc-Ac_4		173–175	−10.1	*g,h*
α-D-Glc	5α-Cholestan-3β-ol (**6**)	226–228	+92.2	*g*
α-D-Glc-Ac_4		184–189	+110.1	*g*
β-D-Glc	5α-Cholestan-3β-ol (**6**)	246–249 dec	−28.3	*g*
β-D-Glc-Ac_4		174–175	+1.9	*g,h*
α-D-Glc	Cholesterol (7)	235–238 dec	+65.7	*i*
α-D-Glc-Ac_4		202–204	+85.5	*h,i*
β-D-Glc	Cholesterol (7)	256–260	−46.7	*i*
β-D-Glc-Ac_4		160–164	−25.7	*h,i*
α-D-Glc	Smilagenin (**8**)	>300	+44.8	
α-D-Glc-Ac_4		193	+34.0	
β-D-Glc	Smilagenin (**8**)	243–244	−52.7	
β-D-Glc-Ac_4		218	−53.7	
β-D-Glc	(2*R*)-Pentanol (9)	120–121	−63.1	
β-D-Glc-Ac_4		88.5–89	−30.3	
β-D-Glc	(2*S*)-Pentanol (**10**)	135	−17.6	
β-D-Glc-Ac_4		107	−8.8	
α-D-Glc	*l*-Menthol (**13**)	160–161	+73.5	
α-D-Glc-Ac_4		Syrup	+40.0	
β-D-Glc	*l*-Menthol (**13**)	Syrup	−84.8	*j*
β-D-Glc-Ac_4		131–132	−53.4	*j*
α-D-Glc	*d*-Menthol (**14**)	143–147	+159.1	
α-D-Glc-Ac_4		Syrup	+99.7	
β-D-Glc	*d*-Menthol (**14**)	141	+24.0	*j*
β-D-Glc-Ac_4		174	+21.5	*j*
β-D-Glc	20α-Hydroxypregn-4-en-3-one (**15**)	263–265	+36.9	
β-D-Glc-Ac_4		189–190	+41.8	
β-D-Glc	20β-Hydroxypregn-4-en-3-one (**16**)	262–263	+38.8	
β-D-Glc-Ac_4		137–138	+34.7	
α-D-Glc	Methyl oleanolate (**19**)	194–196 (amorphous)	+95.6	*k*
α-D-Glc-Ac_4		134 (amorphous)	+79.1	*k*
β-D-Glc	Methyl oleanolate (**19**)	273–275	+33.9	*k,l*
β-D-Glc-Ac_4		217–218	+34.2	*k,l*
β-D-Glc	Alcohol (**22**)	62–67 (amorphous)	−58.7	
β-D-Glc-Ac_4		Syrup	−30.4	
β-D-Glc	Liguloxidol (**24**)	130–132	−34.8	
β-D-Glc-Ac_4		194–195	−30.2	

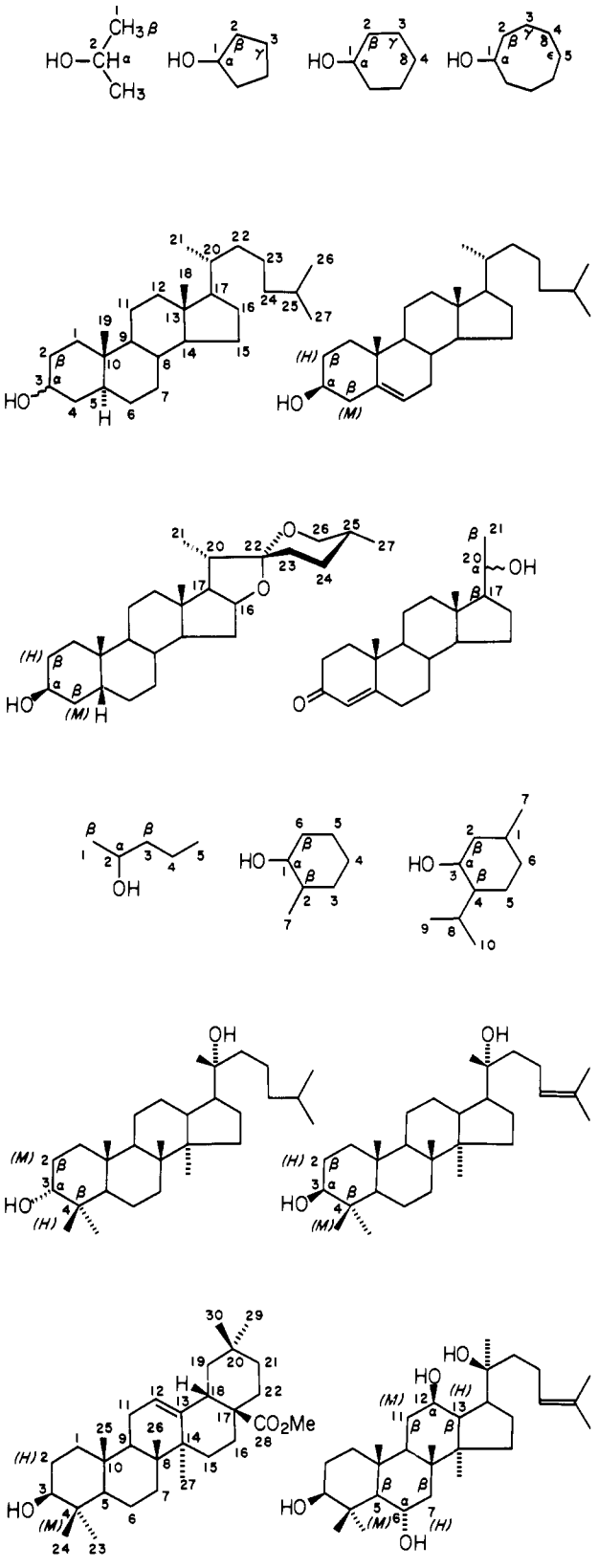
[a] Glc and Glc-Ac_4 stand for glucopyranoside and tetra-*O*-acetylglucopyranoside, respectively. [b] Measured with a Kofler hot-stage apparatus and uncorrected. [c] Measured with a Perkin-Elmer 141 polarimeter in pyridine for the glucopyranosides and in chloroform for tetra-*O*-acetylglucopyranosides at 25–26 °C, $c \sim 1.0$. [d] R. E. Wing and J. N. BeMiller, *Carbohydr. Res.*, **10**, 441–448 (1969). [e] L. C. Kreider and E. Friesen, *J. Am. Chem. Soc.*, **64**, 1482–1483 (1942). [f] R. D. Poretz and I. J. Goldstein, *Biochemistry*, **9**, 2890–2896 (1970). [g] R. P. Linstead, *J. Am. Chem. Soc.*, **62**, 1766–1770 (1940). [h] J. J. Schneider, *Carbohydr. Res.*, **12**, 369–389 (1970). [i] A. Ya. Khorlin, A. F. Bochkov, L. V. Bakinovskii, and N. K. Kochetkov, *Dokl. Akad. Nauk SSSR*, **143**, 1119–1122 (1962). [j] W. Treibs and I. Franke, *Justus Liebigs Ann. Chem.*, **570**, 76–87 (1950). [k] N. K. Kochetkov, A. Ya. Khorlin, and V. I. Snyatkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2028–2036 (1964). [l] E. Hardegger, H. J. Leemann, and F. G. Robinet, *Helv. Chim. Acta*, **35**, 824–829 (1952).

cording to the recommendation of the NMR Data Subcommittee of the Chemical Society of Japan.[7]

Assignments of ^{13}C NMR Signals. The ^{13}C signals were assigned using known chemical shift rules,[8] literature data on analogous compounds (see footnotes of Tables II and III), and the ^1H single-frequency off-resonance decoupling technique.[8] The full signal assignments for a variety of secondary alcohols are shown in Table II. ^{13}C signals of methyl α- (**25**) and β-D-glucopyranosides (**27**), their tetra-*O*-acetyl derivatives (**26** and **28**), and some other typical methyl glycosides are listed in Table III. ^{13}C spectra of secondary alcoholic α- and/or β-D-glucopyranosides and their peracetates were also examined in pyridine-d_5 and chloroform-*d*, respectively. Table IV lists the full signal assignments.

