17, undergo clean α-lithiation as evidenced by the production of the silyl polyenes 18–22.[20] For the alkoxy dienes 11–14 and 16 metalation was achieved with *sec*-butyllithium in THF (–78 °C, 1.5 h). No products arising from either allylic deprotonation[14] or addition of the alkyllithium base[2b,c] to the dienyl system were isolated.[15] Hence, the α-metalation of 1-alkoxy dienes is indeed a general reaction.[21] Noteworthy is the observation that the MOM-substituted diene 12 undergoes metalation faster than the methoxy diene 16.[16] While both these dienes ultimately gave satisfactory yields of α-silylated dienes, the observed rate acceleration of the MOM group is essential in the deprotonation of the trienyl systems.

Treatment of the MOM-substituted triene 15 (entry 5) with *sec*-butyllithium resulted in addition of the alkyllithium base to the trienyl system.[17] After considerable experimentation, it was found that *n*-butyllithium (1.5 equiv) in DME containing TMEDA (1.0 equiv) cleanly deprotonated the MOM triene 15 (–78 °C, 2 h).[18] The resulting silylated triene 21 was isolated as a single isomer, presumably with the 1*Z*,3*E*,5*E* configuration.[22] Extension of these metalation conditions, as well as numerous other deprotonation recipes to the methoxy triene 17, have failed to yield any products resulting from α-lithiation. Therefore, the MOM group is a necessary feature for the successful deprotonation of 1-alkoxy trienes.[18] Furthermore, α-deprotonation of triene 15 represents the first example of vinyl deprotonation on a conjugated triene.

In conclusion, the combination of an efficient, stereoselective synthesis of 1-alkoxy polyenes coupled with the successful α-lithiation of these systems allows for the rapid construction of highly functionalized polyene systems of well-defined configuration. Particularly exciting is the synthesis and metalation of the alkoxy trienes, as the chemistry of these materials is virtually unexplored.[19] Besides exploring the chemistry of these new materials, we are evaluating the use of other highly active chelators to control the lithiation reactions of nonaromatic systems.

Acknowledgment. We gratefully acknowledge the financial support from the National Science Foundation (CHE-8612735). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the research.

(14) For an example of an alkoxy diene which gives only allylic deprotonation, see: Oakes, F. T.; Yang, F.-A.; Sebastian, J. F. *J. Org. Chem.* **1982**, *47*, 3094.

(15) Products resulting from the metalation and silylation of both the (*E*)- and (*Z*)-dienyl ethers (geometry about the enol ether double bond) can be detected by both ^{1}H NMR (300 MHz) and capillary GLC. However, the silylated products are generally enriched in the isomer resulting from the metalation of the (*E*,*E*)-diene. The selective destruction of (*Z*)-dienyl ethers during the metalation reaction has previously been noted (ref 2c).

(16) Initially this was obvious from comparing the time necessary for complete deprotonation at –78 °C (1.5 h for 12 vs 8 h for 16). More substantial data was obtained by reacting 1 mole equiv of *sec*-BuLi with a mixture containing 1 mole equiv of both the methoxy diene 16 and the OMOM diene 12 (2 h, –78 °C). After silylation, the reacting mixture was analyzed by capillary GLC against an internal standard (decane) and found to contain 75% unreacted methoxy diene 16 and 25% unreacted OMOM diene 12.

(17) Increasing the conjugation of a polyene system both lowers its reduction potential (ref 17a) and lowers the energy of the LUMO (ref 17b). It is therefore not surprising that the trienes, relative to the dienes, are more prone to addition relative to deprotonation. (a) Bredas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555. (b) Ann, N. T.; Canadell, E.; Eisenstein, O. *Tetrahedron* **1978**, *34*, 2283.

(18) It has been observed independently (ref 2b) that *n*-BuLi is less prone to add to heterosubstituted dienes than either *t*-BuLi or *sec*-BuLi. For triene 12, employment of *n*-BuLi in THF still yielded only addition products. We had previously found (ref 3b) that DME facilitated the deprotonation process, but in this case the TMEDA additive was also necessary (*t*-BuOK as additive gave only addition products).

