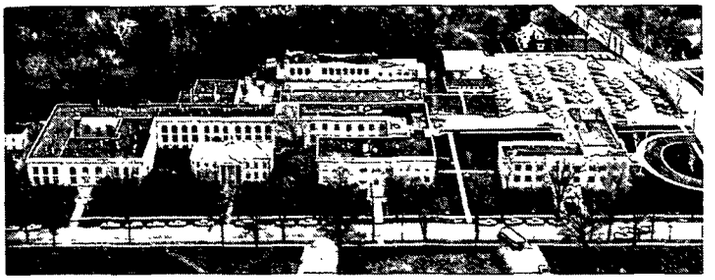

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THE OXIDATION OF METHYL β-D-GLUCOPYRANOSIDE AND METHYL 4-O-METHYL (^{14}C)-β-D-GLUCOPYRANOSIDE WITH ALKALINE PEROXIDE

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JANUARY, 1978

The oxidation of methyl β-D-glucopyranoside and methyl 4-O-methyl (^{14}C)-β-D-glucopyranoside with alkaline peroxide

J. W. Weaver • L. R. Schroeder • N. S. Thompson

INTRODUCTION

The use of oxygen for delignifying and brightening pulps has attracted considerable interest because of the possibility of minimizing the effect of effluents on the environment. Development of the technology is hindered by the oxidative degradation of cellulose and the corresponding decrease in critical physical properties. This degradation is postulated to result from the complex action of reduced states of oxygen on cellulose.

The present paper investigates the role of hydrogen peroxide [a conjectured intermediate] on the degradation of the anhydroglucose unit of cellulose. The products of the oxidation demonstrate that peroxide is indeed a reactive intermediate. This result implies that techniques minimizing peroxide production during delignification will also minimize pulp degradation.

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SUMMARY

The oxidation of methyl β-D-glucopyranoside and methyl 4-O-methyl (^{14}C)-β-D-glucopyranoside with alkaline peroxide revealed a complex kinetic behavior as well as the existence of peroxidic reaction products. The identified reaction products are postulated to be formed from these intermediates (and their equilibrium products) by three competing mechanisms involving catalytic decomposition, alkaline rearrangements and various oxidative degradations. Possible pathways for formation of previously unidentified methoxyacetic acid and 3-O-methyl pentonic acid are presented together with a review of pathways for the formation of the previously identified products described in the literature.

INTRODUCTION

The purpose of this investigation is to expand our knowledge of the cellulosic degradations that occur during oxygen-alkali delignification processes. These harmful reactions pose a threat to the general acceptance of this new pulp and paper technology by the industry. The action of hydrogen peroxide was studied because it has been shown to be a reactive intermediate during oxygen delignification processes [1]. Two glycosides, methyl β-D-glucopyranoside (MBG) and methyl 4-O-methyl (^{14}C)-β-D-glucopyranoside (MeMBG) were chosen as convenient, though limited, models for cellulose degradation.

RESULTS

In order to establish a baseline for the glycoside studies, we determined the spontaneous decomposition of hydrogen peroxide in alkaline solution

in the absence of glycoside. The rate of decomposition of hydrogen peroxide is related to the quantity of trace contaminants in solution and is difficult to control [2]. However, reproducible spontaneous decomposition of the peroxide after variable induction periods can be achieved by the addition of magnesium ion to the reaction mixture. Tests indicated that under suitable circumstances addition of 0.001M $MgSO_4$ gave an acceptably low rate of peroxide decomposition, together with a reproducible rate of MBG degradation. A greater concentration of magnesium ion slowed the rate of peroxide decomposition as well as the rate of glycoside oxidation to unacceptably low values. The effect of unpredictable induction periods on oxidation of the glycosides was eliminated by allowing the alkaline peroxide to decompose to the desired starting concentration before the glycoside was added to the system. The reaction of MBG was shown to be independent of the amount of peroxide that decomposed before glycoside oxidation was initiated. Although the rate of spontaneous decomposition of peroxide (as measured by oxygen evolution) was decreased by the presence of MBG, the peroxide decomposition exhibited approximately first-order dependence on the peroxide concentration and essentially zero-order (0.01) dependence on the MBG concentration.