Results and Discussion

The ^{13}C chemical shifts δ of the glucopyranosides obtained (see Table IV) were compared with those of methyl glucopyranosides (see Table III) and the corresponding parent secondary alcohols (see Table II) to derive the glucosidation shift values as follows: $\Delta\delta_S$ = δ(alcoholic glucoside) − δ(methyl glucoside) for sugar moieties and $\Delta\delta_A$ = δ(alcoholic glucoside) − δ(alcohol) for aglycone moieties.[4] Table V lists the glucosidation shift values for the anomeric carbon in the sugar moiety, $\Delta\delta_S$(C-1′), and the α and β carbons from the secondary hydroxyl in the alcohol moiety, $\Delta\delta_A$(C-α) and $\Delta\delta_A$(C-β), in



pyridine-d_5; these are the only numerical values necessary for the present method. The $\Delta\delta$ values for the peracetyl glucosides are listed in Table VI and will be discussed later. Data from the literature are also included in Table V.

In the case of secondary alcohols having two β-CH_2 (see Table V, the sterically unhindered case), the $\Delta\delta_S$(C-1′) and $\Delta\delta_A$(C-α) values fall in the ranges of -2.1 to -3.0 and $+6.4$ to $+7.9$ ppm, respectively. Furthermore, the $\Delta\delta_A$(C-β) value for the β-CH_2 anti to the pyranose-ring oxygen is always larger (ca. -4 ppm) than that for the β-CH_2 syn to the oxygen (ca. -2 ppm) in the most stable conformation when averaged around the glycosidic linkage[1] (see Figure 1). Thus, the assignments of pro-(*S*)- and pro-(*R*)-β-CH_2 of achiral secondary alcoholic glucosides could be differentiated (see Table V).[3,4]

In this paper, we absolutely designated as the (*H*) and the (*M*) carbon the two β carbons on the left and the right side, respectively, of the secondary alcoholic O-C_α bond, when the C_α-H bond is directed downward from the paper plane (see Figure 1).[9] According to this designation, the $\Delta\delta_A$[C-β-(*M*)] value is larger than that for C-β-(*H*) when β-D- or β-L-glucose (Glc) is used, but the values for C-β-(*M*) and C-β-(*H*) are reversed when Glc is α-D or β-L. The absolute configuration of the secondary hydroxyl can thus be determined from the two observed $\Delta\delta_A$(C-β) values in this case.

When one or two substituents are located at the syn-β carbon in a secondary alcohol (see Table IV, sterically hindered case I), the glucosidation shifts are changed to slightly higher fields because the conformation around the glucosidic linkage in its glucoside changes as the alcohol moiety rotates clockwise (see Figure 1) around the O-C_α bond to avoid steric nonbonded interactions.[1]

When one or two substituents are located at the anti-β carbon (see Table V, sterically hindered case II), the glucosidation shifts move to considerably lower fields, because here the conformational change around the glucosidic bond is caused by the alcoholic moiety rotating counterclockwise around the O-C_α bond to avoid the interactions.[1] Marked changes of $\Delta\delta_S$(C-1′) and $\Delta\delta_A$(C-α) values should particularly be emphasized in this case II. It should be noted that linear chain *sec*-(*R*)- and -(*S*)-alcoholic glucosides belong to sterically hindered cases I and II, respectively. Rotation of the long chain around β-CH_2 must exert a steric effect like a substituent on β-CH_2 in a ring alcohol.

Thus, the strategy for determining the absolute configuration of a secondary hydroxyl should be as follows: (1) measure the ^{13}C NMR spectra of the secondary alcohol in pyridine-d_5; (2) prepare its β-D-glucopyranoside by the usual method; (3) measure the spectra of the glucoside; differentiation between α- and β-D-glucopyranosides is easy from the spectra; (4) obtain the glucosidation shifts; and (5) determine the absolute configuration of the secondary hydroxyl using Table VII, which summarizes the shift rules. Ambiguities, if they occur, could be checked by examining the corresponding α-D-glucopyranoside.

The configuration of the secondary hydroxyl of alcohol **22**

Table II. ^{13}C Chemical Shifts (δ) of Secondary Alcohols Examined in Pyridine-d_5 and Chloroform-*d* (in Parentheses)[a]

Carbon no.	**1**	**2**	**3**	**4**	**9, 10**
C-1	26.0 (25.3)	73.1 (73.9)	69.4 (70.0)	71.2 (72.1)	24.2 (23.5)
C-2	63.2 (63.9)	36.0 (35.5)	36.4 (35.6)	35.3 (34.7)	66.7 (67.8)
C-3		23.8 (23.3)	24.6 (24.5)	23.2 (22.8)	42.3 (41.6)
C-4			26.2 (25.8)	27.9 (27.5)	19.5 (19.0)
C-5				25.5 (25.3)	14.4 (14.1)

	11, 12	**13, 14**[b]	**22**[c] Av	**22**[c] Major	**22**[c] Minor	**24**[d]
C-1	75.6 (76.4)	32.0 (31.7)	127.5 (127.7)	126.5 (126.6)	129.1 (129.1)	51.1 (50.7)
C-2	40.9 (40.3)	46.1 (45.2)	28.2 (28.1)	26.0 (25.9)	31.0 (31.0)	27.4 (27.1)
C-3	34.2 (33.7)	70.7 (71.4)	34.0 (33.7)	31.0 (31.0)	36.2 (36.1)	29.3[j] (29.2)
C-4	26.3 (25.7)	50.7 (50.2)	133.6 (133.8)	133.7 (133.9)	132.4 (132.8)	42.6 (42.5)
C-5	25.8 (25.2)	23.7 (23.2)	48.2 (47.7)	48.1 (47.1)	48.1 (47.1)	92.9 (92.9)
C-6	36.6 (35.5)	35.1 (34.7)	72.2 (73.2)	72.2 (73.8)	67.4 (68.7)	29.2[j] (29.2)
C-7	19.4 (18.6)	22.6 (22.2)	44.4 (43.5)	44.1 (43.5)	38.3 (37.8)	46.2 (45.9)
C-8		26.1 (25.8)	23.7 (23.6)	23.9 (23.8)	19.7 (18.6)	36.6 (36.3)
C-9		16.5 (16.1)	40.0 (39.9)	41.5 (41.2)	35.8 (35.5)	75.4 (75.5)
C-10		21.3 (21.1)	148.7 (148.1)	147.4 (146.8)	149.8 (149.0)	42.5 (42.2)
C-11			27.1 (26.7)	26.9 (26.5)	25.1 (24.7)	81.2 (81.3)
C-12			24.2[j] (23.7)[j]	24.4[j] (24.1)[j]	23.6[j] (23.4)[j]	24.3 (24.1)
C-13			20.1[j] (19.9)[j]	20.3[j] (20.0)[j]	19.2[j] (18.6)[j]	30.9 (30.7)
C-14			16.1 (16.0)	15.6 (15.7)	15.6 (15.7)	20.0 (19.7)
C-15			114.1 (114.6)	113.4 (113.7)	116.2 (116.6)	14.4 (14.3)