(19) The few reactions reported to date all involve 1-siloxy trienes, see: (a) Chan, T. H.; Stossel, D. *J. Org. Chem.* **1986**, *51*, 2423. (b) Fleming, I.; Iqbal, J.; Krebs, E.-P. *Tetrahedron* **1983**, *39*, 841.

(20) The anion from diene 12 also reacts with aldehydes (CH_3CHO, 65%) and ketones (cyclohexanone, 40%). We have not yet been able to effect conjugate addition to cyclohexenone with any of a variety of cuprate reagents.

(21) The stereochemistry of the silylated dienes is more difficult to assign. In accord with the literature precedent (ref 2c), we have used the proton signal at C-2 to assign stereochemistry about the enol ether bond. For compounds which possess the 1*Z* configuration (the major isomers) H-2 resonates downfield (δ 6.1, J = 11.0 Hz) relative to H-2 in the 1*E* isomers (δ 5.7, J = 11.0 Hz). In most compounds, the stereochemistry about the Δ^3 olefin is clearly indicated by a $J_{3,4}$ value of 14.5–15.5 Hz. We have not detected any silylated compounds which have a *Z* configuration about the Δ^3 olefin. The assignment of the 1*Z*,3*E* configuration to all the major isomers is consistent with the idea that deprotonation and silylation occur without isomerization about the double bonds.

(22) For the triene 21 the 400-MHz ^{1}H NMR clearly indicates that one isomer is present. Unfortunately an exact assignment of olefin geometry is impossible due to the overlap of the vinyl proton signals. Hence, the geometry is assigned on the assumption that the major isomer of the starting triene 15 has undergone deprotonation and silylation with retention of olefin geometry.

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Preferred Conformation of C-Glycosides. 1. Conformational Similarity of Glycosides and Corresponding C-Glycosides

Summary: The conformational preference of α(axial)-C-glucosides 3–12 and β(equatorial)-C-glucosides 15–21 was studied by ^{1}H NMR spectroscopy. Axial and equatorial C-glycosides exist predominantly in the conformation **2A** and **14A**, respectively. This conformational preference is parallel to that of corresponding glycosides.

Sir: In connection with structural and synthetic studies on the marine natural product palytoxin,[1-3] we became interested in comparing the conformational preference of glycosides to that of corresponding C-glycosides, since major parts of the palytoxin structure could be viewed as C-oligosaccharides. Regarding the O–R bond at the anomeric center, α(axial)-glycosides are known to prefer

