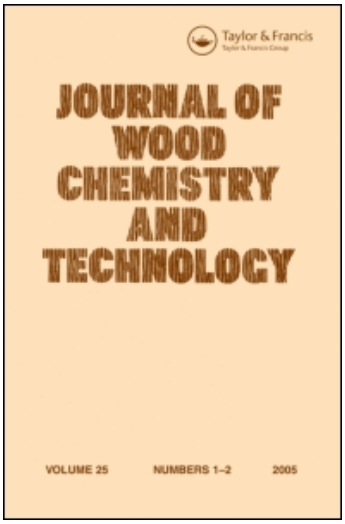

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DEGRADATION OF METHYL ß-D-RIBOPYRANOSIDE AND METHYL ß-D-XYLOPYRANOSIDE BY OXYGEN IN AQUEOUS SODIUM HYDROXIDE SOLUTION

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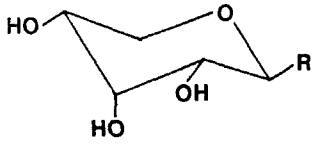
ABSTRACT

Methyl ß-D-ribopyranoside (1) and methyl ß-D-xylopyranoside (2) were degraded by oxygen (0.682 MPa partial pressure) in 1.25 M sodium hydroxide at 120°C. The degradations of 1 and 2 were similar to the previously reported degradations of 1,5-anhydroribitol (3) and 1,5-anhydroxylitol (4), respectively.[4] Both hydrogen peroxide and stable organic peroxides were detected in the reactions of 1 and 2. The riboside 1 degraded faster than the xyloside 2. This difference in reactivity is proposed to be a function of the relative acidity of the glycosides. Ionization of hydroxyl groups is postulated to be favored in 1, thus facilitating the initiation of the free radical degradation. The degradations of both 1 and 2 exhibited complex kinetics indicating autoinhibited reactions. In spite of the differences in reactivity, glycosidic bond cleavage occurred in approximately 60% of the degradations for both 1 and 2. C-1 radicals, resulting from abstraction of the anomeric hydrogen atom, are proposed to cause the observed autoinhibition *via* termination reactions with α-hydroxyhydroperoxyl radicals. However, decomposition of the glycosides *via* C-1 radicals is not believed to constitute a major degradation pathway since the reactivities of 1 and 2 were essentially the same as the analogous 1,5-anhydroalditols, i.e. 3 and 4, respectively. The major acidic degradation products of 1 and 2 were identical, but were formed in different relative ratios. The major acidic products were methoxyacetic acid, lactic acid, glycolic acid, glyceric acid, a methyl 3-*C*-carboxyfuranoside, and two isomeric 2-*C*-carboxyfuranosides.

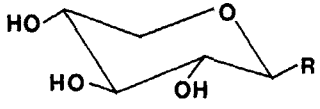
INTRODUCTION

During delignification of wood or pulp by molecular oxygen in alkaline media, degradation of the polysaccharides can be quite severe. The degradation, manifested primarily as a decrease in viscosity caused by depolymerization of the polysaccharides, is a major consideration in oxygen bleaching, necessitating the use of protective additives.[5] It is also an impediment to the development of oxygen pulping. Studies of cellulosics and model compounds[4,6-11] indicate that the depolymerization is caused by oxidation of hydroxyl groups of the monomeric glycose units to form carbonyl-containing intermediates which undergo base-catalyzed ß-elimination reactions to cleave the glycosidic linkages.[12-14]

Previously, we reported a study of the degradation of 1,5-anhydroribitol (3) and 1,5-anhydroxylitol (4) by oxygen in aqueous sodium hydroxide.[4] Using these models, the effects of ring hydroxyl configuration on the rate and mode of pyranoid ring degradation were examined. We now report a study of the degradation of methyl ß-D-ribopyanoside (1) and methyl ß-D-xylopyranoside (2) under the same conditions. By comparing degradation kinetics and products of the methyl glycosides (1 and 2) with those of their 1,5-anhydroalditol analogs (3 and 4), information on the effect of the glycosidic bond on degradation of polysaccharides in oxygen-alkali was obtained. Potential differences in reactivity between the alditols and the glycosides were anticipated because the glycosidic bond can increase the acidity of OH-2[15,16] and enhance radical formation at C-1.[17-19]