Carbon no.	**5**[e]	**6**[e]	**7**[f]	**8**[g]	**15**[h]	**16**[h]	**19**[i]
C-1	33.0 (32.6)	37.8 (37.5)	38.1 (37.6)	30.7 (30.4)	36.1 (36.0)	35.9 (35.9)	39.3 (38.9)
C-2	29.9 (29.4)	32.4 (31.9)	32.6 (32.1)	28.7 (28.1)	34.3 (34.0)	34.3 (34.0)	28.2 (27.6)
C-3	65.9 (66.8)	70.8 (71.5)	71.5 (71.9)	66.3 (67.1)	197.8 (198.7)	197.6 (198.7)	78.6 (79.2)
C-4	37.0[j] (36.4)	39.2 (38.7)	43.5 (42.7)	34.7 (34.0)	124.1 (124.0)	124.0 (123.9)	39.3 (38.9)
C-5	39.7 (39.5)	45.6 (45.4)	142.3 (141.1)	37.1 (36.8)	170.3 (170.7)	170.3 (170.8)	56.2 (55.7)
C-6	29.3 (28.9)	29.4 (29.1)	121.1 (121.6)	27.3[j] (26.8)	33.0 (33.0)	33.0 (33.0)	19.0 (18.6)
C-7	32.6 (32.3)	32.4 (32.4)	32.6 (32.3)	27.1[j] (26.8)	32.5 (32.3)	32.6 (32.4)	33.0 (33.1)
C-8	36.1 (36.0)	36.1 (36.0)	32.4 (32.1)	36.0 (35.7)	35.7 (35.6)	35.9 (35.8)	40.1 (39.7)
C-9	55.1 (54.9)	55.1 (55.0)	51.0 (50.7)	40.7 (40.5)	54.4 (54.2)	54.4 (54.2)	48.4 (48.1)
C-10	36.6 (36.5)	36.1 (36.0)	37.2 (36.8)	35.8 (35.3)	38.9 (38.8)	38.9 (38.8)	37.7 (37.4)
C-11	21.3 (21.1)	21.7 (21.6)	21.6 (21.4)	21.5 (21.1)	21.3 (21.0)	21.4 (21.2)	23.9 (23.7)
C-12	40.7 (40.5)	40.6 (40.5)	40.4 (40.2)	40.7 (40.5)	39.3 (39.0)	40.1 (39.9)	123.0 (122.7)
C-13	43.2 (43.0)	43.1 (43.0)	42.9 (42.7)	41.2 (41.0)	42.0 (41.9)	42.9 (42.6)	144.4 (144.1)
C-14	57.1 (57.0)[j]	57.0 (56.9)	57.3 (57.2)	57.0 (56.8)	56.3 (56.1)	56.0 (55.7)	42.2 (42.1)
C-15	24.6 (24.4)	24.5 (24.4)	24.7 (24.5)	32.3 (32.0)	24.5 (24.2)	24.8 (24.6)	28.4 (28.1)
C-16	28.5 (28.3)	28.4 (28.3)	28.5 (28.3)	81.3 (81.1)	25.8 (25.3)	26.0 (25.7)	23.9 (23.5)
C-17	57.1 (56.8)[j]	57.0 (56.9)	57.0 (56.7)	63.6 (62.9)	59.3 (58.7)	59.0 (58.7)	47.3 (47.1)
C-18	12.5 (12.3)	12.5 (12.3)	12.2 (12.0)	16.6 (16.5)	12.9 (12.7)	12.5 (12.4)	42.2 (41.8)
C-19	11.6 (11.3)	12.5 (12.5)	19.6 (19.5)	24.2 (24.0)	17.5 (17.6)	17.5 (17.6)	46.5 (46.3)
C-20	36.1 (36.0)	36.1 (36.0)	36.1 (35.9)	42.3 (41.9)	68.7 (69.5)	69.6 (70.1)	30.9 (30.8)
C-21	19.1 (18.9)	19.1 (18.9)	19.2 (18.9)	14.8 (14.5)	24.5 (23.8)	24.0 (23.8)	34.4 (34.2)
C-22	36.8[j] (36.4)	36.7 (36.6)	36.8 (36.5)	109.2 (109.3)			33.0 (32.7)
C-23	24.4 (24.2)	24.4 (24.2)	24.4 (24.1)	32.2 (31.8)			28.8 (28.3)
C-24	40.0 (39.8)	39.9 (39.8)	40.0 (39.8)	29.5 (29.1)			16.3 (15.6)
C-25	28.3 (28.2)	28.2 (28.2)	28.3 (28.1)	30.7 (30.5			15.6 (15.4)
C-26	22.7 (22.6)	22.7 (22.6)	22.7 (22.6)	67.1 (67.1)			17.3 (17.1)
C-27	22.8 (22.8)	22.8 (22.8)	22.8 (22.8)	17.2 (17.1)			26.1 (26.1)
C-28							177.8 (178.1)
C-29							33.5 (33.1)
C-30							23.9 (23.7)
OMe							51.3 (51.3)

[a] Alcohols **1–4**, **9–14**, and **24** were measured at 30 °C, and **5–8**, **15**, **16**, and **19** were examined at 100 °C in pyridine-d_5 and at 80 °C in chloroform-*d*. [b] For assignments in chloroform-*d*, see Y. Senda and S. Imaizumi, *Tetrahedron*, **31**, 2905–2908 (1975). [c] Examined at 100 °C in pyridine-d_5 and at 55 °C in dichloromethane-d_2 for the conformationally averaged state, and at −40 °C to study the two conformers.[11] [d] Detailed procedure for signal assignments will be published later. [3] For assignments in chloroform-*d*, see H. Eggert, C. L. VanAntwerp, N. S. Bhacca, and C. Djerassi, *J. Org. Chem.*, **41**, 71–78 (1976). [f] For assignments in chloroform-*d*, see G. Popják, J. Edmond, F. A. L. Anet, and K. R. Easton, Jr., *J. Am. Chem. Soc.*, **99**, 931–935 (1977). [g] For assignments in chloroform-*d*, see H. Eggert and C. Djerassi, *Tetrahedron Lett.*, 3635–3638 (1975). [h] Signal assignments were based on those for progesterone. See N. S. Bhacca, D. C. Giannini, W. S. Jankowski, and M. E. Wolff, *J. Am. Chem. Soc.*, **95**, 8421–8426 (1973). [i] For assignments in chloroform-*d*, see K. Tori, S. Seo, A. Shimaoka, and Y. Tomita, *Tetrahedron Lett.*, 4227–4230 (1974). [j] These assignments may be reversed in each vertical column.

Table III. ^{13}C Chemical Shifts (δ) of Some Methyl Glycopyranosides in Pyridine-d_5[a]

Methyl glycoside	C-1	C-2	C-3	C-4	C-5	C-6	OMe
α-D-Glucopyranoside (**25**)[b]	101.2 (101.2)	73.7 (73.5)	75.3 (75.3)	72.0 (72.4)	73.9 (73.6)	62.7 (63.1)	55.0 (55.2)
Tetra-*O*-acetyl-**25** (**26**)[c,d]	96.9 (97.1)	70.9 (71.1)	70.2 (70.4)	68.8 (69.1)	67.4 (67.5)	62.1 (62.3)	55.3 (55.5)
β-D-Glucopyranoside (**27**)[e,f]	105.4 (105.4)	74.8 (75.0)	78.1 (78.4)	71.4 (72.0)	78.1 (78.0)	62.5 (63.0)	56.7 (56.6)
Tetra-*O*-acetyl-**27** (**28**)[c,d]	101.5 (101.8)	71.3 (71.9)	72.9 (73.4)	68.5 (69.3)	71.8 (72.3)	62.0 (62.5)	56.8 (56.5)
α-D-Mannopyranoside[g]	102.3 (102.6)	71.8 (71.9)	72.8 (73.0)	68.7 (69.5)	74.7 (74.4)	62.8 (63.4)	54.6 (54.7)
β-D-Mannopyranoside[g]	102.9 (102.8)	72.1 (72.9)	75.7 (75.7)	69.0 (69.7)	78.9 (78.4)	63.0 (63.4)	56.5 (56.4)
α-D-Galactopyranoside[h]	101.7 (101.6)	70.5 (70.6)	71.6 (71.7)	70.9 (71.0)	72.5 (72.2)	62.6 (62.8)	55.1 (55.3)
β-D-Galactopyranoside[h]	106.1 (105.9)	72.5 (72.5)	75.2 (75.2)	70.1 (70.3)	76.8 (76.6)	62.3 (62.5)	56.6 (56.4)
α-L-Rhamnopyranoside[e]	102.4 (102.5)	71.9 (72.0)	72.5 (72.7)	73.6 (73.9)	69.4 (69.4)	18.4 (18.3)	54.5 (54.6)
β-L-Rhamnopyranoside	102.7 (102.5)	72.2 (72.1)	75.4 (75.6)	73.8 (74.1)	73.5 (73.4)	18.5 (18.3)	56.5 (56.2)
α-D-Fucopyranoside[h]	101.6 (101.7)	70.0 (70.4)	71.5 (71.8)	73.1 (73.2)	66.9 (67.0)	17.1 (16.8)	55.2 (55.3)
β-D-Fucopyranoside[e]	105.9 (105.6)	72.0 (72.1)	75.2 (75.2)	72.6 (72.6)	71.3 (71.4)	17.2 (16.9)	56.5 (56.3)
α-D-Xylopyranoside[b]	101.5 (101.5)	73.6 (73.7)	75.3 (75.5)	71.3 (71.4)	63.0 (63.2)		55.1 (55.3)
β-D-Xylopyranoside[b]	106.1 (105.8)	74.6 (74.4)	78.1 (77.7)	70.9 (71.0)	66.9 (66.6)		56.6 (56.3)
α-L-Arabinopyranoside[b]	105.9 (105.5)	72.2 (72.3)	74.4 (74.3)	69.1 (68.7)	66.6 (66.1)		56.4 (56.0)
β-L-Arabinopyranoside[b]	102.0 (101.9)	70.1 (69.9)	70.4 (70.8)	70.8 (71.1)	63.9 (63.9)		55.3 (55.5)