The decomposition of MBG in 1.25N NaOH and 0.001M $MgSO_4$ was studied over a range of temperatures (60-90°C), glycoside concentrations (0.01-0.03M), and peroxide concentrations (0.1-0.4M). Each reaction was monitored not only for reactant disappearance but also for methanol formation, various peroxides, and evolved oxygen. Acidic reaction products were analyzed by gas-liquid chromatography (GLC) and gas chromatography interfaced with mass spectrometry (GLC-MS). The oxidation of 0.01M MeMBG was studied in 1.25N NaOH and 0.001M $MgSO_4$ at 60°C with 0.2M H_2O_2. In addition to analyses described for MBG, the proportion of ^{14}C-labelled methanol in the methanol liberated in the reaction of MeMBG was measured by scintillation techniques.

The dependence of the rate of MBG decomposition on the MBG concentration and the peroxide concentration was determined by conventional kinetic procedures [3] and is summarized in Equation (1).

$$- d[MBG]/dt \propto [MBG]^a[H_2O_2]^b \quad (1)$$

where initially a = b = 1 and finally a = 1 and b ≃ 0.4.

Although the rate of MBG degradation exhibited first-order dependence on the glycoside concentration throughout the whole reaction, the dependence on peroxide concentration shifted from first order to a fractional order. Thus, complex reaction mechanisms are apparently involved in the degradation of MBG in alkaline hydrogen peroxide.

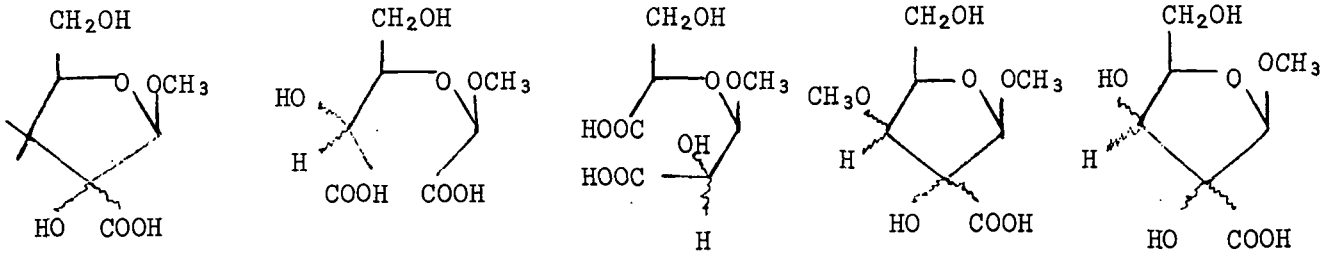
Figures 1 and 2 illustrate that both MBG and MeMBG degrade very rapidly at first and then at very slow rates at longer reaction times as anticipated from Equation (1). Although the production of methanol from MBG follows the expected pattern, no more than 60% of the glycoside degradation is accompanied by methanol formation (see Fig. 1). This confirms observations already in the literature [4, 5]. Figure 2 illustrates that loss of the C-4 methoxy substituent in MeMBG is favored over loss of the C-1 methoxy substituent. Kolmodin [6] observed a similar preference for C-4 bond cleavage relative to glucosidic bond cleavage in the oxygen-alkali reaction of ethyl 4-O-methyl-β-D-glucopyranoside.

[Fig. 1 and 2 here]

Organic peroxides were detected at early reaction times in oxidations of both MBG and MeMBG by a colorimetric, titanium sulfate method [7, 8]. The peroxides were detected at all the reaction conditions studied. These observations have been described in greater detail elsewhere [9]. The stability of the organic peroxides was considerably less than that of the organic peroxides

formed in the reaction of MBG with oxygen and alkali at greater extents of reaction [10]. Thus, the two types of peroxides resulting from the degradation of MBG by the two oxidative processes are not the same.

Reaction products other than methanol and organic peroxides were analyzed by GLC and GLC-MS as their trimethylsilyl (TMS) derivatives [11, 12, 13, 14]. An analysis of MBG reaction products at 0.5 h is illustrated in Fig. 3. The reactions of MeMBG were investigated in less detail than the reactions of MBG. The acidic products identified in oxidations of MBG and MeMBG with alkaline peroxide are listed in Table 1. Those products previously reported for similar reactions of MBG [4] and MeMBG [12] were readily identified except for methyl 2-C-carboxy-β-D-pentafuranosides (20) in the reactions of MBG. The difference in results may be due to the fact that the present oxidations of MBG were conducted under significantly different oxidative conditions or to the possibility that magnesium ion could influence the degradative pathways through formation of intermediate complexes [16]. However, the analog of (20), methyl 2-C-carboxy-3-O-methyl-β-D-pentafuranoside (19) was formed in reactions of MeMBG.