1: R = Me
3: R = H



2: R = Me
4: R = H

RESULTS

General

The methyl glycosides (1 and 2) were degraded under the same conditions used previously with the 1,5-anhydroalditols (3 and 4): 1.25 M NaOH at 120°C, 0.682 MPa partial oxygen pressure, and 0.1 M carbohydrate.[4] The solubility of oxygen at the reaction conditions was 2.9×10^{-3} M and was not decreased by the presence of 0.1 M methyl ß-D-ribopyranoside (1), the more reactive of the two glycosides. Thus, with proper agitation, diffusion of oxygen into solution did not control the reactions of 1 and 2. Previous investigators have also reported that properly agitated reactions of carbohydrates with oxygen in alkali are not rate-controlled by oxygen diffusion.[4,20,21]

As illustrated in Figure 1, the degradations of 1 and 2 were reproducible and showed only minor differences to the degradation of the analogous 1,5-anhydroalditols, 3 and 4, respectively. Thus, the glycosidic bond apparently has only a minor effect on the initial degradation rate of a pyranoid ring in an alkaline, oxygenated solution. Consistent with observations of previous workers,[4,11] the methyl riboside (1), having *cis*-1,2-glycol groups, degraded more rapidly than the methyl xyloside 2 which has only *trans*-1,2-glycol groups. Also, consistent with previous reports,[4,8,10] slight induction periods were noted in the degradations.

Kinetic Analyses

To determine the order of the reaction with respect to the glycoside, it was assumed that the concentrations of oxygen and sodium hydroxide remained essentially constant during the reactions. Thus, the basic rate expression given in Equation 1 could be expressed as in Equation 2 or Equation 3:

$$-d[G]/dt = k[G]^a[O_2]^b[NaOH]^c \quad (1)$$

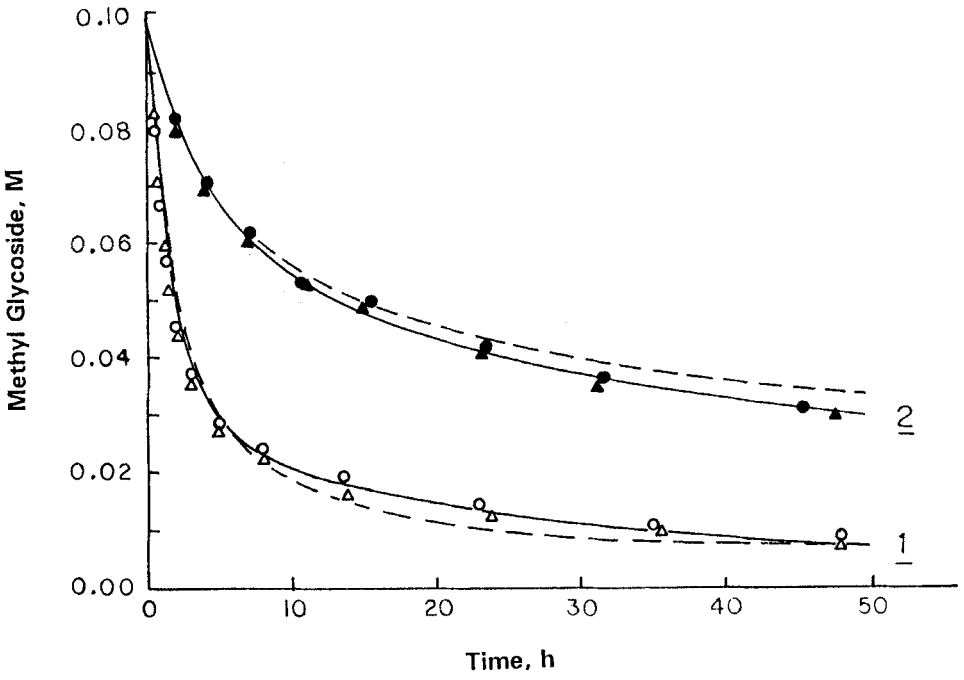


FIGURE 1. Duplicate reactions of 0.10 M methyl ß-D-ribopyranside (1) and 0.10 M methyl ß-D-xylopyranoside (2) in 1.25 M NaOH at 120°C and 0.682 MPa O_2 partial pressure. Reactions of the corresponding 1,5-anhydroalditols (dashed lines) are included for comparison.

$$-d[G]/dt = k'[G]^a \quad (2)$$

$$\log(-d[G]/dt) = \log k' + a \log[G] \quad (3)$$

where G is 1 or 2; t is time; k is the rate constant; a, b, and c are the orders of the reaction with respect to the indicated reactant; and $k' = k[O_2]^b[NaOH]^c$ and is essentially constant.

The concentration of oxygen was determined to remain constant at 2.9×10^{-3} M during the reactions. At long reaction

times the assumption that the sodium hydroxide concentration remains essentially constant is in error, but Millard, *et al.*[4] demonstrated that for the degradation of the 1,5-anhydroalditols this slight drop in alkali strength did not affect the kinetic analysis.