[a] Measured at 30 and 100 °C (in parentheses). [b] For signal assignments in deuterium oxide, see P. A. J. Gorin and M. Mazurek, *Can. J. Chem.*, **53**, 1212–1223 (1975). [c] Measured in chloroform-*d* at 30 and 80 °C (in parentheses). [d] For signal assignments, see D. Y. Gagnaire, F. R. Taravel, and M. R. Vignon, *Carbohydr. Res.*, **51**, 157–168 (1976). [e] Reference 2. [f] S. Yahara, R. Kasai, and O. Tanaka, *Chem. Pharm. Bull.*, **25**, 2041–2047 (1977). [g] For signal assignments in deuterium oxide, see J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 461–462. [h] For signal assignments in deuterium oxide, see T. E. Walker, R. E. London, T. W. Whaley, R. Barker, and N. A. Matwiyoff, *J. Am. Chem. Soc.*, **98**, 5807–5813 (1976).

Table IV. ^{13}C Chemical Shifts (δ) of Glucopyranosides Examined in Pyridind2-d_5 and Their Peracetates in Chloroform-*d* (in Parentheses)[a]

Carbon no.	α-D-Glc-**1**	β-D-Glc-**1**	α-D-Glc-**2**	β-D-Glc-**2**	β-D-Glc-**3**[c]	β-D-Glc-9	β-D-Glc-**10**
C-1	21.6 (20.6)	23.8 (23.3)	79.5 (80.3)	80.4 (81.6)	76.5 (77.9)	19.8 (19.8)	22.0 (21.6)
C-2	69.7 (71.5)	70.8 (73.0)	32.0 (31.9)	33.6 (33.2)	34.1 (33.2)	73.7 (75.7)	75.8 (78.1)
C-3	23.6 (23.1)	22.0 (22.0)	23.5[b] (23.0)[b]	23.7[b] (23.3)[b]	24.3[b] (23.6)	39.8 (39.0)	39.2 (38.9)
C-4			23.8[b] (23.4)[b]	23.6[b] (23.1)[b]	25.9 (25.5)	18.8 (18.4)	18.7 (18.4)
C-5			33.5 (32.9)	32.4 (32.1)	24.1[b] (23.6)	14.2 (13.9)	14.2 (14.0)
C-6					32.2 (31.6)		
C-1′	98.3 (94.3)	102.4 (99.6)	99.1 (94.5)	103.0 (99.6)	102.4 (99.4)	102.0 (99.3)	103.9 (101.1)
C-2′	73.5 (71.1)	75.0 (71.6)	73.8 (71.1)	75.0 (71.5)	75.1 (71.6)	74.9 (71.7)	75.1 (71.7)
C-3′	75.2 (70.3)	78.2 (73.0)	75.4 (70.4)	78.3 (73.0)	78.2 (73.0)	78.3 (73.1)	78.3 (73.0)
C-4′	72.2 (68.9)	71.6 (68.7)	72.5 (68.9)	71.5 (68.7)	71.6 (68.7)	71.7 (68.9)	71.7 (68.7)
C-5′	74.0 (67.3)	78.1 (71.6)	74.3 (67.3)	78.2 ((71.7)	78.2 (71.6)	78.0 (71.7)	78.0 (71.7)
C-6′	62.9 (62.1)	62.7 (62.2)	63.1 (62.1)	62.7 (62.2)	62.8 (62.2)	62.8 (62.3)	62.8 (62.3)

	β-D-Glc-**4**[c]	α-D-Glc-**11**[d]	β-D-Glc-**11**[d]	α-D-Glc-**12**[d]	β-D-Glc-**12**[d]	α-D-Glc-**13**	β-D-Glc-**13**[d]
C-1	78.8 (80.5)	85.5 (87.5)	81.4 (83.6)	79.6 (82.1)	85.5 (87.6)	31.9 (31.7)	31.6 (31.5)
C-2	33.3 (32.3)	39.3 (38.4)	38.3 (37.5)	38.4 (37.6)	39.3 (38.1)	43.6 (42.9)	41.1 (40.8)
C-3	23.3 (22.6)[b]	34.1 (33.7)	33.9 (33.6)	34.1 (33.7)	33.9 (33.6)	81.1 (83.0)	77.0 (79.0)
C-4	27.8[b] (27.4)	25.7 (25.3)	25.6 (25.1)	25.7 (25.3)	25.6 (25.1)	49.4 (48.5)	48.5 (47.5)
C-5	25.4 (25.1)	25.4 (25.0)	24.9 (24.7)	24.9 (24.6)	25.4 (25.1)	23.3 (22.9)	23.5 (23.0)
C-6	27.5[b] (27.4)	34.1 (33.7)	31.6 (31.3)	30.6 (30.6)	34.8 (33.6)	34.6 (34.2)	34.7 (34.2)
C-7	23.0 (22.4)[b]	19.1 (18.4)	19.2 (18.7)	19.7 (19.4)	19.2 (18.4)	22.5 (22.4)	22.5 (22.2)
C-8	31.0 (30.8)					24.9 (25.0)	25.4 (25.0)
C-9						16.3 (15.8)	16.1 (15.5)
C-10						21.4 (21.0)	21.2 (20.8)
C-1′	102.8 (99.7)	102.3 (97.6)	101.5 (98.8)	96.0 (92.7)	106.0 (101.9)	102.3 (97.7)	101.4 (98.7)
C-2′	75.2 (71.7)	74.2 (71.3)	75.1 (71.6)	73.7 (71.1)	75.6 (71.6)	74.3 (71.3)	75.0 (71.6)
C-3′	78.5 (73.0)	75.2 (70.3)	78.5 (73.1)	75.4 (70.3)	78.5 (73.1)	75.2 (70.3)	78.5 (73.1)
C-4′	71.7 (68.8)	72.4 (69.0)	72.0 (68.9)	72.4 (69.0)	71.8 (68.9)	72.5 (69.0)	72.1 (69.0)
C-5′	78.3 (71.1)	74.2 (67.4)	78.2 (71.6)	74.4 (67.6)	78.1 (71.6)	74.3 (67.5)	77.9 (71.6)
C-6′	62.8 (62.2)	63.0 (62.1)	63.1 (62.2)	63.0 (62.1)	63.0 (62.2)	63.1 (62.4)	63.2 (62.5)