12 13 14 19 20

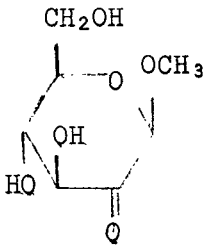
[Fig. 3 and Table 1 here]

Methoxyacetic acid, previously unreported as a product of alkaline peroxide oxidation of MBG and MeMBG, was identified in both systems. In addition, a 3-O-methyl-pentonic acid was a product of MeMBG degradation.

Two products with GLC retention times of ca. 53 and 60 min (Fig. 3 and 4) had mass spectra similar to two dicarboxylic acids characterized by Ericsson, et al. [4] and are believed to be isomers of dicarboxylic acids (13) and (14).

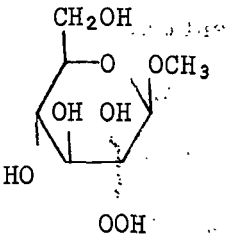
[Fig. 4 here]

As illustrated in Fig. 4, one of the MBG reaction products (11, T_r ca. 43 min) accounts for a substantial portion of the products in the early stage of the reaction, but with reaction time it is diminished to insignificance. The reactive intermediate was identified as a methyl hexopyranosidulose in which the carbonyl group is probably at C-2 [9], e.g., 11. The known lability of



11

aldopyranosiduloses in alkali [15] makes it unlikely that the methyl hexopyranosidulose existed to any significant extent per se in the alkaline peroxide solution, although its limited stability could potentially be enhanced by formation of a magnesium complex [16]. Both the organic peroxide described earlier and the methyl hexopyranosidulose were present in greater amounts during the initial periods of the reaction. This parallel between the two compounds, described in more detail previously [9], suggests that the aldopyranosidulose, which was detected by GLC, was formed from the organic peroxide during preparation of the analytical sample. The most likely type of peroxide precursor is an α-hydroxyhydroperoxide, e.g., 21 and its conjugate base, analogous to those which can be prepared from other ketones, e.g., acetone [17] and cyclohexanone by reaction with hydroperoxide ion. Similar species have often been postulated as intermediates in carbohydrate-peroxide reactions [18].



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The methyl pyranosidulose (11) detected by GLC-MS, is believed to be derived from this hydroxyhydroperoxide (21) during the treatment of the sample with sodium hydrogen sulfite. The pyranosidulose (11) could result either from the reduction of the α-hydroxyhydroperoxide [Equation (2)] or from the

$$HO-\overset{|}{\underset{|}{C}}-OOH + HSO_3^- \longrightarrow \overset{|}{\underset{|}{C}}=O + H_2O + HSO_4^- \qquad (2)$$

$$HO-\overset{|}{\underset{|}{C}}-OOH \rightleftharpoons \overset{|}{\underset{|}{C}}=O + H_2O_2 \qquad (3)$$

α-hydroxyhydroperoxide as the hydrogen peroxide is decomposed by the bisulfite [Equation (3)]. After liberation, the methyl pyranosuloside would be stabilized by the formation of its hydrogen sulfite adduct.

The analyses of MeMBG reactions were less exhaustive than those for MBG reactions, and no attempt was made to identify the suspected methyl 4-O-methyl-β-D-hexopyranosidulose product except by chromatographic mobility.

Changes in the yield of the oxidation products with time of reaction were determined for an oxidation of MBG with 0.3M peroxide at 60°C. The results show a rapid increase of organic peroxide and its subsequent decomposition, as well as the formation of various acidic degradation products (Table 2). The data also demonstrate that methoxyacetic acid, glycolic, 3-hydroxypropionic, glyceric, dicarboxylic acids (13) and (14) and methyl 2-C-carboxy-3-deoxy-β-D-pentafuranosides continue to increase throughout the interval investigated. The yields of 2,4-dihydroxybutyric acid and tetronic and pentonic acids reached a maximum and then decreased significantly after prolonged reaction.

[Table 2 here]

When the quantity of transition metal ion present during the peroxide oxidation was increased above that of the background level, the distribution of the reaction products was greatly altered, indicating a change in the relative importance of the reaction mechanisms involved. The results shown in Table 3 contrast the catalytic effects of Mg^{2+} and Cr^{3+} ions on the degradation of MBG by alkaline peroxide after about 10 h reaction.