The reactions were analyzed by the differential method[22,23] using Equation 3. The variable induction periods made it impractical to utilize the differential method involving variation of initial reaction conditions. However, as the degradation rate attained after the induction period was essentially the same for duplicate experiments (see Fig. 1), the differential method employing single kinetic trials was applicable. Analysis entailed measuring the reaction rate at various reaction times corresponding to a number of reactant concentrations, and plotting the data according to Equation 3, as illustrated in Figure 2. The slope of the resulting line is *a*, the order of the reaction with respect to methyl glycoside concentration. The values of *a* obtained for reactions of the methyl riboside **1** and methyl xyloside **2** were 2.75 and 3.47, respectively, and were interpreted to indicate autoinhibition.[4]

Products

Methanol - The formation of methanol in the degradations of **1** and **2** was determined by quantitative g.l.c. Methanol liberation was taken as an indication of the extent of glycosidic bond cleavage. The fractions of **1** and **2** degrading with concomitant methanol formation were equivalent (ca. 60%) and constant with respect to the extent of reaction. The methanol yield agrees well with that reported for the degradation of methyl ß-D-glucopyranoside in oxygen-alkali.[24] The equivalent yields of methanol in the degradations of **1** and **2** indicates that the proportion of glycosidic bond cleavage is unaffected by the stereochemistry of the hydroxyl group at C-3.

Peroxides - The formation of hydrogen peroxide and organic peroxides in the methyl glycosidic oxidations was determined by a

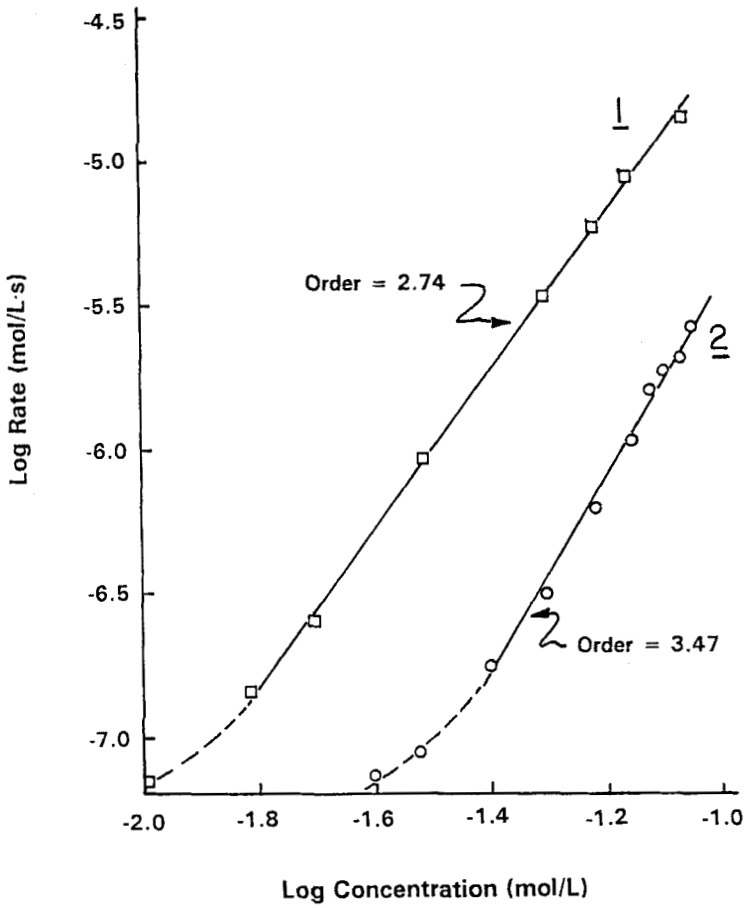


FIGURE 2. Determination of the reaction order with respect to the glycoside concentration.

modified acidic titanium sulfate method.[19,25,26] As illustrated in Figure 3, hydrogen peroxide was formed in the reactions of both 1 and 2, but the concentration of hydrogen peroxide in the reaction of the methyl riboside 1 achieved a much higher level than in the reaction of the methyl xyloside 2. This result parallels hydrogen peroxide formation in degradations of the analogous 1,5-