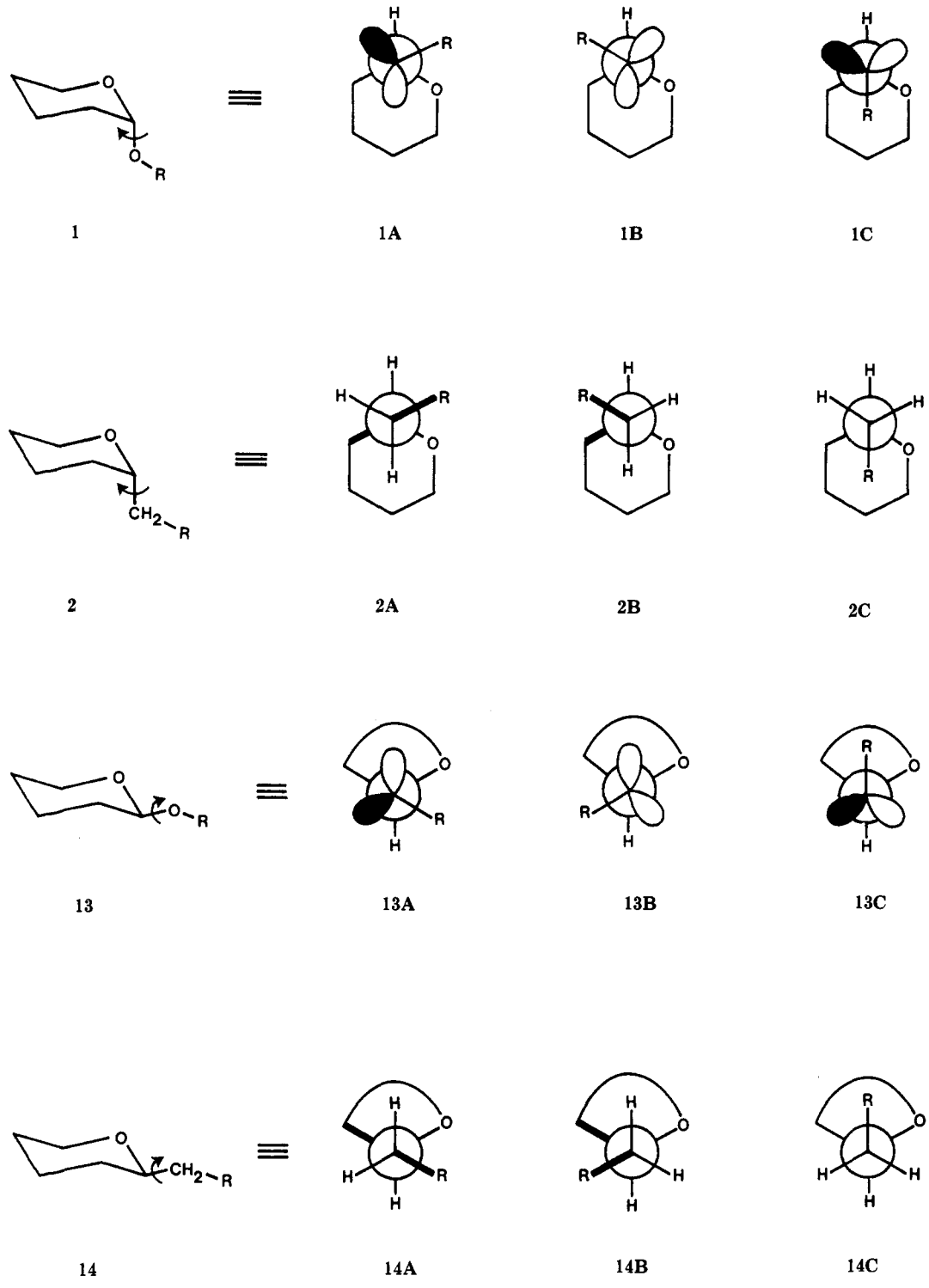
(1) For the gross structure of palytoxin, see: (a) Uemura, D.; Ueda, K.; Hirata, Y.; Naoki, H.; Iwashita, T. *Tetrahedron Lett.* **1981**, *22*, 2781 and references cited therein. (b) Moore, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491 and references cited therein. For the structures of minor constituents, see: Uemura, D.; Hirata, Y.; Iwashita, T.; Naoki, H. *Tetrahedron* **1985**, *41*, 1007.

(2) For the stereochemistry assignment primarily based on organic synthesis, see: Cha, J. K.; Christ, W. J.; Finan, J. M.; Fujioka, H.; Kishi, Y.; Klein, L. L.; Ko, S. S.; Leder, J.; McWhorter, W. W., Jr.; Pfaff, K.-P.; Yonaga, M.; Uemura, D.; Hirata, Y. *J. Am. Chem. Soc.* **1982**, *104*, 7369 and preceding papers. For the stereochemistry assignment primarily based on spectroscopic methods, see: Moore, R. E.; Bartolini, G.; Barchi, J.; Bothner-By, A. A.; Dadok, J.; Ford, J. *J. Am. Chem. Soc.* **1982**, *104*, 3776.

(3) For synthetic studies on palytoxin, see: (a) Jin, H.; Uenishi, J.-I.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644 and references cited therein. (b) Still, W. C.; Galynker, I. *J. Am. Chem. Soc.* **1982**, *104*, 1774.

0022-3263/87/1952-4819$01.50/0

Chart I



the conformer **1A** over the conformers **1B** and **1C** due to (1) steric destablization of **1C** over **1A** and **1B** (Chart I), (2) stereoelectronic stabilization of **1A** (and **1C**) over **1B**, referred to as the exo-anomeric effect,[4,5] and (3) steric destabilization of **1B** over **1A**. Thus, the similarity or dissimilarity between the conformational behavior of parent glycosides and corresponding C-glycosides depends primarily upon the stereoelectronic effect—compare **1A–C** with **2A–C**. To the best of our knowledge, however, there is no rigorous experimental data available to estimate the degree of the stabilization due to the exo-anomeric effect.[6]

(4) Lemieux, R. U.; Pavia, A. A.; Martin, J. C.; Watanabe, K. A. *Can. J. Chem.* **1969**, *47*, 4427. Also see: Lemieux, R. U.; Koto, S. *Tetrahedron* **1974**, *30*, 1933.