[Table 3 here]

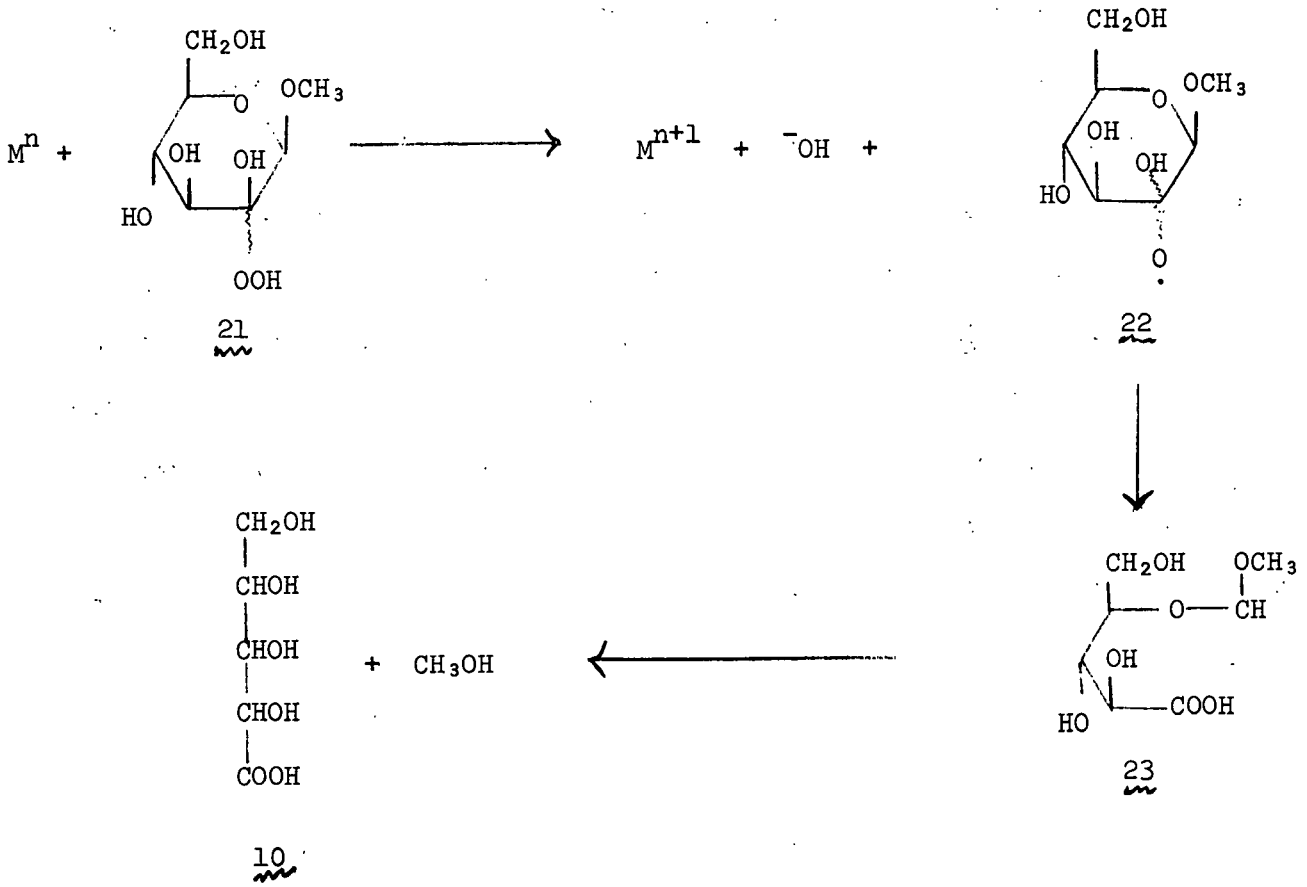
The chromium ions catalyse the degradation of MBG in an unexpected manner. The initial rate of degradation of MBG is not significantly changed from that of the control. This limited response of the initial rate of degradation to catalysis is probably due to the protective action of the Mg^{2+} stabilizer and to the less effective catalytic action of various chromium ions compared to many other transition metal ions. The yield of methoxyacetic acid was greatly diminished whereas the yield of pentonic acids and methanol was increased by the presence of the chromium ions. Since no hexonic acids or their corresponding lactones were detected by GLC, it is likely that a loss of a terminal carbon atom is accelerated by the presence of the chromium ions. The significant yield of dicarboxylic acids (13) and (14) suggests that the reaction pathways leading to those acids has not been as adversely affected as those leading to methoxyacetic acid. Using other transition metal ions, it is possible to cause 95% of the degradation of MBG to occur with methanol liberation instead of the 75% for Cr^{3+} catalysis and 50% for Mg^{2+} stabilization. This research will be part of another publication.

