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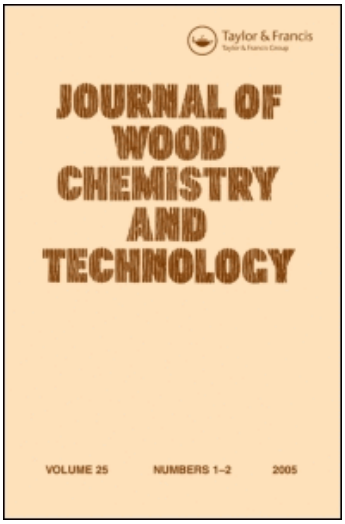

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Leland R. Schroeder[a]; Eugene C. Millard[bc]
[a] Paper Science and Engineering Faculty, SUNY College of Environmental Science and Forestry, Syracuse, New York, USA [b] Institute of Paper Science and Technology, Atlanta, Georgia, USA [c] Interstate Paper Corporation, Savannah, GA

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Stereoselective Formation of 1,4-Anhydro-2-C-carboxytetritols in the Degradation of 1,5-Anhydroribitol and 1,5-Anhydroxylitol with Oxygen in Aqueous Alkali

Leland R. Schroeder
Paper Science and Engineering Faculty, SUNY College of Environmental Science and Forestry, Syracuse, New York, USA

Eugene C. Millard
Institute of Paper Science and Technology, Atlanta, Georgia, USA

Abstract: In addition to other acid products, degradation of 1,5-anhydroribitol (*5*) and 1,5-anhydroxylitol (*6*) with oxygen in 1.25 M NaOH produced diastereomeric 1,4-anhydro-2-C-carboxy-D-erythritol (*7*) and 1,4-anhydro-2-C-carboxy-D-threitol (*8*) and their enantiomers as major products. However, the ratio of the diastereomers differed for the two reactants. Thus, their formation could not proceed solely by benzilic acid-type rearrangements through α-dicarbonyl intermediates as typically proposed for formation of alkyl C-carboxyfuranosides from alkyl glycopyranosides in similar reactions. The α-dicarbonyl species that can form from *5* and *6* are identical. Potential mechanisms to account for stereoselective formation of *7* and *8* are presented.

Keywords: 1,5-anhydroribitol, 1,5-anhydroxylitol, oxygen, alkali, 1,4-anhydro-2-C-carboxytetritols

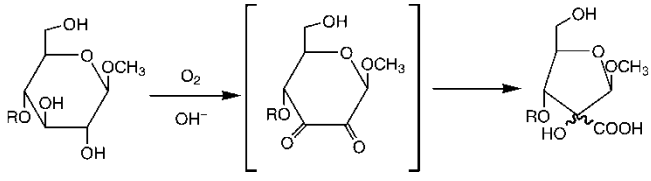
Current address for Eugene C. Millard is Interstate Paper Corporation, Savannah, GA.

Address correspondence to Leland R. Schroeder, Faculty of Paper Science and Engineering, SUNY College of Environmental Science and Forestry, 1 Forestry Drive, Syracuse, NY 13210, USA. E-mail: lrschroeder@juno.com or lrschroeder@esf.edu

INTRODUCTION

To take full advantage of the use of oxygen and alkali for delignifying and brightening wood pulps the oxidative degradation of the wood polysaccharides has to be minimized. This article is an extension of earlier studies of the basic questions of how the monomeric pyranoid ring is degraded by oxygen in an alkaline medium and whether the degradation is affected by the stereochemistry of the hydroxyl groups on the ring.