(5) There are excellent reviews on this subject. For example, see: (a) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983. (b) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983.

(6) In this paper, we adopt the definition of exo-anomeric effect as the additional stabilization of 1 over 2 at a given conformation due to the stereoelectronic effect. For some theoretical treatment of this subject, see: (a) Thogersen, H.; Lemieux, R. U.; Bock, K.; Meyer, B. *Can. J. Chem.* **1982**, *60*, 44 and references cited therein. (b) Jeffrey, G. A.; Pople, J. A.; Binkley, J. S.; Vishveshwara, S. *J. Am. Chem. Soc.* **1978**, *100*, 373 and references cited therein. (c) Tvaroska, I. *Carbohydr. Res.* **1984**, *125*, 155 and references cited therein.

Table I.[8] Spin–Spin Coupling Constants (Hz)[a]

compd	solv	temp, °C	1–X	1–Y	X–2′α	X–2′β	Y–2′α	Y–2′β
3	D_2O	84	3.6	11.1	b	b	b	b
		64	3.5	11.3	b	b	b	b
		44	3.4	11.6	b	b	b	b
		24	3.2	11.8	b	b	b	b
	DMSO-d_6	24	3.2	11.2	b	b	b	b
	CD_3OD	44	3.5	10.1	b	b	b	b
		24	3.2	11.4	b	b	b	b
		0	2.8	11.7	b	b	b	b
n		−20	2.7	12.0	b	b	b	b
		−33	2.6	12.0	b	b	b	b
	C_5D_5N	24	3.9	10.6	b	b	b	b
4	CD_3OD	24		11.6			9.8	4.7[c]
5	D_2O	84	3.2	11.3		9.6		3.3
		64	3.2	11.5		9.9		3.2
		44	3.1	11.8		10.2		3.0
		24	2.9	11.9		10.5		2.7
	DMSO-d_6	24	2.9	11.5		10.1		2.6
	CD_3OD	44	3.5	11.0		9.8		3.1
		24	3.3	11.4		10.3		3.0
		0	3.2	11.7		10.4		2.7
		−20	3.0	12.0		10.7		2.3
		−36	2.8	12.3		10.9		2.2
	C_5D_5N	24	3.8	10.7		9.6		3.5
6	CD_3OD	24		11.6				2.7
7	CD_3OD	24	3.5	11.2		9.9		2.8
8	CD_3OD	24		11.3				2.8
9	CD_3OD	24	4.2	10.0	6.1		6.4	
		0	4.3	10.1	6.3		6.3	
		−20	4.7[c]	10.0[c]	6.6[c]		6.3	
		−41	b	b	b		b	
10	CD_3OD	24	3.7		5.8			
11	CD_3OD	44	5.9	8.8	4.9		7.7	
		24	6.0	8.7	5.0		7.7	
		0	6.3	8.6	5.2		7.9	
		−20	6.3[c]	8.6[c]	5.5[c]		8.0[c]	
		−36	6.4[c]	8.6[c]	5.6[c]		8.0[c]	
12	CD_3OD	24	5.6		4.7			
15	D_2O	24	8.6	2.5	b	b	b	b
	DMSO-d_6	24	8.3	2.3	b	b	b	b
	CD_3OD	44	8.1	2.5	b	b	b	b
		24	8.5	2.2	b	b	b	b
		0	8.7	2.0	b	b	b	b
		−20	8.8	1.7	b	b	b	b
		−36	8.8	1.5	b	b	b	b
	C_5D_5N	24	8.4	2.4	b	b	b	b
16	CD_3OD	24	9.7	2.5	3.0		9.7	
17	CD_3OD	44	9.3		3.0			
		24	9.7		3.0			
		0	10.2		2.8			
		−43	10.7		2.3			
18	CD_3OD	24	9.5	2.8	3.0		9.5	
19	CD_3OD	24	8.9	2.8		6.9		5.3
20	CD_3OD	24		2.7				5.6
21	CD_3OD	44	7.5	5.0		7.5		5.0
		24	7.6	5.1		7.6		5.1
		0	7.7	5.2		7.7		5.2
		−20	7.7	5.2		7.7		5.2
		−40	7.7	5.4		7.7		5.4

[a] Spectra were recorded on a Bruker AM-500 (500 MHz) spectrophotometer. The spin–spin coupling constants were obtained by first-order analysis. [b] Chemical shifts are too close to apply the first-order analysis. [c] An approximate value.