DISCUSSION

The complexity of the reaction of MBG with alkaline peroxide is illustrated by the production of an organic peroxide which behaves as a reactive intermediate. GLC-MS analysis of the reaction mixtures did not reveal the presence of this unstable organic peroxide. Instead, methyl 1-5-pyranosiduloses

were detected which are believed to be derived from α-hydroxyhydroperoxides by the treatment of the reaction mixture with sodium bisulfite before analysis [19]. The acidic reaction products can be postulated to arise from the intermediate organic peroxides by catalytic decomposition, alkaline rearrangement, or further oxidation. Of these three types of reactions, catalytic degradation appears at first sight to be the most obvious.

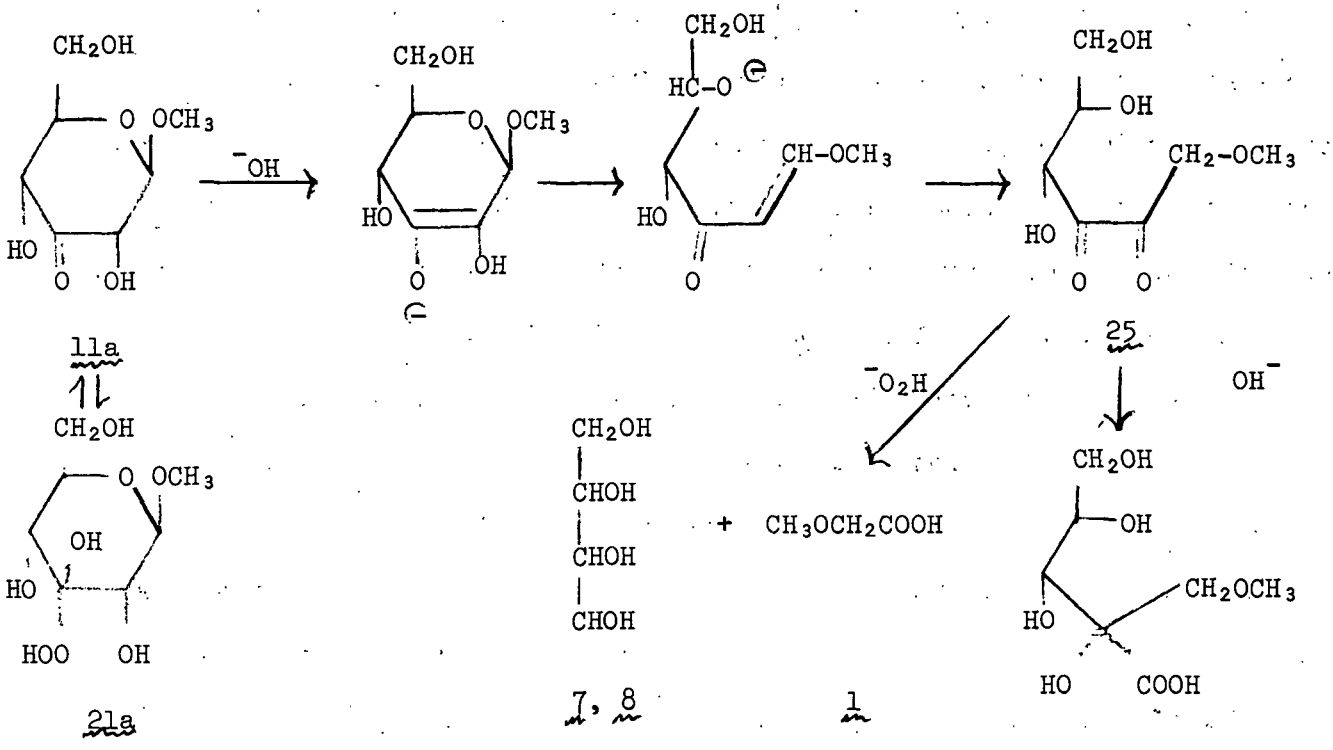
Catalytic degradation of organic peroxides by transition metal ions are widely recognized but often incompletely understood reactions [19]. Addition of Cr^{3+} to the degradation of MBG led to greater yields of pentonic acids and methanol. The oxidation of MeMBG under these conditions yields 3-O-methyl pentonic acid and methanol. A potential mechanism to explain these observations is illustrated in Scheme I. According to this scheme, transition metal ion is



Scheme I

oxidized by the organic peroxide (21), and the resulting alkoxyl radical (22) rearranges to a resonance stabilized carbon radical (23). The radical (23) would readily react with oxygen, hydroxy radicals, or perhydroxyl radicals [20] and subsequently give a pentonic acid and methanol. If however the radical (23) abstracted a hydrogen atom from one of the carbohydrate species in the system, an acetal, stable toward alkali, would be formed. No evidence for this type of product has been found yet. Since it is unlikely that all reactions are initiated at the 2-position, the decomposition of peroxides in other positions must also be considered. These could lead to the production of species containing an aldehydic group in addition to the carboxylic acid group shown in Scheme I. The new intermediates could decompose to low molecular weight acids and methanol by mechanisms proposed by Isbell, et al. [18, 21].

