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7(S)-Acetoxy-2(S)-methoxy-1(S)-3,6,8-trioxabicyclo-[3.2.1]octane.[1] Characterization of the Product from Periodic Acid Oxidation of Methyl β-L-Arabinopyranoside in Methyl Sulfoxide[3]

Jacques Gelas,[4] Derek Horton,* and Joseph D. Wander

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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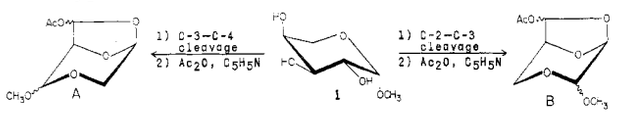
It was shown by Yu and Bishop[2] that methyl β-L-arabinopyranoside (1) in methyl sulfoxide containing excess periodic acid consumes only one mole per mole of oxidant, presumably through C-3–C-4 glycol cleavage, as borohydride reduction and subsequent acid hydrolysis of the product gave a volatile compound chromatographically indistinguishable from ethylene glycol. The lack of further oxidation was attributed to rapid internal cyclization of the initial dialdehyde to afford a tricyclic product containing no group labile to the glycol-cleavage oxidant. Acetylation of the oxidized 1 gave a mixture from which was isolated a 38% yield of a crystalline monoacetate 2, mp 89–90°, $[\alpha]^{22}D$ +44° (chloroform). Based on the presumption of C-3–C-4 cleavage in 1, a structure of type A was assigned.[2] However, the modest yield of 2 leaves open the conceivable possibility that it could have arisen *via* C-2–C-3 cleavage in 1, to generate an acetate having a structure of type B.

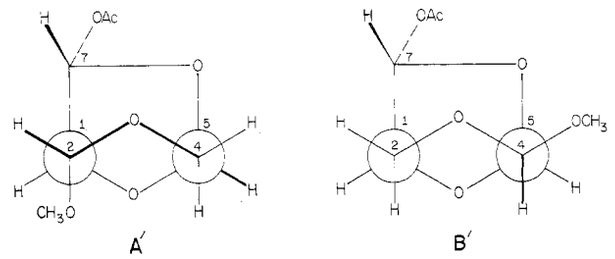


The present investigation was designed to place the structural characterization of compound 2 on a firm basis. Such products are useful matrices in which to examine, with dioxolane and 1,4-dioxane ring systems, the types of anomeric equilibria and polar anomeric effects that have already been studied extensively in this laboratory with respect to polysubstituted tetrahydropyran ring systems derived from sugars.[5] Related equilibria have also been investigated by one of us in racemic tricyclic analogs obtained from glycerol and dicarbonyl compounds.[6]

Mass spectral data for 2 include a weak (0.3% of the base peak) molecular ion (*m/e* 204) consistent with a formulation of $C_8H_{12}O_6$, relatively small fragments corresponding to the loss of $CH_3O\cdot$ at *m/e* 173 (0.3%) and of $CH_3CO_2\cdot$ at *m/e* 145 (4.7%), more prominent fragments at *m/e* 43 (100%), 103 (21%), and 145 (4.7%) characteristic of acetate groups, and a metastable-verified elimination of ketene at *m/e* 129–87 (m*, 58.8). These data accord with the formulation of a monomeric, monoacetylated, methyl acetal structure for 2.

Also consistent with the formulation $CH_3O(C_5H_6O_3)O-COCH_3$ for compound 2 is the 22.3-MHz ^{13}C nmr spectrum in chloroform-*d*, which exhibits eight separate resonances assignable, respectively, to the acetate methyl group [δ^c (Me_4Si) +27.0], the *O*-methyl group (61.4), singly oxygenated methylene (69.1) and methine (85.8) carbon atoms, three doubly oxygenated carbon atoms (100.3, 101.5, and 109.0), and an acetate carbonyl carbon atom (176.7). Lacking appropriate reference compounds, specific assignments of the three acetal carbon atoms must be deferred. The shift of the methylene carbon atom corresponds fairly closely to the shifts (66.7–66.8) measured[7] for the resonance of the analogous methylene carbon atoms in some 4-alkoxy-5-methyl-3,6,8-trioxabicyclo[3.2.1]octanes in which the alkoxyl group has been shown[6] to adopt the axial disposition.