			β-D-Glc-**22**[e]			
	α-D-Glc-**14**	β-D-Glc-**14**	Av	Major	Minor	β-D-Glc-**24**
C-1	31.5 (31.3)	31.8 (31.7)	127.3 (127.3)	124.3 (126.2)	126.9 (129.1)	50.1 (50.2)
C-2	40.2 (40.3)	44.3 (42.9)	28.0 (28.0)	36.1 (25.9)	30.7 (30.8)	28.7 (28.5)
C-3	75.4 (77.9)	81.1 (83.0)	33.5 (33.4)	30.7 (30.8)	35.7 (36.0)	29.5 (29.5)[b]
C-4	48.5 (47.6)	49.4 (48.1)	134.1 (134.2)	134.6 (134.2)	132.8 (133.2)	43.2 (42.7)
C-5	23.1 (22.6)	23.3 (22.9)	43.7 (43.5)	43.7 (42.8)	43.7 (42.8)	92.5 (92.2)
C-6	34.8 (34.3)	34.7 (34.2)	79.9 (80.5)	80.9 (81.7)	75.7 (76.7)	29.5 (29.4)[b]
C-7	22.5 (22.2)	22.5 (22.3)	44.3 (43.5)	43.7 (43.5)	37.9 (37.4)	46.9 (46.3)
C-8	25.5 (25.5)	24.9 (25.0)	23.0 (22.9)	24.3 (23.5)	19.7 (20.0)	36.5 (35.4)

Table IV (*Continued*)

Carbon no.	α-D-Glc-**14**	β-D-Glc-**14**	β-D-Glc-**22**[e] Av	β-D-Glc-**22**[e] Major	β-D-Glc-**22**[e] Minor	β-D-Glc-**24**
C-9	15.8 (15.2)	16.3 (15.9)	40.3 (39.9)	41.6 (41.0)	35.7 (35.3)	84.3 (85.5)
C-10	21.4 (21.2)	21.3 (20.9)	148.1 (147.2)	146.7 (145.7)	149.9 (148.2)	42.4 (41.6)
C-11			27.1 (27.2)	26.8 (27.5)	25.2 (25.2)	80.9 (80.6)
C-12			23.9[b] (23.7)[b]	24.4[b] (23.9)[b]	23.7[b] (23.5)[b]	25.1 (24.6)
C-13			20.0[b] (19.7)[b]	20.3[b] (20.0)[b]	19.2[b] (18.6)[b]	32.2 (31.8)
C-14			16.0 (15.9)	15.7 (15.6)	15.7 (15.6)	19.6 (19.0)
C-15			114.7 (115.2)	114.0 (114.5)	*f* (117.1)	14.1 (13.9)
C-1′	96.1 (92.9)	106.0 (101.9)	102.9 (99.5)	103.5 (99.0)	*f* (99.4)	107.8 (103.5)
C-2′	73.7 (71.0)	75.6 (71.6)	75.2 (72.0)	75.1 (70.7)	*f* (71.0)	75.2 (71.5)
C-3′	75.2 (70.2)	78.5 (73.1)	78.7 (73.4)	78.7 (72.3)	*f* (72.3)	78.3 (73.1)
C-4′	72.2 (68.6)	71.7 (68.8)	72.6 (69.6)	70.8 (68.3)	70.9 (68.8)	72.2 (68.7)
C-5′	74.4 (67.9)	78.0 (71.7)	77.7 (72.6)	78.7 (72.0)	*f* (72.0)	78.0 (71.9)
C-6′	63.0 (62.1)	62.9 (62.5)	63.5 (63.0)	62.0 (62.5)	62.5 (63.2)	63.5 (61.9)
	α-D-Glc-**5**	β-D-Glc-**5**	α-D-Glc-6	β-D-Glc-6	α-D-Glc-7	β-D-Glc-7
C-1	33.0 (32.3)	33.1 (32.7)	37.5 (37.2)	37.5 (37.1)	37.6 (37.3)	37.8 (37.3)
C-2	28.1 (27.8)	26.0 (25.7)	28.4 (28.3)	30.1 (29.3)	28.5 (28.2)	30.4 (29.5)
C-3	73.2 (73.2)	73.8 (74.6)	77.5 (79.0)	78.0 (79.7)	78.2 (79.2)	78.7 (80.0)
C-4	33.7 (33.2)	35.1 (34.5)	36.8 (36.5)	35.2 (34.7)	40.8 (40.1)	39.6 (39.0)
C-5	40.1 (39.8)	39.8 (39.5)	45.6 (45.5)	45.2 (44.9)	141.5 (140.7)	141.4 (140.4)
C-6	29.1 (28.9)	29.0 (28.6)	29.3 (29.1)	29.2 (28.9)	121.8 (122.2)	121.7 (122.0)
C-7	32.3 (32.3)	32.3 (32.1)	32.5 (32.3)	32.5 (32.1)	32.4 (32.2)	32.4 (32.0)
C-8	36.1 (35.9)	36.0 (35.9)	36.1 (35.9)	36.0 (35.6)	32.4 (32.2)	32.4 (32.0)
C-9	54.8 (54.8)	54.5 (54.7)	55.0 (54.9)	55.0 (54.6)	50.8 (50.6)	50.8 (50.3)
C-10	36.3 (36.5)	36.0 (35.9)	36.1 (35.9)	36.0 (35.6)	37.2 (36.9)	37.2 (36.8)
C-11	21.3 (21.1)	21.2 (21.0)	21.8 (21.5)	21.7 (21.3)	21.5 (21.3)	21.5 (21.1)
C-12	40.5 (40.3)	40.5 (40.4)	40.7 (40.4)	40.6 (40.1)	40.3 (40.1)	40.3 (39.9)
C-13	43.1 (43.0)	43.0 (42.9)	43.2 (43.0)	43.1 (42.7)	42.8 (42.7)	42.8 (42.4)
C-14	57.1[b] (56.8)	57.0 (56.8)	57.1 (56.8)	56.9 (56.5)	57.2 (57.1)	57.2 (56.9)
C-15	24.4 (24.3)	24.3 (24.3)	24.6 (24.4)	24.5 (24.2)	24.6 (24.4)	24.6 (24.3)
C-16	28.4 (28.3)	28.4 (28.3)	28.4 (28.1)	28.4 (28.3)	28.5 (28.2)	28.4 (28.2)
C-17	56.9[b] (56.8)	57.0 (56.7)	57.1 (56.8)	56.9 (56.5)	56.9 (56.6)	56.9 (56.3)
C-18	12.4 (12.3)	12.4 (12.2)	12.5 (12.3)	12.4 (12.1)	12.1 (12.0)	12.1 (11.9)
C-19	11.6 (11.5)	11.6 (11.5)	12.5 (12.4)	12.4 (12.3)	19.5 (19.4)	19.5 (19.3)
C-20	36.1 (35.9)	36.0 (35.9)	36.1 (35.9)	36.0 (35.6)	36.1 (35.9)	36.0 (35.8)
C-21	19.1 (18.9)	19.1 (18.9)	19.2 (18.9)	19.1 (18.7)	19.2 (18.9)	19.1 (18.8)
C-22	36.8 (36.2)	36.7 (36.4)	36.8 (36.2)	36.7 (36.3)	36.7 (36.5)	36.7 (36.3)
C-23	24.4 (24.1)	24.3 (24.0)	24.4 (24.1)	24.3 (23.9)	24.3 (24.1)	24.3 (23.9)
C-24	40.0 (39.8)	39.8 (39.7)	40.0 (39.8)	39.9 (39.6)	39.9 (39.8)	39.9 (39.6)
C-25	28.2 (28.2)	28.2 (28.1)	28.4 (28.1)	28.2 (28.0)	28.3 (28.2)	28.2 (28.0)
C-26	22.7 (22.6)	22.7 (22.6)	22.7 (22.6)	22.7 (22.6)	22.7 (22.6)	22.7 (22.6)
C-27	22.7 (22.8)	22.8 (22.8)	22.8 (22.8)	22.8 (22.8)	22.8 (22.8)	22.8 (22.8)
C-1′	98.7 (94.0)	102.7 (99.3)	98.5 (94.8)	102.4 (99.6)	98.6 (94.6)	102.7 (99.7)
C-2′	73.8 (71.7)	75.1 (72.1)	73.8 (71.6)	75.2 (71.8)	73.8 (71.5)	75.2 (71.8)
C-3′	75.6 (71.0)	78.4 (73.4)	75.7 (70.8)	78.4 (73.1)	75.6 (70.7)	78.4 (73.1)
C-4′	72.9 (69.6)	72.1 (69.4)	73.0 (69.6)	72.2 (68.9)	72.8 (69.5)	72.1 (68.9)
C-5′	74.0 (67.8)	77.6 (72.1)	73.8 (67.7)	77.8 (71.8)	73.9 (67.7)	77.8 (71.8)
C-6′	63.4 (62.6)	63.2 (62.5)	63.5 (62.6)	63.3 (62.3)	63.4 (62.5)	63.2 (62.2)
	α-D-Glc-**8**	β-D-Glc-**8**	β-D-Glc-**15**	β-D-Glc-**16**	α-D-Glc-**19**	β-D-Glc-**19**
C-1	31.2 (30.4)	31.0 (30.5)	36.0 (35.9)	36.0 (36.0)	38.8 (38.5)	39.0 (38.7)
C-2	24.9 (24.0)	27.0 (26.7)	34.3 (34.0)	34.4 (34.1)	23.8 (23.8)	26.5 (25.9)
C-3	73.7 (73.5)	74.7 (74.9)	197.8 (198.5)	198.1 (198.9)	84.6 (86.1)	89.1 (90.5)
C-4	32.8 (32.0)	31.0 (30.5)	124.1 (124.0)	124.0 (124.0)	39.0 (38.8)	39.5 (39.0)
C-5	37.9 (37.4)	37.2 (37.1)	170.3 (170.5)	170.7 (171.0)	56.3 (56.0)	56.2 (55.9)
C-6	27.1 (26.8)	27.1 (26.7)	32.9 (32.9)	33.0 (33.1)	18.8 (18.6)	18.6 (18.4)
C-7	27.1 (26.8)	27.1 (26.7)	32.4 (32.2)	32.7 (32.4)	33.4 (33.1)	33.3 (33.1)
C-8	36.0 (35.7)	35.9 (35.7)	35.7 (35.6)	36.0 (36.0)	40.1 (39.8)	40.0 (39.6)
C-9	40.8 (40.5)	40.6[b] (40.6)	54.2 (54.0)	54.6 (54.3)	48.2 (48.0)	48.1 (47.9)
C-10	36.0 (35.7)	35.4 (35.3)	38.9 (38.7)	39.0 (38.9)	37.5 (37.2)	37.2 (37.0)
C-11	21.5 (21.1)	21.3 (21.2)	21.2 (21.0)	21.5 (21.2)	23.2 (22.9)	23.8 (23.6)
C-12	40.8 (40.5)	40.8[b] (40.6)	39.3 (38.9)	39.7 (38.9)	123.0 (122.6)	122.9 (122.5)
C-13	41.2 (41.0)	41.1 (41.0)	42.9 (41.6)	43.0 (42.6)	144.4 (144.2)	144.3 (143.9)
C-14	57.0 (56.8)	56.8 (56.9)	56.2 (55.9)	56.2 (55.8)	42.2 (42.1)	42.0 (41.9)
C-15	32.4 (32.0)	32.3 (32.0)	24.3 (24.1)	24.6 (24.4)	28.3 (28.0)	28.2 (27.9)
C-16	81.4 (81.1)	81.3 (81.1)	26.7 (26.2)	26.0 (25.7)	23.8 (23.5)	23.8 (23.4)
C-17	63.6 (62.9)	63.5 (63.0)	58.3 (57.2)	57.0 (56.2)	47.3 (47.1)	47.1 (46.9)
C-18	16.6 (16.5)	16.5 (16.5)	12.8 (12.6)	12.0 (11.5)	42.3 (41.7)	42.2 (41.6)
C-19	24.1 (24.0)	23.9 (24.0)	17.4 (17.5)	17.6 (17.6)	46.5 (46.3)	46.4 (46.2)
C-20	42.3 (41.9)	42.2 (42.0)	80.5 (82.1)	74.9 (75.6)	30.9 (30.8)	30.8 (30.7)
C-21	14.8 (14.5)	14.8 (14.5)	22.9 (22.1)	18.9 (18.4)	34.3 (34.2)	34.2 (34.1)
C-22	109.3 (109.3)	109.2 (109.3)			33.1 (32.7)	32.9 (32.5)
C-23	32.2 (31.8)	32.1 (31.8)			29.1 (28.9)	28.4 (27.9)