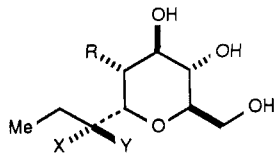
For this reason the ^1H NMR spectra of C-glycosides **3**,[7] **5**, and **9** were studied (Table I[8]). The spin–spin coupling constants were obtained by first-order analysis. The values of spin–spin coupling constants[8] clearly demonstrate that the tetrahydropyran ring of **3**, **5**, and **9** adopts a chair conformation (Chart II). The spin–spin coupling constants $J_{1,X}$ and $J_{1,Y}$ are crucial in determining the conformation around the C1–C1′ bond. The assignment of these couplings was made unambiguously by using the corresponding specifically deuterated α-C-glucosides **4**, **6**, and **10**. The observed values, i.e., $J_{1,Y}$ = 10–12 Hz and $J_{1,X}$ = 3–4 Hz, could be translated into a dihedral angle by using the Karplus equation,[9] yielding about 55° for the O1–C1–C1′–C2′ torsional angle. This value is remarkably close to the corresponding torsional angle (55 ± 5° in solution; 63° in crystal) of methyl α-glucopyranoside.[6]

(7) All the compounds reported were synthesized by using the methods developed in our laboratory in connection with the palytoxin synthesis. The details of synthesis will be published elsewhere.

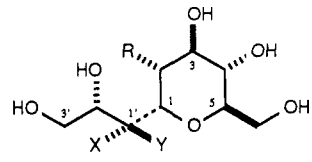
(8) The complete Table I listing spin–spin coupling constants is included in the supplementary material.

(9) For a refinement of the spin–spin coupling constant and dihedral angle correlation, see, for example: Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783. According to this procedure, the dihedral angles H(C1)–C1–C1′–YH(C1′) and H(C1)–C1–C1′–XH(C1′) are approximately 175° and 50°, respectively.

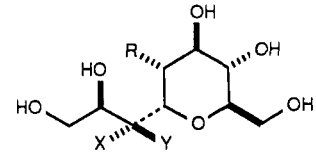
Chart II



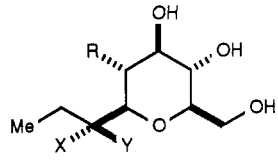
3: X = Y = H, R = OH
4: X = D, Y = H, R = OH



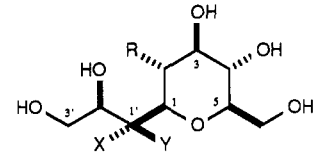
5: X = Y = H, R = OH
6: X = D, Y = H, R = OH
7: X = Y = R = H
8: X = D, Y = R = H



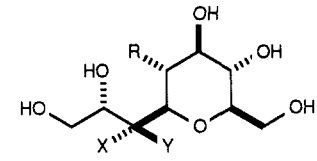
9: X = Y = H, R = OH
10: X = H, Y = D, R = OH
11: X = Y = R = H
12: X = R = H, Y = D



15: X = Y = H, R = OH



16: X = Y = H, R = OH
17: X = H, Y = D, R = OH
18: X = Y = R = H



19: X = Y = H, R = OH
20: X = D, Y = H, R = OH
21: X = Y = R = H

For the case of **3**, **5**, and **9**, however, one additional effect might destabilize the conformer **2B** over **2A**: 1,3-diaxial-like interactions which arise between the C2–O and C1′–C2′ bonds in the conformer **2B**.[10] Thus, the NMR spectra of 2-deoxy-α-*C*-glucosides **7** (**8**) and **11** (**12**) were examined (Table I). The preferred conformation of **7** corresponds to the predicted conformer **2A**—note $J_{1,X}$ = 3.5 Hz and $J_{1,Y}$ = 11.2 Hz. In the case of **11**, $J_{1,Y}$ = 8.7 Hz and $J_{1,X}$ = 6.0 Hz indicate that it adopts a slightly deviated conformation from the ideal **2A** to avoid steric interactions between the C1–O and C2′–O bond.