Several studies of degradation of glycosidic model compounds by oxygen in alkaline media have been done. In addition to other aspects of the reactions, degradation of methyl β-D-glucopyranoside (*1*),[1,2] methyl 4-0-methyl-β-D-glucopyranoside (*2*),[3] and various other methyl glucopyranosides[4] with oxygen in alkaline media yield significant amounts of methyl C-carboxyfuranosides, e.g., *3*, which have been postulated to form from α-dicarbonyl intermediates, for example, *4*, by benzilic acid-type rearrangements.[1–4]



1 R = H
2 R = CH_3

4

3

RESULTS AND DISCUSSION

Reactions of 1,5-anhydroribitol (*5*) and 1,5-anhydroxylitol (*6*) with oxygen in aqueous 1.25 M sodium hydroxide at 120°C produced a variety of acid products including formic, acetic, lactic, glycolic, glyceric, 3-O-(carboxymethyl)-glyceric, 3-hydroxypropanoic, 2-hydroxybutanoic, and 2,4-dihydroxybutanoic acids. In addition, diastereomeric 1,4-anhydro-2-C-carboxytetritols (*7* and *8*) were identified as major products in both reactions, with each stereoisomer probably being a mixture of the D and L enantiomers.[5] The carboxytetritols, *7* and *8*, subsequently tentatively identified as 1,4-anhydro-2-C-carboxy-D-erythritol and 1,4-anhydro-2-C-carboxy-D-threitol, and their enantiomers, respectively, are analogous to the carboxyfuranosides, for example, *3*, formed in reactions of the methyl glycosides.

The reactions of the two anhydropentitols (*5* and *6*) were similar in that the total concentration of the carboxytetritol products (*7* and *8*) went through a maximum in both systems. However, distinct differences in the ratio of the isomeric carboxytetritols as the reactions progressed were

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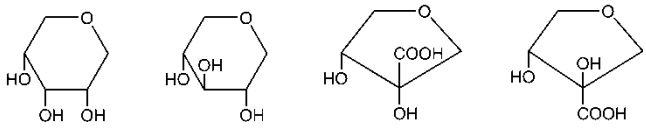
evident, as illustrated by the series of chromatographic analyses as a function of the percent reactions shown in Figure 1.



5 *6* *7* *8*

Initially, carboxytetritol *7* dominated in the reaction of 1,5-anhydroribitol (*5*), but it became increasingly less important as the reaction progressed. Conversely, throughout the reaction of 1,5-anhydroxylitol (*6*), the dominant carboxytetritol product was *8*. As the reaction of *6* proceeded, the relative amount of *7* continually decreased to where it was not detectable chromatographically. The data indicate that carboxytetritol *8* is formed preferentially in the 1,5-anhydroxylitol (*6*) reaction whereas carboxytetritol *7* is selectively formed in the 1,5-anhydroribitol (*5*) reaction. Also, it is apparent that *7* reacts more rapidly than *8* to form other products under these reaction conditions. The fact that the erythritol isomer, *7*, degrades more rapidly than the

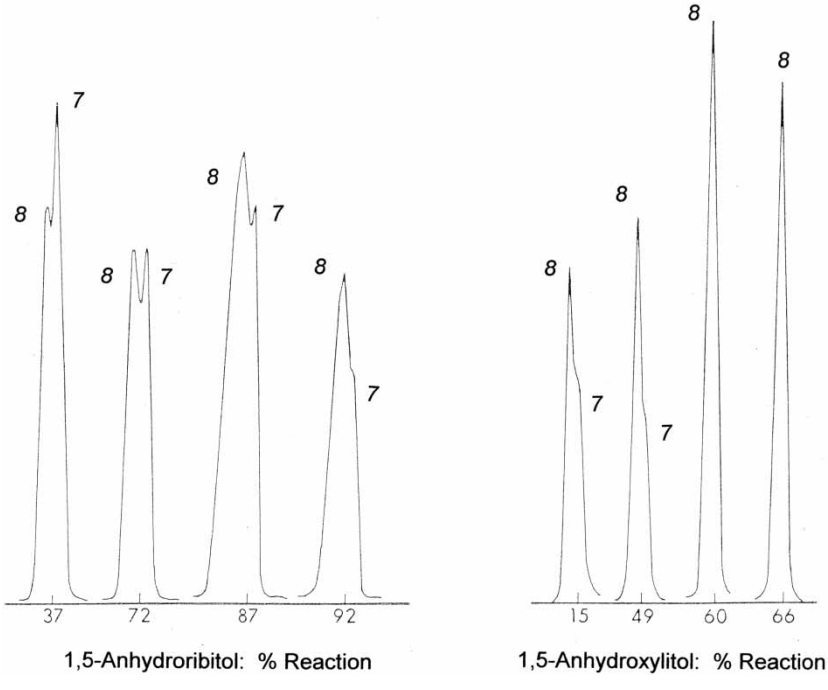


Figure 1. Gas-liquid chromatographic analysis of diastereomeric 1,4-anhydro-2-C-carboxytetritols (*7* and *8*, Me_3Si derivatives) formed in the alkaline oxygen reactions of 1,5-anhydroribitol and 1,5-anhydroxylitol.