Four pairs of diastereoisomers could, in principle, exist for structure A, and a similar number for B. In actuality, however, a number of these possibilities may be excluded because the stereochemistry at the anomeric carbon atom of 1 and at the hydroxylated carbon atom that is *not* oxidized is retained in the final product; furthermore, the stereochemistry at the bridgehead acetal carbon atom is determined by the orientation of the unoxidized alcoholic center. These considerations decrease the possibilities to two pairs of compounds epimeric at C-7. In each pair the endo isomer would presumably experience sufficient destabilization due to repulsive interactions with O-3 to preclude the formation of this isomer. This conclusion is supported by the earlier observation that the resonance of H-7 in this molecule gives rise to a very narrow singlet, an observation consistent only with the location of this proton in the endo orientation[2] because of the ~90° dihedral relationship between the bond to the adjacent bridgehead proton (H-1) and the 7 endo bond.



Only two structural possibilities remain for 2, namely, A′ and B′. Specific evidence permitting selection between these two structures is suggested in the 60-MHz ^1H nmr spectrum of 2 published by Yu and Bishop,[2] although the resolution in that spectrum is insufficient to permit extraction of the necessary coupling information. The ^1H nmr spectrum of 2 in chloroform-*d* was redetermined at 100 MHz with a sample that had been deoxygenated with a stream of nitrogen. Well-separated signals are observed for each of the six ring protons, permitting[8] extraction of a complete set of reliable, first-order coupling constants for this molecule. These values, which were measured from 100-Hz sweeps, were verified by double-irradiation experiments. As with other examples[9,10] of bicyclo[3.2.1]octane derivatives, long-range coupling interactions of the "W" and extended-"W" type[8] abound. See Table I.

A closely related compound, (racemic) 1,4,4-trimethyl-3,6,8-trioxabicyclo[3.2.1]octane (3), exhibits[10] two long-range couplings whose presence or absence can be used to

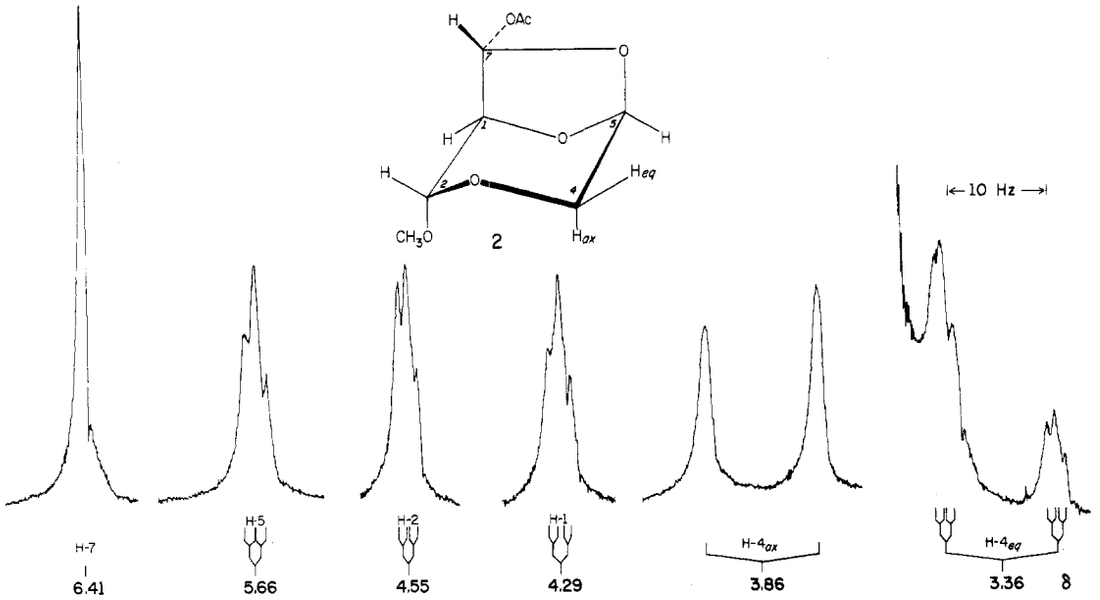
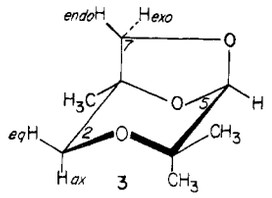


Figure 1. Expanded portions of the 100-MHz ^1H nmr spectrum of compound **2** in chloroform-*d*; the edge of the O-CH_3 resonance at δ 3.49 is visibly distorting the low-field portion of the H-4 eq signal.