With respect to the C1′ and C2′ moiety, the spin–spin coupling constants show that **5**, **7**, and probably **3**,[11] prefer the extended, zig-zag conformation. However, the data suggest that **9** and **10** adopt a conformation slightly distorted from the ideal extended, zig-zag conformation to avoid the steric interactions between the C2′–O and C1–O bonds. It is interesting to note that $J_{5,6}$ values[8] of all these compounds are very close to those observed for α(1–6)- and β(1–6)-D-diglucopyranosides.[12]

It is worth mentioning that temperature had some, although small, effect on the spin–spin coupling constants (Table I). Upon lowering temperature the spin–spin coupling constant $J_{1,X}$ of **3** decreased and reached a constant value (2.6 Hz) while $J_{1,Y}$ increased and reached a constant value (12.0 Hz) at about −20 °C. It is also interesting to note that solvent did not show dramatic effects on the conformation of these substances (Table I).[13]

Encouraged by these results, we decided to examine the conformational preference of β(equatorial)-C-glycosides. On the basis of a similar analysis, we anticipated the conformer **14A** to be preferred over the conformers **14B** and **14C**. Assuming the degree of stabilization due to the stereoelectronic effect not to be overwhelming once again, the conformational behavior of β-C-glycosides should be similar to that of corresponding β-glycosides—compare **13A–C** with **14A–C**.

As before, the ^{1}H NMR spectra of **15–21** were examined (Table I). The spin–spin coupling constants lead to the conclusion that **15–20** exist preferentially in the predicted conformation with respect to the C1–C1′ moiety and in the extended, zig-zag conformation with respect to the C1′–C2′ moiety. As a result of the 1,3-diaxial-like interactions, **21** appears to take a conformation slightly deviated from **14A**. Temperature and solvent effects on the equatorial C-glucosides were also very similar to those on the axial C-glucosides (Table I).

The NMR studies outlined here clearly show that α-(axial)- and β(equatorial)-C-glycosides exist predominantly in the conformation of **2A** and **14A**, respectively. The C-glycoside is, like the corresponding glycoside, not conformationally rigid. Nonetheless, the weighted average of available conformers corresponds extremely well to the one predicted solely on the basis of the consideration of steric interactions. Thus, although our results do not preclude the existence of a stereoelectronic stabilization, the exo-anomeric effect is not the major factor why glycosides adopt preferentially the conformation **1A** or **13A**. The conformational preference of C-glycosides is parallel to that of corresponding glycosides, which may suggest a number of interesting potentials for the use of C-glycosides.

Acknowledgment. Financial support from the National Institutes of Health (NS 12108) and the National Science Foundation (CHE 86-105050) is gratefully acknowledged).

Registry No. **3**, 110352-30-2; **4**, 110316-51-3; **5**, 110352-31-3; **6**, 110316-52-4; **7**, 110316-53-5; **8**, 110316-54-6; **9**, 110352-32-4; **10**, 110352-33-5; **11**, 110352-34-6; **12**, 110352-35-7; **15**, 3736-73-0; **16**, 54503-51-4; **17**, 110352-36-8; **18**, 110352-37-9; **19**, 54548-38-8; **20**, 110352-38-0; **21**, 110352-39-1.

Supplementary Material Available: The complete Table I listing spin–spin coupling constants (3 pages). Ordering in-

(10) The importance of this type of 1,3-diaxial-like interactions for the conformational preference of carbohydrates was first recognized by Horton and co-workers. For example, see: El Khadem, H. S.; Horton, D. *J. Org. Chem.* **1968**, *33*, 734.

(11) Chemical shifts of the protons in question were too close to obtain precise spin–spin coupling constants needed to reach a definite conclusion.