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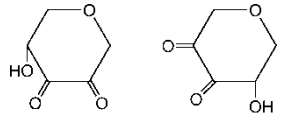
threitol isomer, *8*, is consistent with observations that carbohydrates having *cis* vicinal hydroxyl groups are more reactive than the trans isomers with oxygen in aqueous alkali.[4–6]

If the reactions of anhydropentitols (*5* and *6*) to form the carboxytetritols (*7* and *8*) proceeded solely through α-dicarbonyl intermediates as postulated for analogous glycosidic reactions,[1–4] the differences in the ratios of *7* and *8* formed in the two reactions would not be expected because the α-dicarbonyl species that can form from the anhydropentitols *5* and *6* are identical. The two α-dicarbonyl compounds that could be formed from either *5* or *6* are the enantiomers *9* and *10*. Thus, although the α-dicarbonyl compounds (*9* and *10*) could potentially be intermediates in the reactions of *5* and *6*, they cannot be exclusive. Other reaction intermediates that have a stereochemical directing effect because of the configuration of substituents at C-3 must be important to account for the observed differences in formation of the diastereomeric carboxytetritol products.



9 *10*

Potential reaction schemes that account for stereoselective formation of diastereomeric carboxytetritols in reactions of *5* and *6* are shown in Figures 2 and 3. The initial step of both reactions is postulated to be oxidation of a hydroxyl group to a carbonyl group *via* an α-hydroxyhydroperoxide as discussed previously.[5,6] The reactions are illustrated for initial oxidation at C-2; initial oxidation at C-4 would produce the enantiomeric product. Initial oxidation at C-3 is also possible, but would produce identical intermediates from *5* and *6*, thereby eliminating any potential for different ratios of *7* and *8* to be formed from the two anhydropentitols.

The next step postulated for both reactions is reversible addition of hydroxide ion to the carbonyl group. In both systems, the species in which the oxyanion of the resulting *gem*-diol is *cis* to OH-3 (*11* and *11a*) should be stabilized by effective hydrogen bonding as illustrated.[5] Abstraction of H-3 from *11* or *11a* by any of several radical species®·) in the system[5] would produce a hydroxyalkyl radical at C-3 (*12* and *12a*). Stereoselective addition of oxygen to *12* and *12a* to form the α-hydroxyhydroperoxyl radicals *13* and *13a*, respectively, would be facilitated by stabilization of the C-3 radical to inversion by the hydrogen bonding. In addition, reaction of the hydroxyalkyl radicals (*12* and *12a*) with oxygen would be very rapid because it would be expected to have an essentially zero activation energy.[7–9] The hydroperoxyl radicals *13* and *13a* would readily abstract hydrogen atoms from other substrates to form the key α-hydroxyhydroperoxide intermediates, *14* or *14a*,