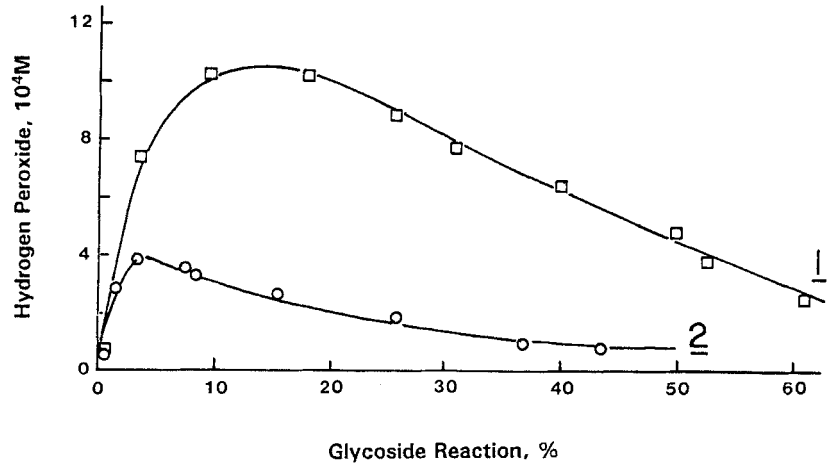


FIGURE 3. Hydrogen peroxide formation.

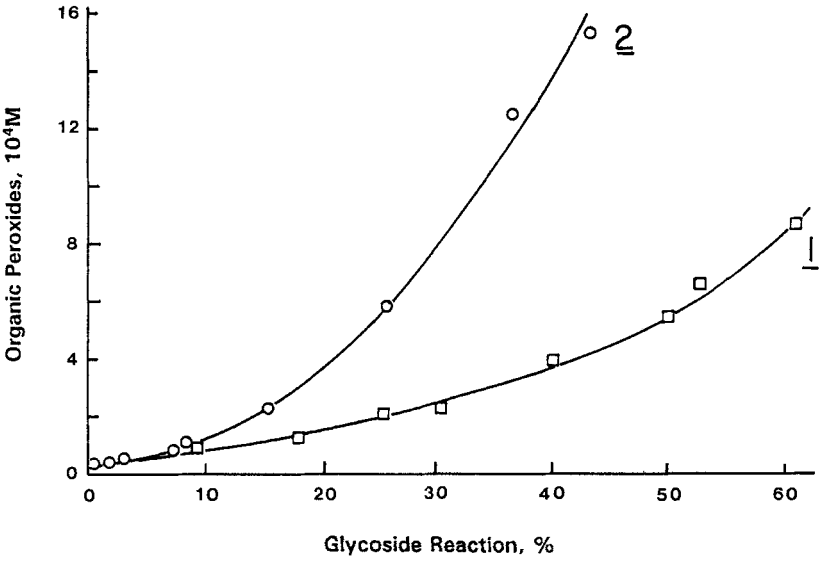
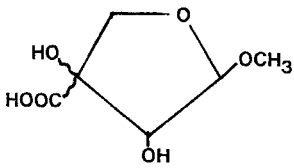


FIGURE 4. Organic peroxide formation.

anhydroalditols.[4] Organic peroxides were also formed in the oxidations of 1 and 2 (see Fig. 4). In contrast to hydrogen peroxide formation, organic peroxide formation from the methyl xyloside 2 was greater than from the methyl riboside 1. These organic peroxides appeared to be stable, similar to those reported in the oxygen degradation of methyl ß-D-glucopyranoside in alkali.[8] No formation of organic peroxides of intermediate stability was observed even though several different test conditions were invoked. This pattern of organic peroxide formation is in sharp contrast with the oxidations of the 1,5-anhydroalditols[4] in which intermediate organic peroxides were formed but few stable organic peroxides.

Carboxylic acids - The products from 1 and 2 were identical. The major products were methoxyacetic acid (3), lactic acid (4), glycolic acid (5), glyceric acid (6), a methyl 3-*C*-carboxy-ß-D-tetrafuranoside (7), and two isomeric methyl 2-*C*-carboxy-ß-D-tetrafuranosides (8,9). Several other very minor products were apparent by g.l.c. analysis, but were not identified.



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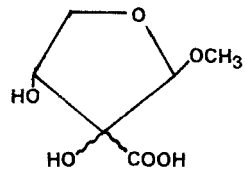


8, 9

Products 3-6 were identified as their trimethylsilyl (Me_3Si) derivatives. Their g.l.c. retention times and g.l.c.-m.s. spectra were comparable to those of authentic samples. The major diagnostic peaks for 3 were *m/e* 162 (P^+), 147 (P^+-CH_3), 117 ($P^+-CH_3OCH_2$),

and 89 (P^+-Me_3Si). The mass spectra of **4**-**7** also compared favorably with those reported by Petersson.[27]

The methyl *C*-carboxyfuranosides were also identified as their Me_3Si derivatives by g.l.c.-m.s. The important diagnostic peaks were *m/e* 394 (P^+), 379 (P^+-CH_3), and 334 (P^+-$OCHOCH_3$). The mass spectra were in general agreement with previously reported spectra,[11] except that contrary to these reports assignment of the carboxyl group position could not be made from the mass spectra. This assignment was made from p.m.r. spectra of the Me_3Si derivatives of **7**-**9** collected by preparative g.l.c. In the p.m.r. spectrum of **7** the anomeric proton was a doublet centered at 4.74 ppm. For **8** and **9** the anomeric protons were singlets at 4.95 ppm.