(12) For example, see: Ohrui, H.; Nishida, Y.; Watanabe, M.; Hori, H.; Meguro, H. *Tetrahedron Lett.* **1985**, *26*, 3251 and references cited therein.

(13) Because of poor solubility, we were unable to record meaningful spectra in either $CDCl_3$ or C_6D_6.

formation is given on any current masthead page.

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Preferred Conformation of C-Glycosides. 2. Preferred Conformation of Carbon Analogues of Isomaltose and Gentiobiose

Summary: The preferred conformation of the methyl C-glycosides **1** and **2**, carbon analogues of methyl isomaltoside and methyl gentiobioside, was shown to be **1A** and **2A**, respectively, by ^{1}H NMR spectroscopy.

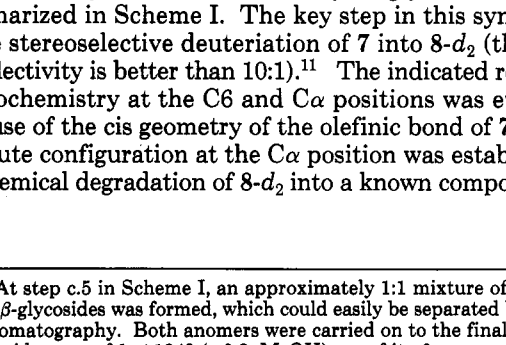
Sir: In the preceding paper, we have demonstrated that both α(axial)- and β(equatorial)-C-glycosides exist predominantly in the conformers bearing the C1′–C2′ bond antiperiplanar to the C1–C2 bond.[1] This conformational preference is very similar to that of corresponding parent glycosides. Obviously, this analysis can be extended to the methyl glycosides **1** and **2** of $\alpha(1'\rightarrow6)$- and $\beta(1'\rightarrow6)$-*C*-diglucoses, which are the carbon analogues of isomaltose (**3**) and gentiobiose (**4**) (Chart I). On the basis of the results reported in the preceding paper, the conformational preference around the C1′–Cα and C5–C6 bonds of **1** and **2** is predicted to be such that the Cα–C6 bond is antiperiplanar to the C1′–C2′ bond and also to the C5–C4 bond. With respect to the Cα–C6 bond, one would expect a priori an extended, zig-zag conformation to be preferred.[2] Thus, we anticipate that **1** and **2** should exist predominantly in the conformers **1A** and **2A**, respectively. In this paper, we would like to present experimental support for this prediction.

For the case of $\alpha(1'\rightarrow6)$-*C*-diglucose, we needed first of all to develop a reliable chemical synthesis and have found that the route summarized in Scheme I meets well with our requirements. The key step in the synthesis is the $NiCl_2/CrCl_2$-mediated coupling[3,4] of the vinyl iodide **5**[5,6] with the aldehyde **6**[7] to yield stereoselectively the allylic alcohol **7** (the stereoselectivity is better than 15:1). The methyl glycoside **1** (α_D +134° in CH_3OH)[8] was isolated and purified by polystyrene gel column chromatography.

The 500-MHz NMR spectrum in CD_3OD–D_2O (9:1) of **1** shows good resolution of all the signals without apparent higher order effects. The C6 and Cα methylene protons appear at 1.59, 1.69, 1.83, and 1.93 ppm. All the spin–spin coupling constants can be measured directly from the spectrum, resulting in the spin relationship summarized in Chart II.[9,10]

The values of spin–spin coupling constants[9] clearly show that both pyranose rings adopt a chair conformation; the vicinal spin–spin coupling constants between the C1′ and Cα protons (J = 11.7 and 3.2 Hz) and also between the C5 and C6 protons (J = 9.5 and 2.2 Hz) demonstrate that one of the two Cα protons is antiperiplanar to the C1′ proton and one of the two C6 protons is antiperiplanar to the C5 proton. The vicinal spin–spin coupling constants between the Cα and C6 protons, i.e., J = 10.8, 10.8, 5.2, and 3.6 Hz, lead to the conclusion that the extended, zig-zag conformation is preferred around the Cα–C6 bond as anticipated. Thus, among 27 ideal staggered conformers possible around the C1′–Cα, Cα–C6, and C6–C5 bonds, only the two conformers **1A** and **1B** are consistent with the observed NMR data.