In the relative absence of transition metal ions and in the presence of magnesium ions, other more complex reactions occur which yield reaction products such as methoxyacetic acid (1), 2,4-dihydroxybutyric acid (6), tetronic acids, methyl 2-C-carboxy-3-deoxy-β-D-pentafuranosides and the dicarboxylic acids 13 and 14. The formation of methoxy acetic acid could arise from the alkaline rearrangement of the hexopyranosidulose (11a) which would be in equilibrium with the organic α-hydroxyhydroperoxide (21a). This potential mechanism, shown in Scheme II, would also account for the formation of some of the 2-O-methyl tetronic acid (7, 8) detected after the oxidation of MeMBG.

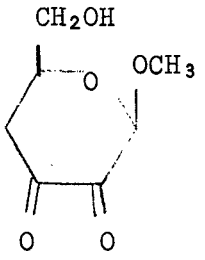


Scheme II

The postulated dicarbonyl intermediate, 25, produced by an elimination reaction at the C-5 position of both MBG and MeMBG, can undergo either oxidative degradation or a benzylic acid rearrangement. In these experiments, oxidation of 25 must predominate since tetronic acids and methoxy acetic acid are produced. In the presence of less peroxide and more alkali, the rearrangement reaction might predominate and could account for other product mixtures. The many different combinations of reaction products that may be formed by different reaction conditions is illustrated by the pattern of oxidation products isolated from the oxidation of methyl β-D-ribohexapyranosid-3-ulose with oxygen and alkali reported in the literature [4].

Methyl 2-C-carboxy-3-deoxy-β-D-pentafuranoside (12), a reaction product from the oxidation of both MBG and MeMBG, has been reported previously [12]. The mechanism proposed by Ericsson and Malinen [12] for the formation of (12) involved the elimination of hydroxyl or methoxyl groups from the C-4 position of

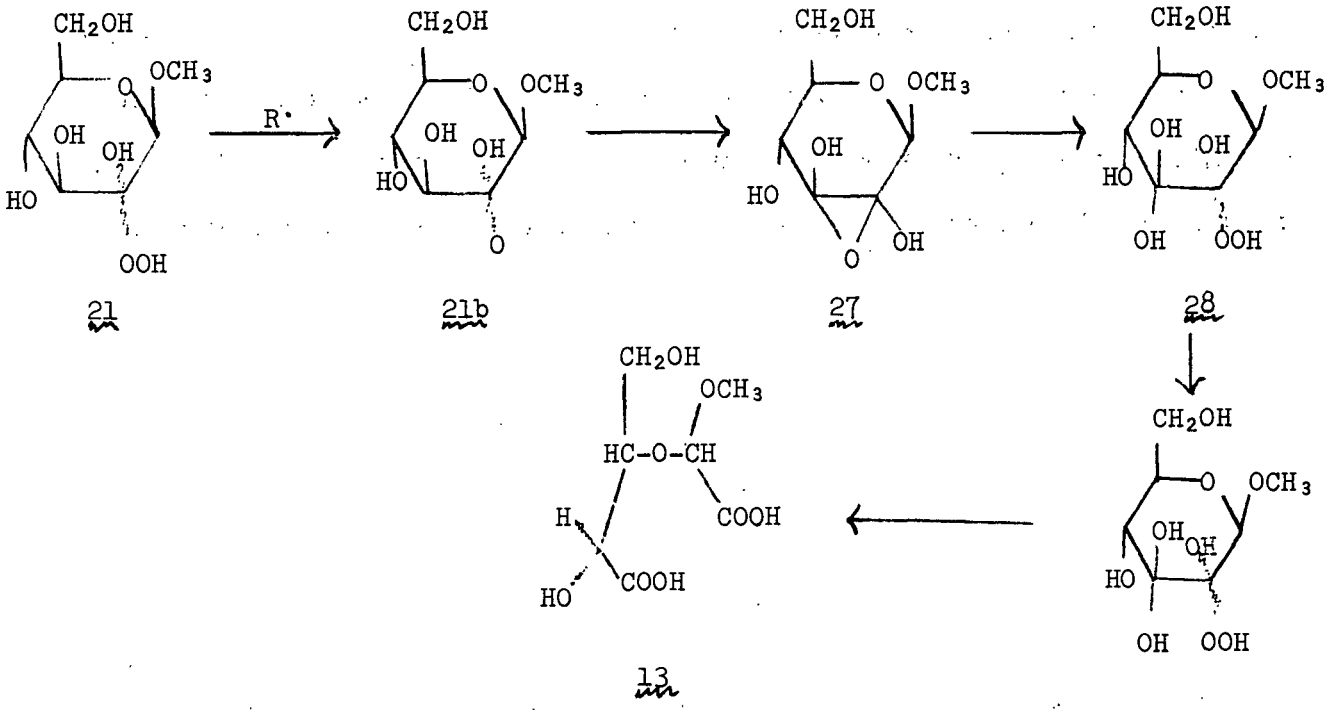
the 2-keto oxidation product to give a 4-deoxy-dicarbonyl intermediate (26). This postulated intermediate could either be oxidized further or undergo a benzylic acid rearrangement. It was speculated [12] that the greater yield of acid (12) from the oxidation of MeMBG compared to that from the oxidation of MBG was due to the better leaving group ability of the methoxy group compared to the hydroxyl group. 3,4-Dihydroxybutyric acid, detected as a product in the reaction of peroxide with MeMBG both in the present work and previously [12], could potentially be formed by further oxidation of the dicarbonyl intermediate (26). However, thus far 3,4-dihydroxybutyric acid has not been detected in alkaline peroxide reactions of MBG.