Table IV (*Continued*)

Carbon no.	α-D-Glc-**8**	β-D-Glc-**8**	β-D-Glc-**15**	β-D-Glc-**16**	α-D-Glc-**19**	β-D-Glc-**19**
C-24	29.5 (29.1)	29.4 (29.1)			17.0 (16.7)	16.9 (16.4)
C-25	30.8 (30.5)	30.7 (30.5)			15.5 (15.4)	15.5 (15.3)
C-26	67.2 (67.1)	67.1 (67.0)			17.4 (17.1)	17.3 (17.0)
C-27	17.2 (17.1)	17.2 (17.1)			26.2 (26.0)	26.2 (25.9)
C-28					177.9 (178.2)	177.8 (177.9)
C-29					33.1 (33.1)	33.1 (33.1)
C-30					23.8 (23.8)	23.8 (23.7)
OMe					51.4 (51.4)	51.3 (51.3)
C-1′	98.7 (93.8)	103.1 (99.3)	105.3 (102.2)	100.9 (97.8)	97.4 (93.7)	106.3 (102.9)
C-2′	73.9 (71.5)	75.2 (72.2)	75.6 (71.9)	75.2 (71.9)	73.8 (71.6)	75.6 (71.8)
C-3′	75.7 (70.9)	78.5 (73.4)	78.4 (73.4)	78.5 (73.4)	75.6 (70.7)	78.5 (73.2)
C-4′	72.9 (69.4)	72.3 (69.5)	72.3 (69.3)	72.7 (69.6)	72.7 (69.4)	72.1 (69.3)
C-5′	74.1 (67.7)	77.7 (72.2)	77.6 (72.2)	77.6 (72.1)	74.3 (68.2)	77.6 (72.2)
C-6′	63.5 (62.5)	63.3 (62.6)	63.4 (62.6)	63.7 (62.6)	63.4 (62.5)	63.3 (62.5)

[a] The glucosides of **1–4**, **9–14**, and **24** were measured at 30 °C, and those of **5–8**. **15**, **16**, and **19** were examined at 100 °C in pyridine-d_5 and at 80 °C in chloroform-*d*. [b] These assignments may be reversed in each vertical column. [c] We thank Dr. H. Arita of this laboratory for the samples. [d] These data were taken from the spectra of a diastereomeric mixture of α-D-Glc-**11** and -**12** and that of β-D-Glc-**11** and -**12**. [e] Examined at 100 °C in pyridine-d_5 and at 55 °C in dichloromethane-d_2 (in parentheses) for the conformationally averaged state, and at −40 °C to study the two conformers.[11] [f] Not assignable owing to signal broadenings.