The differentiation of **1A** from **1B** should be possible by an NMR study with a substrate specifically deuteriated at the Cα or C6 or both positions. Namely, $J_{1',\alpha}$ = 11.7 Hz is attributed to the vicinal spin–spin coupling between the C1′ and Cα *pro-S* protons in the conformer **1A** whereas between the C1′ and Cα *pro-R* protons in the conformer **1B**. A similar analysis can also be applied for $J_{5,6}$ = 9.5 and 2.2 Hz.



1B

Experimentally, this was accomplished by synthesizing the selectively dideuteriated methyl C-glycoside 1-d_2 as summarized in Scheme I. The key step in this synthesis is the stereoselective deuteriation of **7** into 8-d_2 (the stereoselectivity is better than 10:1).[11] The indicated relative stereochemistry at the C6 and Cα positions was evident because of the cis geometry of the olefinic bond of **7**. The absolute configuration at the Cα position was established by chemical degradation of 8-d_2 into a known compound.[12]

(1) Wu, T.-C.; Goekjian, P. G.; Kishi, Y. *J. Org. Chem.*, preceding paper in this issue.
(2) The anti conformation of *n*-butane is known to be favored over the gauche conformation by about ΔG = 0.8 kcal/mol.
(3) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, **5644**. Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am.* Chem. *Soc.* **1986**, *108*, 6048.
(4) Attempted couplings utilizing more conventional organometallic reagents including acetylene anion and vinyllithium did not yield the desired products.
(5) This substance was synthesized from 2,3,4,6-tetra-*O*-benzyl-D-glucose *p*-nitrobenzoate in 30% overall yield in six steps: (1) $CH{\equiv}CCH_2TMS/BF_3{\cdot}Et_2O/MeCN/0$ °C → room temperature;[16] (2) $O_3/MeOH{-}CH_2Cl_2/{-}78$ °C, followed by $(Me)_2S$ workup; (3) $CBr_4/(Ph)_3P/CH_2Cl_2/O$ °C; (4) *n*-BuLi/THF/−78 °C; (5) I_2/morpholine/C_6H_6/45 °C; (6) $KO_2CN{=}NCO_2K$/AcOH/dioxane/room temperature.
(6) Satisfactory spectroscopic data were obtained for all the new compounds reported in this paper.
(7) This substance was synthesized from L-xylose diethyl dithioacetal in 75% overall yield in five steps: (1) *p*-MeOPh$(Ph)_2$CCl/py/room temperature; (2) BnBr/NaH/THF–DMF/room temperature; (3) HCl/THF–H_2O/room temperature (4) (*t*-Bu)$(Me)_2$SiCl/imidazole/DMF/room temperature; (5) NBS/$AgNO_3$/collidine/acetone–H_2O/0 °C.
(8) At step c.5 in Scheme I, an approximately 1:1 mixture of methyl α- and β-glycosides was formed, which could easily be separated by silica gel chromatography. Both anomers were carried on to the final methyl C-glycosides: α_D of **1**, +134° (*c* 0.3, MeOH); α_D of its β-anomer, +38.2° (*c* 0.3, MeOH).
(9) The complete table listing chemical shifts and spin–spin coupling constants is included in the supplementary material.
(10) It is worthwhile to note that the hepta-*O*-benzyl derivative of **1** adopts preferentially the conformation corresponding to **1A**, based on the ^{1}H NMR spectrum in $CDCl_3$ (shifts in ppm): H5, 3.60 (ddd, 9.7, 9.7, 2.2 Hz); H6 (*pro-S*), 1.53 (dddd, 13, 11.5, 9.7, 4.1); H6 (*pro-R*), 1.78 (dddd, 13, 11.5, 4.8, 2.2); Hα (*pro-S*), 1.95 (dddd, 14, 11.9, 11.5, 4.1); Hα (*pro-R*), 1.62 (dddd, 14, 11.5, 4.8, 3.2); H1′, 3.99 (ddd, 11.9, 5.7, 3.2).
(11) For examples of hydroxyl group directed heterogeneous hydrogenation, see: Fujimoto, R.; Kishi, Y.; Blount, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 7154 and references cited therein.
(12) The summary of this assignment is included in the supplementary material.

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