Glycoside Acidity

As a means of investigating the possibility of **1** and **2** exhibiting different hydroxyl ionization in alkali, ^{13}C-n.m.r. spectra were taken of **1** and **2** in both D_2O and D_2O/NaOD. The carbon resonances of **1** and **2** are tabulated in Tables 1 and 2, respectively. Assignments of the carbon resonances were based on the work of Bock and Pederson[28] and were confirmed by selective decoupling experiments. As can be seen from the tables, the carbon resonances of **1** shifted more in alkali than did those of **2**. This was interpreted to imply that the hydroxyl groups of **1** ionize more readily to form the oxyanion. To eliminate the possibility that the observed resonance shifts were the result of a salt effect, a spectrum of **1** was also taken in D_2O/NaCl. No significant peak resonance shifts were observed in this case.

The question of glycoside acidity (hydroxyl group ionization) was also addressed by ion-exchange chromatography. The methyl riboside **1** and methyl xyloside **2** were analyzed as a mixture by chromatography on Amberlite CG-400 (OH^-). The elution time of the more acidic riboside **1** was 1.37 times that of the xyloside **2**.[29]

TABLE 1

^{13}C-N.m.r. Analysis of Methyl ß-D-Ribopyranoside[a]

Carbon	D_2O ppm[b]	D_2O/NaOD ppm[b]	Shift ppm[c]
C-1	104.4	104.8	0.4
C-2	73.2	73.6	0.4
C-3	70.8	71.3	0.5
C-4	70.7	70.8	0.1
C-5	66.1	66.5	0.4
CH_3	59.1	58.9	-0.2

[a]0.53 M NaOD, 200 mg/mL glycoside
[b]relative to 3-(trimethylsilyl)propane sulfonic acid
[c]positive shift means downfield shift

TABLE 2

^{13}C-N.m.r. Analysis of Methyl ß-D-Xylopyranoside[a]

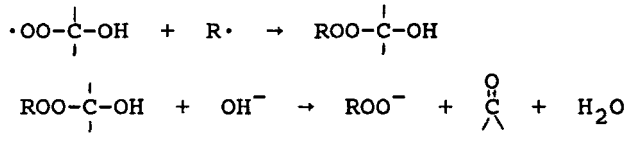
Carbon	D_2O ppm[b]	D_2O/NaOD ppm[b]	Shift ppm[c]
C-1	106.9	107.0	0.1
C-3	78.8	78.9	0.1
C-2	76.0	76.1	0.1
C-4	72.3	72.3	0.0
C-5	68.2	68.3	0.1
CH_3	60.3	60.3	0.0

[a]0.59 M NaOD, 200 mg/mL glycoside
[b]relative to 3-(trimethylsilyl)propane sulfonic acid
[c]positive shift means downfield shift

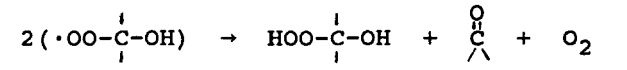
DISCUSSION

The mechanism proposed previously for alkaline oxygen degradation of 1,5-anhydroribitol (3) and 1,5-anhydroxylitol (4)[4] was assumed to be generally applicable to the degradation of the glycosides 1 and 2. The mechanism can account for the observed formation of hydrogen peroxide and acidic products, but does not account for stable organic peroxide formation. In addition, the mechanism would also predict a second-order kinetic dependence on the methyl glycoside concentration in a minimum metal-catalyzed system.