26

This research confirms previous reports [4, 12] that the dicarboxylic acids 13 and 14 represent a significant fraction of the degradation products from the oxidation of MBG but not from the oxidation of MeMBG. These two acidic substances (13 and 14) and methyl 2-C- (and 3-C-) carboxy β-D-penta-furanosides (acids 19 and 20) are thought to be derived from common hypothetical 2,3- and 3,4-dicarbonyl intermediates by oxidations or benzylic acid rearrangements. The inability to detect the products of this benzylic acid rearrangement (acid 20) in the reaction of MBG in this research may result from the different experimental conditions used here or to the presence of magnesium ion in these experiments. In the latter case, a magnesium complex of either the keto derivatives as proposed by Defaye, et al. [16] or of their α-hydroxyhydroperoxides might diminish the susceptibility of the intermediates to alkaline rearrangement to a greater extent than to oxidation.

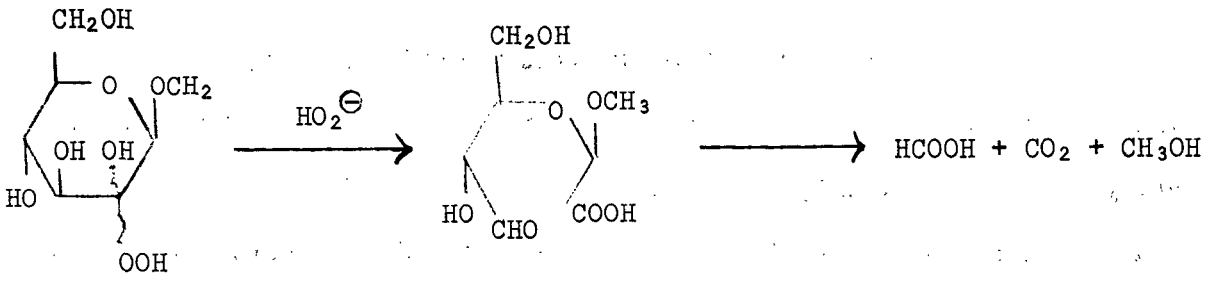
The dicarboxylic acids 13 and 14 detected in this research could arise from an α-dicarbonyl intermediate [4] which could form by reaction pathways similar to those proposed by Isbell, et al. [18] for the oxidation of pentahydroxycyclohexanone with alkaline peroxide. The reaction (Scheme III)



Scheme III

would proceed via an epoxide intermediate (27) and the hydrated α-diketone (28). Similarly, oxidation at C-3 or C-4 of MBG could lead to the formation of dicarboxylic acid 14.