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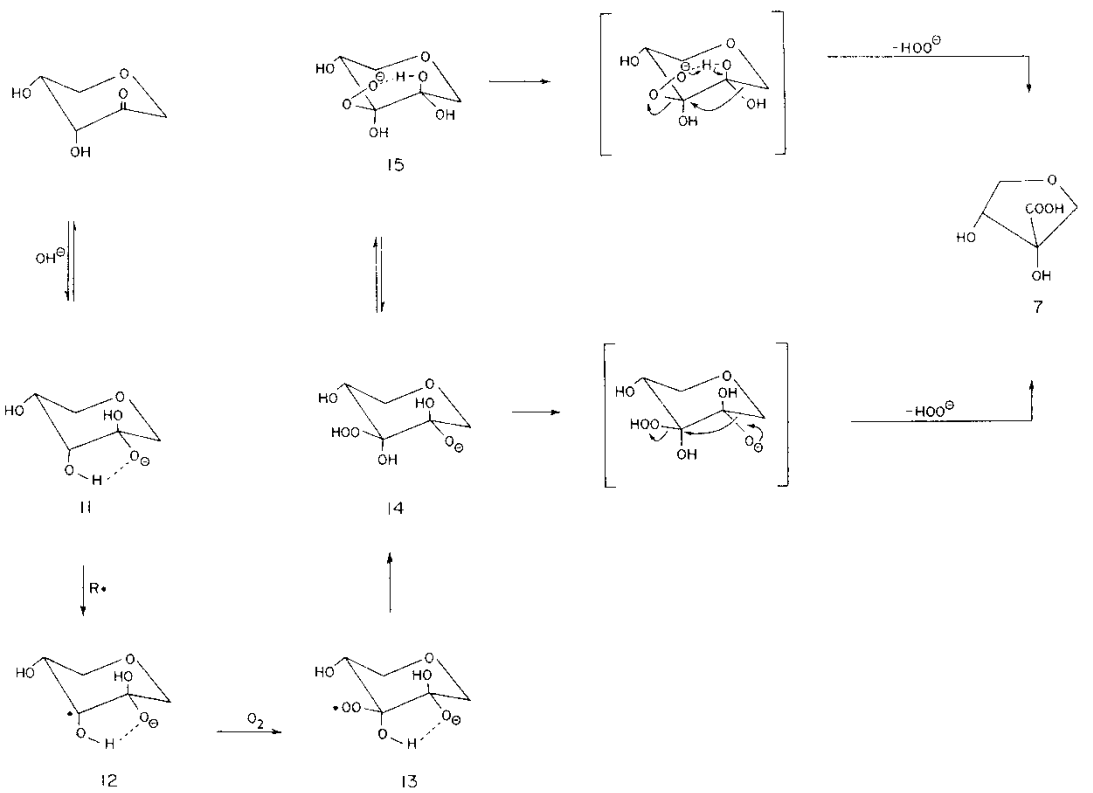

Figure 2. Potential mechanism for stereoselective formation of 1,4-anhydro-2-C-carboxy-D-erythritol from 1,5-anhydroribitol.