The oxidations of 1 and 2 exhibited kinetic orders higher than 2.0 with respect to the glycosides (Fig. 2) indicating complex kinetic behavior. The greater time-dependent kinetic orders with respect to the glycosides suggest autoinhibition of the reactions.[4,22] Autoinhibition occurs when a reaction intermediate slows the reaction down in some fashion. Autoinhibition observed in the alkaline oxygen degradation of 1,5-anhydroxylitol was postulated to be the result of stabilized α-hydroxyhydroperoxy radicals entering into radical chain termination reactions as in (4) and (5).[4]



(4)

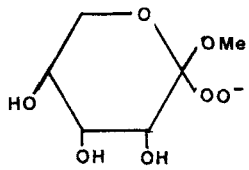


(5)

Reactions of this type have frequently been observed in hydrocarbon autoxidations.[30] These reactions produce only non-radical

species, thus causing the radical chain to slow down and thereby retarding the rate of degradation. Of the termination reactions (4) and (5), the initial reaction (5) was considered to be the more predominant in the alkaline oxidations of 1,5-anhydroxylitol.[4]

Similarly, α-hydroxyhydroperoxyl radicals are probably involved in chain termination reactions in the alkaline oxygen degradations of **1** and **2**. However, in the methyl glycoside degradations, reaction (4) is believed to cause the observed autoinhibition and stable organic peroxide formation. For this reaction to be viable, two criteria must be met: first, the alkyl radical (R·) in reaction (4) must be stable and second, because oxygen is an efficient radical scavenger, its concentration must be low.[30] The C-1 radical formed by abstraction of the anomeric hydrogen from the glycoside is a stable radical due to the adjacent ring and glycosyl oxygens.[31] The saturation oxygen concentration was determined to be *ca.* 3% of the initial glycoside concentration. Therefore, the autoinhibition exhibited in the alkaline oxygen degradations of **1** and **2** is believed to be a result of a radical chain termination reaction (4) between an α-hydroxyhydroperoxyl radical and a glycosidic C-1 radical (R·) to ultimately yield the conjugate base of a diester of a peroxyorthoacid, *e.g.* **10**. Compound **10** could also be formed by reaction of the C-1 radical with oxygen but this would not disrupt the radical chain reaction.



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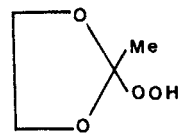

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That the diester of the peroxyorthoacid **10** would have the observed stability of the organic peroxides detected in the degradations of

the glycosides could be called to question, particularly in the peroxide analysis with acidic titanium sulfate. However, 2-methyl-2-hydroperoxy-1,3-dioxolane (11) requires rather severe conditions (1 N H_2SO_4, 20°, 2 h) to yield hydrogen peroxide.[32]

The formation of stable organic peroxides in the degradations of 1 and 2 (see Fig. 4) is consistent with the above hypothesis. Furthermore, the higher kinetic order with respect to glycoside (i.e. more autoinhibition) in the reaction of 2 (Fig. 2) correlates well with the greater organic peroxide formation from 2 (see Fig. 4). This increase in organic peroxide from 2, relative to the reaction of 1, is probably related to greater stabilization of intermediate α-hydroxyhydroperoxyl radicals from 2 relative to those from 1, similar to the enhanced stabilization proposed for α-hydroxyhydroperoxyl radicals from degradation of 1,5-anhydroxylitol.[4]

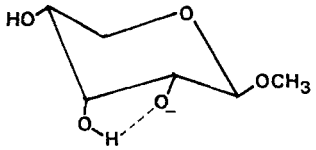
Although the C-1 radical is postulated to give rise to the observed autoinhibition, formation and decomposition of the C-1 radical apparently does not represent a major degradative pathway for 1 and 2. The overall degradation rate and reaction pathways of 1 and 2 were similar to the analogous 1,5-anhydroalditols, 3 and 4, respectively. If the C-1 radical were a major degradation route the rates of degradation of the glycosides would have been much greater than those of the 1,5-anhydroalditols. Additionally no major products associated with the C-1 radicals were identified. A similar conclusion was made by Kano, *et al.*[33] in a study of the alkaline oxygen degradation of cellobiitol.

Autoinhibition accounts for the observed kinetic orders and organic peroxide formation, but it does not account for the reactivity difference between 1 and 2. The most rational explanation for the difference in reactivity of the glycosides reactivity difference is based on their relative acidities. The first step in the mechanism proposed for alkaline oxygen degradation of carbohydrates is ionization of a hydroxyl group.[4] The most acidic hydroxyl group in the two methyl pentopyranosides is probably OH-2.[34-36] The arguments presented here will refer to ioni-