Table V. Glucosidation Shifts in Pyridine-d_5 ($\Delta\delta$ in ppm)[a]

Glc	Alcohol	$\Delta\delta_S$(C-1′)	$\Delta\delta_A$(C-α)	$\Delta\delta_A$[C-β-(*H*)]	$\Delta\delta_A$[C-β-(*M*)]
			Achiral Secondary Alcoholic Glucosides		
α-D	**1**	−2.9	+6.5	−4.4	−2.4
α-D	**2**	−2.1	+6.4	−4.0	−2.5
β-D	**1**	−3.0	+7.6	−2.2	−4.0
		[−3.1	+7.6	−1.8	−3.6][b]
β-D	**2**	−2.4	+7.3	−2.4	−3.6
β-D	**3**	−3.0	+7.1	−2.3	−4.2
β-D	**4**	−2.6	+7.6	−2.0	−4.3
			Chiral Secondary Alcoholic Glucosides		
			Sterically Unhindered Case		
α-D	**5** (*R*)	−2.5	+7.3(C-3)	−3.3(C-4)	−1.8(C-2)
α-D	6 (*S*)	−2.7	+6.7(C-3)	−4.0(C-2)	−2.4(C-4)
β-L	6 (*S*)	[−3.1	+7.2(C-3)	−4.1(C-2)	−2.7(C-4)][b]
α-D	7 (*S*)	−2.6	+6.7(C-3)	−4.1(C-2)	−2.7(C-4)
α-D	**8** (*S*)	−2.5	+7.4(C-3)	−3.8(C-2)	−1.9(C-4)
β-D	**5** (*R*)	−2.7	+7.9(C-3)	−1.9(C-4)	−3.9(C-2)
		[−3.1	+7.5	−1.9	−4.3][b]
β-D	6 (*S*)	−3.0	+7.2(C-3)	−2.3(C-2)	−4.0(C-4)
		[−3.5	+6.7	−2.5	−4.4][b]
β-D	7 (*S*)	−2.7	+7.2(C-3)	−2.2(C-2)	−3.9(C-4)
		[−3.0	+7.0	−2.3	−4.0][b]
β-D	**8** (*S*)	−2.3	+7.7(C-3)	−1.7(C-2)	−3.7(C-4)
			Sterically Hindered Case I		
α-D	**12** (*S*)	−5.2	+4.3(C-1)	−6.0(C-6,CH_2)	−2.5(C-2,CH)
α-D	**14** (*S*)	−5.2	+4.2(C-3)	−5.9(C-2,CH_2)	−2.2(C-4,CH)
β-L	**18** (*S*)	[−3.2	+6.9(C-3)	−4.2(C-2,CH_2)	−0.8(C-4,C)][b]
α-D	**19** (*S*)	−3.8	+6.0(C-3)	−4.4(C-2,CH_2)	−0.3(C-4,C)
β-D	**9** (*R*)	−3.4	+7.0(C-2)	−2.5(C-3,CH_2)	−4.4(C-1,Me)
β-D	**11** (*R*)	−3.9	+5.8(C-1)	−2.6(C-2,CH)	−5.0(C-6,CH_2)
β-D	**13** (*R*)	−4.0	+6.3(C-3)	−2.2(C-4,CH)	−5.0(C-2,CH_2)
		[−4.0	+6.4	−2.1	−4.9][b]
β-D	**16** (*R*)	−4.5	+5.3(C-20)	−2.0(C-17,CH)	−5.1(C-21,Me)
β-D	**17** (*R*)	[−3.3	+6.8(C-3)	−0.6(C-4,C)	−3.7(C-2,CH_2)][b]
α-D	**20**[c] (*R*)	[−5.1	+7.4(C-12)	−1.9(C-13,CH)	−4.0(C-12,CH_2)][b]
β-D	**22**[d] (*R*)	Av −2.5	+7.7(C-6)	−0.1(C-7,CH)	−4.5(C-5,CH_2)
		Major −1.9	+8.7	−0.4	−4.4
		Minor −2.4	+8.3	−0.4	−4.4
			Sterically Hindered Case II		
α-D	**11** (*R*)	+1.1	9.9(C-1)	−1.6(C-2,CH)	−2.5(C-6,CH_2)
α-D	**13** (*R*)	+1.1	+10.4(C-3)	−1.3(C-4,CH)	−2.5(C-2,CH_2)
β-D	**10** (*S*)	−1.5	+9.1(C-2)	−2.2(C-1,Me)	−3.1(C-3,CH_2)
β-D	**12** (*S*)	+0.6	+9.9(C-1)	−1.8(C-6,CH_2)	−1.6(C-2,CH)
β-D	**14** (*S*)	+0.6	+10.4(C-3)	−1.8(C-2,CH_2)	−1.3(C-4,CH)
		[+0.4	+10.5	−1.8	−1.1][b]
β-D	**15** (*S*)	−0.1	+11.8(C-20)	−1.6(C-21,Me)	−1.0(C-17,CH)
β-D	**18** (*S*)	[+1.4	+10.8(C-3)[e]	−1.2(C-2,CH_2)	+0.3(C-4,C)][b]

Table V (*Continued*)

Glc	Alcohol	$\Delta\delta_S$(C-1′)	$\Delta\delta_A$(C-α)	$\Delta\delta_A$[C-β-(*H*)]	$\Delta\delta_A$[C-β-(*M*)]
β-D	**19** (*S*)	+0.9	+10.5(C-3)	−1.7(C-2,CH_2)	+0.2(C-4,C)
β-D	**20**[f] (*S*)	[+0.4	+10.4(C-6)	−2.2(C-7,CH_2)	−0.3(C-5,C)][b]
β-D	**24** (*S*)	+2.4	+8.9(C-9)	−0.1(C-8,CH_2)	−0.1(C-10,CH)

[a] Plus sign denotes a downfield shift. [b] Data taken from ref 3. [c] Glc at C-12 (chikusetsu-saponin-L_{10}).[3] [d] See footnote *c*, Table II. [e] Revised value (O. Tanaka, private communication). [f] Glc at C-6 (ginsenoside-Rh_1).[3]

Table VI. Tetra-*O*-acetylglucosidation Shifts in Chloroform-*d* ($\Delta\delta$ in ppm)[a]

Glc-Ac_4	Alcohol	$\Delta\delta_S$(C-1′)	$\Delta\delta_A$(C-α)	$\Delta\delta_A$[C-β-(*H*)]	$\Delta\delta_A$[C-β-(*M*)]
			Achiral Secondary Alcoholic Tetra-*O*-acetylglucosides		
α-D	**1**	−2.6	+7.6	−4.7	−2.2
α-D	**2**	−2.4	+6.4	−3.6	−2.6
β-D	**1**	−1.9	+9.1	−2.0	−3.3
β-D	**2**	−1.9	+7.7	−2.3	−3.4
β-D	**3**	−2.1	+7.9	−2.4	−4.0
β-D	**4**	−1.8	+8.4	−2.4	−3.9
			Chiral Secondary Alcoholic Tetra-*O*-acetylglucosides		
			Sterically Unhindered Case		
α-D	**5** (*R*)	−3.1	+6.4(C-3)	−3.2(C-4)	−1.6(C-2)
α-D	**6** (*S*)	−2.3	+7.5(C-3)	−3.6(C-2)	−2.2(C-4)
α-D	**7** (*S*)	−2.5	+7.3(C-3)	−3.9(C-2)	−2.6(C-4)
α-D	**8** (*S*)	−3.3	+6.4(C-3)	−4.1(C-2)	−2.0(C-4)
β-D	**5** (*R*)	−2.5	+7.8(C-3)	−1.9(C-4)	−3.7(C-2)
β-D	**6** (*S*)	−2.2	+8.2(C-3)	−2.6(C-2)	−4.0(C-4)
β-D	**7** (*S*)	−2.1	+8.1(C-3)	−2.6(C-2)	−3.7(C-4)
β-D	**8** (*S*)	−2.5	+7.8(C-3)	−1.4(C-2)	−3.5(C-4)
			Sterically Hindered Case I		
α-D	**12** (*S*)	−3.8	+5.7(C-1)	−4.9(C-6,CH_2)	−2.7(C-2,CH)
α-D	**14** (*S*)	−4.0	+6.5(C-3)	−4.9(C-2,CH_2)	−2.6(C-4,CH)
α-D	**19** (*S*)	−3.4	+6.9(C-3)	−3.8(C-2,CH_2)	−0.1(C-4,C)
β-D	**9** (*R*)	−2.2	+7.9(C-2)	−2.6(C-3,CH_2)	−3.7(C-1,Me)
β-D	**11** (*R*)	−2.7	+7.2(C-1)	−2.8(C-2,CH)	−4.2(C-6,CH_2)
β-D	**13** (*R*)	−2.8	+7.6(C-3)	−2.7(C-4,CH)	−4.4(C-2,CH_2)
β-D	**16** (*R*)	−4.0	+5.5(C-20)	−2.5(C-17,CH)	−5.4(C-21,Me)
β-D	**22**[b] (*R*)	Av −2.3	+7.3(C-6)	0.0(C-7,CH)	−4.2(C-5,CH_2)
		Major −2.5	+7.9	0.0	−4.3
		Minor −2.1	+8.0	−0.4	−4.3
			Sterically Hindered Case II		
α-D	**11** (*R*)	+1.1	+11.1(C-1)	−1.9(C-2,CH)	−1.8(C-6,CH_2)
α-D	**13** (*R*)	+0.8	+11.6(C-3)	−1.7(C-4,CH)	−2.3(C-2,CH_2)
β-D	**10** (*S*)	−0.4	+10.3(C-2)	−1.9(C-1,Me)	−2.7(C-3,CH_2)
β-D	**12** (*S*)	+0.4	+11.2(C-1)	−1.9(C-6,CH_2)	−2.2(C-2,CH)
β-D	**14** (*S*)	+0.4	+11.6(C-1)	−2.3(C-2,CH_2)	−2.1(C-4,CH)
β-D	**15** (*S*)	+0.4	+12.6(C-20)	−1.7(C-21,Me)	−1.5(C-17,CH)
β-D	**19** (*S*)	+1.1	+11.3(C-3)	−1.7(C-2,CH_2)	+0.1(C-4,C)
β-D	**24** (*S*)	+2.0	+10.0(C-9)	−0.9(C-8,CH_2)	−0.6(C-10,CH)