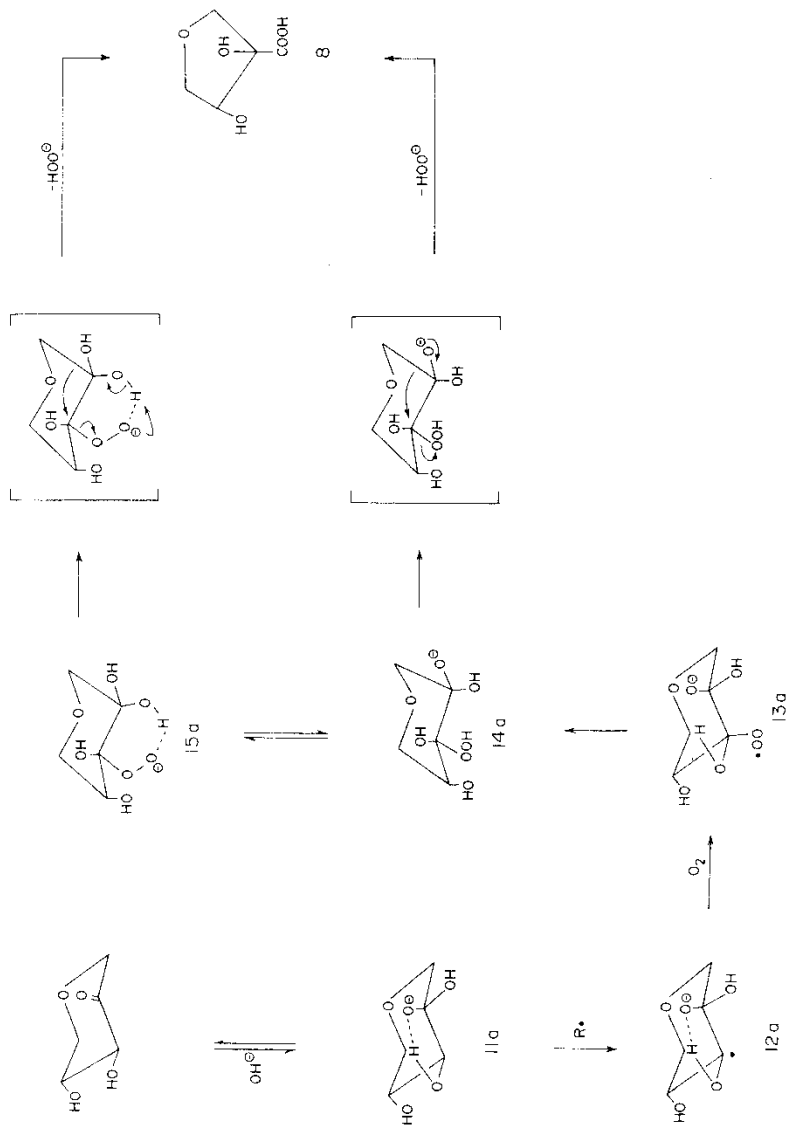

Figure 3. Potential mechanism for stereoselective formation of 1,4-anhydro-2-C-carboxy-D-threitol from 1,5-anhydroxylitol.

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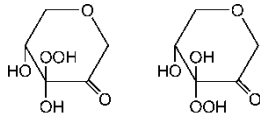
which in the alkaline medium should readily form the conjugate bases of the hydroperoxides, *15* and *15a*, also.

The carboxytetritols *7* and *8* could be formed readily from *14* and *14a* or *15* and *15a*, respectively, by a semibenzilic type mechanism.[10,11] Transfer of the hydroxyl proton to the peroxy anion of *15* and *15a* could precede or be concerted with the ring contraction. Formation of the carboxylic acid carbonyl moiety would be concerted with ring contraction and displacement of the hydroperoxy anion, as shown in Figures 2 and 3. The concerted rearrangements must occur from the conformations [$^4C_1$ for *5* and $_4C^1$ for *6*] in which the (C-1)-(C-2) bond and the carbon-oxygen bond of the hydroperoxide are antiperiplanar. In the conformations necessary for rearrangement, the bulky hydroperoxide groups are equatorial, thus helping to stabilize the molecule in that conformation.

Naturally, the potential exists for the α-hydroxyhydroperoxide moiety of *14*, *14a*, *15*, or *15a* to form a carbonyl group[5] prior to the ring contraction, thus forming the α-dicarbonyl species (i.e., *9* or *10*, or their hydrates), which could undergo benzilic acid type rearrangements. In those reactions in which this occurs, the proportion of *7* and *8* formed from the anhydropentitols *5* and *6* would be the same.

Compounds *14* and *15* can also potentially exist in equilibrium with *16*. Similarly *14a* and *15a* could exist in equilibrium with *16a*. Thus, the Favorskii rearrangement[10,11] involving *16* and *16a* was also considered for formation of *7* and *8*. This would involve initial formation of a carbanion at C-1 and subsequent migration of C-1 to C-3 with displacement of the hydroperoxy anion from C-3 to form the cyclopropanone intermediate. Ring-opening of the cyclopropanone intermediates to form C-1 carbanions would result in formation of the 1,4-anhydro-2-C-carboxytetritols (*7* and *8*). Because of potential elimination reactions, alternate ring-opening of the cyclopropanone intermediates would yield several compounds, none of which were found in the product mixtures.