zation of OH-2, but the same arguments apply equally well to ionization at other positions. The oxyanions of 1 and 2 [G^-(1) and G^-(2), respectively] can be stabilized by hydrogen bonding to the neighboring hydroxyl group. But hydrogen bonding in the case of G^-(1) seems to be favored over hydrogen bonding in G^-(2) since the riboside 1 was demonstrated to be more acidic than the xyloside 2. The oxygen-oxygen distances between neighboring hydroxyl groups in 1 and 2 are approximately the same providing 2 exists primarily in the $^4C_1$ conformer as would be expected from conformational analysis.[37] The postulate of increased hydrogen bonding in G^-(1) is believed to arise from the contraction of internuclear distances which occurs upon hydrogen bond formation.[39] Kuhn[40] described a similar situation when he found evidence for more intramolecular hydrogen bonding in *cis*-cyclohexane-1,2-diol than in *trans*-cyclohexane-1,2-diol. In the case of the *trans*-1,2-glycol, hydrogen bond formation and subsequent contraction of internuclear distances decreases the dihedral angle between the adjacent hydroxyl groups and accentuates ring puckering. An increase in ring puckering leads to adverse 1,3-diaxial hydrogen interactions. For the *cis*-1,2-glycol, this same reduction in dihedral angle tends to flatten the ring and no increase in 1,3-diaxial interactions is observed. Additionally, the reduction of the dihedral angle is assisted by the more frequent interconversion of the riboside 1 between the two chair conformers.

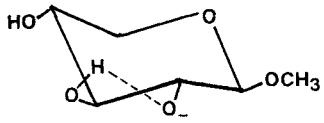
The next step in the proposed mechanism is abstraction of the hydrogen geminal to the oxyanion by oxygen. Formation of the oxyanion facilitates abstraction of the geminal hydrogen atom. This reaction yields a perhydoxyl radical (HOO·) and a ketyl radical [$G^{\cdot}$(1) or $G^{\cdot}$(2)]. The ketyl radical can subsequently react with oxygen to form the α-hydroxyhydroperoxyl radical.[4] The perhydroxyl radical (HOO·) would exist in base as the superoxide radical ($O_2^{-}\cdot$).[41] A higher concentration of oxyanions from 1 would effectively increase the number of initiation reactions. The increase in initiation reactions would, in turn, increase the concentration of superoxide radical which is involved in the

subsequent radical chain propagation (1). The hydrogen peroxide data from the reactions of 1 and 2 support this view (see Fig. 3).



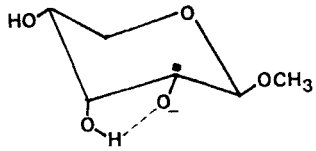
O---O ≃ 2.7 Å

G^{-}(1)

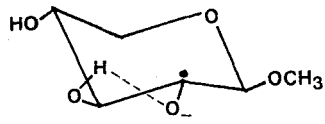


O---O ≃ 2.9 Å

G^{-}(2)



$G^{\cdot}$(1)



$G^{\cdot}$(2)

EXPERIMENTAL

Analytical Methods

Melting points were determined on a calibrated Thomas-Hoover capillary apparatus. Optical rotations were determined with a Perkin-Elmer 141 MC polarimeter. Colorimetric analyses were performed with a Cary Model 15 recording spectrophotometer. N.m.r. spectra were determined on a Jeol FX-100 pulse Fourier transform spectrometer.

G.l.c. analyses were performed with a Varian 1200 instrument equipped with a hydrogen flame-ionization detector. The columns were housed in 0.125-in. stainless-steel tubing. The following

columns and operating conditions were employed: (A) on-column injection, 10% SE-30 on 60-80 mesh DMCS-AW Chromosorb W (5 ft); nitogen 15 mL/min; and column 170°C; (B) off-column injection; 5% Carbowax 20M on 80-100 mesh Chromosorb 101 (4 ft); nitrogen 35 mL/min; and column 70°C; (C) on-column injection; 3% OV-17 on 80-100 mesh Supelcoport (15 ft); nitrogen 20 mL/min; and column 60 → 160°C at 2°/min.

Mass spectra were determined with a DuPont Instruments 21-491 spectrometer interfaced with a Varian 1440 gas chromatograph. G.l.c. conditions *C* were used with helium as the carrier gas.

Substrates

Methyl ß-D-ribopyranoside (1) was prepared by debenzoylating methyl 2,3,4-tri-*O*-benzoyl-ß-D-ribopyranoside[42] with sodium methoxide in methanol-chloroform (20:1, vol). Crystallization twice from ethyl acetate yielded 1 (73% yield); m.p. 81-2°C, $[\alpha]_D$ = -106.2° (H_2O). Literature:[43] m.p. 83°C, $[\alpha]_D$ = -105.0°.

Methyl ß-D-xylopyranoside (2) (Pfanstiehl) was recrystallized twice from ethanol; m.p. 156-7.5°C, $[\alpha]_D$ = -65.8° (H_2O. Literature:[44] m.p. 156.7°C, $[\alpha]_D$ = -65.8° (H_2O).