$|^5J_{2eq,5}|$ 1.1 Hz

$|^4J_{2ax,7exo}|$ 1.4 Hz

$|^2J_{2ax,2eq}|$ 11.2 Hz

specify the location of the exocyclic substituents of **2**. The first of these, a four-bond interaction between H-2 ax and H-7 exo, is not observed for **2**, as the foregoing discussion of this proton requires. The other coupling, acting through five bonds between an equatorially disposed methylene proton and the remote bridgehead proton, provides a means for differentiating between A′ and B′ on the basis of the appearances of the signal for the proton geminal to the methoxyl group. In A′ this proton (H-2) would exhibit couplings to H-1, to H-5 (indicated by intensified bond lines), and possibly to H-4 eq, whereas the corresponding proton (H-4) in the isomeric representation B′ is axial and would, therefore, experience only a single coupling interaction, $^3J_{4,5}$. The observation that H-5 resonates as a slightly broadened doublet of doublets ($J_{2,5}$ = 1.1, $J_{4,5}$ = 1.1 Hz, see Figure 1) establishes that **2** has the structure A′ and validates the previous[2] tentative assignment.

There is evidence[6] for the operation of a strong anomeric effect[11] in 4-alkoxy-3,6,8-trioxabicyclo[3.2.1]octanes. Accordingly, it may be possible to account for the apparent singularity of **2**, as the only isolated product of this type formed from reaction of a methyl pentopyranoside with periodate in methyl sulfoxide, on the principle that analogous cyclization processes that would generate an equatorially disposed methoxyl group would be prohibitively disfavored. On the basis of this rationalization one would expect the analogous oxidation of methyl β-D-xylopyranoside to produce the 4 epimer of B′, as the appropriate C-2–C-3 cleavage is reported[2] to be favored.

Preparations of **2**, which had physical constants in acceptable agreement with literature[2] values, were made by Dr. R. H. Bell and by E. W. Rhode, III. Some preliminary ^1H nmr experiments were performed by Dr. J. H. Lauterbach. The ^{13}C Fourier transform nmr spectrum of **2** was recorded by Mr. J. M. Geckle with a Bruker HX-90 spectrometer; the spectrum was measured in a 10-mm tube at ~25° and is referenced to internal tetramethylsilane.

Table I
Chemical Shifts and Coupling Constants Measured for 7(*S*)-Acetoxy-2(*S*)-methoxy-1(*S*)-3,6,8-trioxabicyclo[3.2.1]octane (2) in Chloroform-*d* Solution at 100 MHz

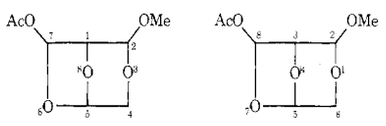
Chemical shifts	δ^a	Coupling constants	Hz
H-4 eq	3.36	$^3J_{1,2}$	0.8
H-4 ax	3.86	$^5J_{1,4eq}$	1.4
H-1	4.29	$^5J_{2,5}$	1.1
H-2	4.55	$^2J_{4eq,4ax}$	11.5
H-5	5.66	$^3J_{4eq,5}$	1.1
H-7	6.41	$^4J_{1,5}$	<0.5

[a] Expressed in parts per million downfield from internal Me_4Si.

Registry No.—**1**, 1825-00-9; **2**, 51271-13-7.

References and Notes

(1) The conventional numbering (a) for this ring system places the smallest numbers at the bridgehead positions along the longest ring leg; an earlier report[2] described an alternative notation (b) in which precedence was given to the heteroatoms of the 1,4-dioxane ring.



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