16 *16a*

However, the Favorskii mechanism does not appear to be as viable as the semibenzilic mechanism for the formation of *7* and *8*. For example, if a C-1 carbanion did form, it would be expected to undergo inversion. Carbanions stabilized by adjacent carbonyl groups usually give racemization no matter what the solvent.[11,12] Although inversion of the C-1 carbanion would not affect the final products in reactions of the anhydropentitols (*5* and *6*), in glycosidic systems carbanion inversion would result in formation of anomeric mixtures of the alkyl C-carboxyfuranosides. Such anomeric product mixtures have not be reported.[1–4] In addition, only

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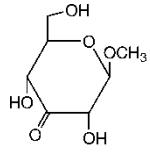
the β-anomers of the methyl C-carboxyfuranoside products were formed from alkaline oxygen degradation of methyl β-D-ribopyranoside and methyl β-D-xylopyranoside.[6]

The mechanisms shown in Figures 2 and 3 are consistent with *7*, 1,4-anhydro-2-C-carboxy-D-erythritol and its L-enantiomer forming preferentially in reactions of 1,5-anhydroribitol (*5*) and *8*, 1,4-anhydro-2-C-carboxy-D-threitol and its L-enantiomer forming preferentially in reactions of 1,5-anhydroxylitol (*6*). In contrast to the proposed mechanisms, Ericsson et al.[1,2] have questioned the importance of monocarbonyl species as precursors to C-carboxyfuranoid species. Because glycosiduloses (e.g., *17* and *18*), are extremely labile in alkaline solution,[13,14] it was postulated that for the reaction of methyl β-D-glucopyranoside with oxygen in alkali, the α-dicarbonyl intermediate, that is, *4*, must be formed by simultaneous introduction of the two carbonyl groups.[2] However, on reaction with oxygen in aqueous alkali, methyl β-D-ribo-hexopyranosid-3-ulose (*17*), which eliminates the aglycon more rapidly[13,14] and is probably less likely to form initially than the 2-ulose (*18*), formed 35–65% of the C-carboxyfuranosides generated from methyl β-D-glucopyranoside under comparable conditions.[1,2] Thus, postulating monocarbonyl species as intermediates in these types of oxidations is not unrealistic.



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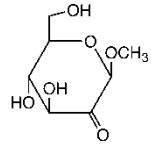

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EXPERIMENTAL

Reactants

The 1,5-anhydroribitol (*5*) and 1,5-anhydroxylitol (*6*) were prepared by hydrogenations of 2,3,4-tri-O-benzoyl-β-D-ribopyranosyl bromide[15] and phenyl 2,3,4-tri-O-acetyl-1-thio-β-D-xylopyrnoside,[16] respectively, as described previously.[5]

Sodium hydroxide solutions were freshly prepared from a carbonate-free 50% (wt) stock solution by dilution with carbon dioxide-free, triply-distilled water under a nitrogen atmosphere.

Reactions

The reactor consisted of a 250-mL capacity, Teflon-lined reactor that could be sampled while hot and under pressure, and an oil-bath assembly that controlled the reactor temperature at 120 $\pm$ 0.2°C. The reactor was assembled

and loaded in a nitrogen atmosphere, connected to the sampling system and oil bath apparatus, and allowed to equilibrate thermally. After a zero-time sample was taken the reaction was initiated by pressurizing the reactor to a partial oxygen pressure of 75 lb/in^2 (25°C).

Disappearance of the anhydropentitols (*5* or *6*) was monitored by glc. Samples (≈1.5 mL) of the reaction solution containing an internal standard were deionized on a column (6–8 mL) of Amberlite MB-3 (H^+, OH^-) resin, evaporated *in vacuo*, and the residues acetylated with acetic anhydride in pyridine.[5] The acetylated sugars were analyzed on columns (5 ft) of 10% SE-30 on 60–80 mesh DMCS-AW Chromosorb W.

Product Analyses

With the exception of formic and acetic acids which were analyzed as their benzyl esters,[17] the 1,4-anhydro-2-C-carboxytetritols (*7* and *8*) and other acidic products were analyzed by glc and glc-ms as their pertrimethylsilyl ethers. A sample (≈3.0 mL) of the reaction solution was eluted with distilled water (15 mL) through a column (5 mL) of Amberlite IR-120 (H^+) resin. The eluate was concentrated *in vacuo* to a syrup that was dissolved in dimethyl sulfoxide (0.3 mL) and treated with Tri-Sil concentrate (0.5 mL). The mixture was shaken for 24 h and then the top layer of the two-phase system was analyzed by glc on a column (10 ft) of 3% OV-17 on 80–100 mesh Supelcoport.[5]

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