Kinetic Analyses

General - A stock solution of low metals NaOH was prepared following the procedure of Reiner and Poe.[45] The stock solution was stored in a paraffin-lined container under nitrogen.

Triply-distilled water used in the reactions was prepared by a method to minimize trace organic contaminants.[46]

The reactor system, described in detail elsewhere,[47] consisted of a 250-mL capacity, Teflon-lined brass reactor that could be sampled while hot and under pressure, and an oil-bath assembly that controlled the reactor at 120±0.2°C.

The reactor was loaded and assembled in a nitrogen atmosphere, connected to the sampling system and the oil-bath apparatus, lowered into the heated oil bath, and allowed to equilibrate

thermally. A zero-time sample was then taken and the reaction was initiated by pressurizing the reactor with oxygen.

Glycoside Analysis - The size of the samples and the amount of internal standard (n-propyl ß-D-xylopyranoside) were determined gravimetrically. Samples (*ca.* 1 mL) of the reaction solution containing the internal standard were deionized on a column (5 mL) of Amberlite MB-3 (H^+, OH^-) resin, evaporated *in vacuo*, and the residues acetylated with acetic anhydride (0.3 mL) in pyridine (0.8 mL) for 18 h. The acetylation mixture was mixed with cold distilled water, shaken for 0.5 h, and extracted with chloroform (2 x 5 mL). The chloroform extracts were washed with M hydrochloric acid (15 mL) and water (10 mL), dried (sodium sulfate), and evaporated *in vacuo*. The dried samples were dissolved in chloroform (*ca.* 0.5 mL) and analyzed by g.l.c. using conditions A.

Product Analyses

Methanol Analysis - The sample size was determined gravimetrically and the internal standard (ethanol) was added volumetrically. The samples were analyzed directly by g.l.c. using conditions *B*.[48]

Peroxide Analysis - The concentration of peroxides (hydrogen and organic peroxides) was determined by a colorimetric method involving a complex between hydrogen peroxide and titanium(IV) sulfate.[25,26] The test was conducted at two pH levels to correspond with that used by Millard, *et al.*[4,47] (pH 1) and that used by Sinkey and Thompson[8] (pH 0). The initial absorbance of the samples treated with the titanium sulfate reagent was taken as a measure of hydrogen peroxide. With time, the absorbance usually increased and the difference between the initial and final absorbance was taken as a measure of organic peroxides. The method was calibrated against standard dilute hydrogen peroxide solutions.

Acidic Product Analysis - The acidic products of the methyl glycoside degradations were analyzed by g.l.c., g.l.c.-m.s. or by preparative g.l.c. in conjunction with n.m.r.

The samples (*ca.* 4 mL) were taken directly into tared 8-mL vials containing 1 M $NaHSO_3$ (1 mL). The sample size was determined gravimetrically and then internal standard (n-propyl ß-D-xylopyanoside, as an aqueous solution) was added gravimetrically. The sample was then passed over an Amberlite IR-120 (H^+) resin column (10 mL) and eluted with distilled water (3 x 8 mL). The pH of the combined eluant was immediately adjusted to *ca.* 7-8 by addition of NH_4OH. The sample was concentrated to dryness *in vacuo* (35°C) using coevaporation with 1,2-dichloroethane to remove the last traces of water.[49]

A portion (30-50 mg) of the sample was dissolved in dimethylsulfoxide (0.5 mL, silylation grade, Pierce Chemical Co.) with warming. Tri-Sil Concentrate (0.5 mL, Pierce Chemical Co.) was added to the sample and the sample was mechanically shaken for 12 h.[50] The top layer of the mixture was analyzed by g.l.c. using conditions *C*, g.l.c.-m.s. using conditions *C*, or by preparative g.l.c. in conjunction with n.m.r.

Preparative g.l.c. was performed on a Varian 200 instrument using a 10 ft x 0.25-in. stainless-steel column filled with 5% OV-17 on 80-90 mesh Anakrom ABS and rigged for on-column injection. The nitrogen flow rate was 20 mL/min and the column temperature was 60 → 150°C at 2°/min.

Oxygen Solubility

The solubility of oxygen at the reaction conditions was determined by employing equipment developed by Green and Thompson.[51] Reaction solutions were withdrawn from the reactor by a hydraulic piston which then transferred the solution into a pressurized trap (N_2, 200-250 psig). In the trap, the reaction solution was allowed to react with Winkler solutions[52] while the nitrogen pressure insured that the oxygen would not come out of solution. The final sodium thiosulfate titration was done at atmospheric pressure.

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