[a] Plus sign denotes a downfield shift. [b] See footnote *c*, Table II.

prepared from preisocalamenediol (**21**) by reduction with lithium aluminum hydride was earlier reported to be β-(*S*).[10] However, the β-D-glucosidation shifts of **22**[11] showed that the C-β-(*M*) is assigned to C-5, not C-7 (see Table V, sterically hindered case I), for both major and minor conformers of the ten-membered ring at −40 °C, demonstrating that the configuration is apparently α-(*R*). The β-D-glucosidation shifts of liguloxidol (**24**)[12] were observed to belong to sterically hindered case II, showing that the reported β configuration[12] of the hydroxyl is correct (see Table V). However, the $\Delta\delta$ values for these two cases are somewhat different from the normal ones shown in Table VII. These values probably result from the sterically more crowded environment around the glucosidic linkages. In fact, 9α-hydroxyliguloxide (**23**),[12] an epimer of liguloxidol, formed no glucoside but an ortho ester only. Caution should therefore be exercised for such a sterically crowded alcohol, although the rule is still almost valid.

In a manner similar to the method described above, tetra-*O*-acetylglucosidation shifts can be used for the present purpose, as can be seen from Table VI. However, these shift values have a few more ambiguities owing probably to the contribution of conformation of the *O*-acetyl group at the C-2′ position.

It is reasonably suggested that the present method can be extended to a more general one, where all glycopyranosides having an equatorial hydroxy group at C-2′, such as galactopyranosides and xylopyranosides, can at least be used generally, and probably the other glycopyranosides[13] may be applied.

The glycosidation shift rules should thus be useful for determining not only the absolute configuration of a secondary hydroxyl in an alcohol but also the glycosidation position as well as the kind of saccharide in an unknown glycoside. Thus, it seems worthwhile to compile ^{13}C NMR data for some popular methyl glycopyranosides in pyridine-d_5 in Table III.

In conclusion we emphasize that with the present method, it is not necessary to examine both epimeric alcohols, and that this method is particularly powerful for determining the absolute configuration of hydroxyl in aliphatic-chain, five-membered ring, and flexible medium- and macroring secon-

Table VII. β-D-Glucosidation Shift Rules for Secondary Alcohols in Pyridine ($\Delta\delta \pm 1$ ppm)[a]

	$\Delta\delta_S$(C-1′)	$\Delta\delta_A$(C-α)	$\Delta\delta_A$[C-β-(*H*)]	$\Delta\delta_A$[C-β-(*M*)]
Sterically unhindered case[b]	−2.6	+7.2	−2.2 (CH_2,Me)	−4.0 (CH_2,Me)
Sterically hindered case I[c]	−4.2	+5.5 (±1.5)	−2.2 (CH) −0.5(C)	−5.1 (CH_2,Me)
Sterically hindered case II	0(±1.5)	+10.4 (±1.5)	−1.7 (CH_2,Me)	−1.3(CH) 0(C)

[a] These rules are also valid for α-L-glucosides, but the $\Delta\delta_A$[C-β-(*H*)] and $\Delta\delta$ [C-β-(*M*)] as well as sterically hindered cases I and II are exchanged when α-D- or β-L-glucosides are used. [b] A little lower field shift values should be expected when the *sec*-hydroxyl is axial in an aglycone alcohol. [c] Higher and lower field shift values should be applied according as the anomeric configuration is respectively axial and equatorial in the sugar moiety.

dary alcohols, because the usual NMR method using *J* values may not generally be applicable for these compounds. This method should be worth confirming results obtained by other methods[14] which may, in some cases, give ambiguous results. Other cases having substituents on both β carbons or having an sp^2 or sp-β carbon(s) should be studied in the future.

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Three-Dimensional Aromaticity of Polyhedral Boranes

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Received August 15, 1977

Abstract: Resonance energies of typical polyhedral boranes with a general formula of $B_nH_n^{2-}$ have been calculated by means of a graph-theoretical theory of aromaticity previously reported by Aihara. Hückel-type molecular orbitals employed are those of Kettle and Tomlinson with three-center BBB localized orbitals as basis functions. Most polyhedral boranes investigated are predicted to be aromatic with positive resonance energies, in general agreement with their chemistry. The present resonance energy is fairly proportional to the logarithm of the number of valence structures allowed for the polyhedral borane.

The closed polyhedral boranes have long been of great theoretical and experimental interest.[1,2] Some kinds of three-center bonds have been found to play an important role in molecular orbital (MO) calculations of boranes.[3,4] Such a three-center bond formalism has also been established in describing their valence structures.[3,4] Especially, the use of a central three-center BBB bond, in which all the three boron atoms are pairwise neighbors and topologically equivalent, serves as a theoretical basis for the energy consideration of polyhedral boranes.

A spherical network of the central three-center BBB bonds is known to stabilize polyhedral borane ions with a general formula of $B_nH_n^{2-}$ to a considerable extent.[1-5] In this connection, a graph-theoretical theory of aromaticity has been developed by Aihara,[6-11] and has been remarkably successful in predicting aromaticities of planar conjugated compounds.[6,9] One of the most important applications of the three-center bond formalism may be the graph-theoretical approach to aromatic stabilization of these borane dianions. In this paper, we show how it can be used to estimate aromaticity of a three-dimensional network of the central three-center BBB bonds.

Theory

In order to apply the graph-theoretical theory of aromaticity to polyhedral boranes, a Hückel-type MO theory is needed to estimate the ground-state bonding characters. Among the MO theories based on the three-center bond formalism, that of Kettle and Tomlinson[12,13] is most suitable for the present purpose. They used localized three-center BBB bonding orbitals as basis functions in a Hückel-type MO description of the bonding in polyhedral boranes.

When three boron atoms are triangularly bound to each other, a localized three-center BBB bonding orbital is often stabilized with respect to the zeroth-order energies of the valence shell atomic orbitals of which it is a linear combination.[1]

0002-7863/78/1500-3339$01.00/0