Other smaller acids detected in the reaction mixtures could arise from competing reaction pathways described by Isbell, et al [18] for oxidation at C-2 of MBG and illustrated in Scheme IV. The aldehyde group in 13a for example would react further with the alkaline peroxide to produce formic acid and methanol [21]. The number of stable products formed by these pathways will depend upon the location of the peroxide group in the molecule.



21 13a

Scheme IV

EXPERIMENTAL

Reagents

Methyl β-D-glucopyranoside (MBG) (Pfanstiehl Laboratories, Inc.) was recrystallized twice from ethanol to remove traces of methanol; m.p. 109-110°C, $[\alpha]_D^{21}$ = 33.5 (C = 1, H_2O). Literature [24]: m.p. 111°C, $[\alpha]_D$ -34.2° (C=1, H_2O).

Methyl 4-O-methyl (^{14}C)-β-D-glucopyranoside (MeMBG) was prepared according to the procedure of Bouveng, et al. [22] using $C^{14}H_3I$ in the methylation stage. The crude product was purified by column chromatography (silica gel 60-200 mesh) using ethyl acetate — absolute ethanol (20:1) as eluant; m.p. 101-2°C, $[\alpha]_D^{21}$ = -18° (C = 1, H_2O). Literature [22]: m.p. 101-3°, $[\alpha]_D$ -18° (C=1, H_2O).

Stock solutions of 25% (w/w) NaOH were prepared by dissolving analytical grade sodium hydroxide in triply distilled water. The solution was further purified by complexing metal ions with alcoholic phenyl 2-pyridyl ketoxime [23]. The complexes were removed by extraction with isoamyl alcohol and chloroform. After treatment with hydrogen peroxide, the stock solution was boiled and stored in a paraffin-lined container under nitrogen.

Alkaline peroxide reactions

Alkaline peroxide reactions of the glucosides were carried out in a Teflon-lined reactor equipped with a sampling port, a gas exit port, and a magnetic stirring device [25].

Reaction solutions (1.25N NaOH and 1 mM $MgSO_4$) were prepared by diluting the stock solutions to 300 ml with triply-distilled water. An appropriate quantity of unstabilized hydrogen peroxide (30%) was added and the reactor sealed. As the reactor equilibrated in the temperature-controlled oil bath, the decomposition of alkaline peroxide was monitored for the desired initial concentration level (100-400 mM) by measuring oxygen evolution. At the appropriate time the reaction was initiated by addition of the glucoside (10-30 mM). During the reaction, samples were withdrawn through a sampling port and associated valve system while evolved gases were measured with a water-jacketed gas buret connected to the gas exit port [25].

Analysis of reaction solutions

The concentrations of unreacted glucoside, residual hydrogen peroxide, oxygen evolution, organic peroxides, and methanol were monitored throughout each alkaline peroxide reaction. In addition, after each reaction was terminated, an aliquot of the solution was analyzed for transition metal by atomic absorption spectroscopy [26].

Methanol analysis was conducted on distillates of the reaction samples and involved a modification of the chromotropic acid method of Boos [27].

Analysis of the unreacted glucosides was performed by quantitative gas chromatography of the acetylated glucosides using an internal standard. The reaction samples were deionized with Amberlite MB-3 (OH^-, H^+) resin, concentrated to dryness, and acetylated for analysis. Gas chromatography was conducted on a Varian Aerograph 1200-1 chromatograph equipped with hydrogen flame ionization detector and a Honeywell Electronic 16 recorder with Disc integrator. A 10% SE-30 on 60/80 mesh Chromosorb W column (5' x 1/8", SS) was used with the following operating conditions: nitrogen carrier gas, 8 ml/min; injector temperature, 250°C; column temperature, 160-200°C at 4°C/min; and detector temperature, 260°C.

The concentration of peroxides (hydrogen peroxide and organic peroxides) was determined by a colorimetric titanium sulfate method [7, 8]. The rate of H_2O_2 decomposition was determined by measurement of evolved oxygen. The volume of oxygen was measured by displacement of mercury from a water-jacketed gas buret. Proof that only oxygen was evolved during the alkaline peroxide reaction of the glucosides was shown by pyrogallic acid absorption [28].

The quantity of ^{14}C in a reaction sample was determined from a comparison of the specific activity of the isolated methanol with the specific activity of the reactant MeMBG using a Beckman LS-100 Liquid Scintillation Counter. After corrections, the concentration of $^{14}CH_3OH$ was determined by the technique described by Arnoff [29].

Mass spectroscopy and identification of reaction products

The products of the glucoside reactions were separated by gas chromatography of the trimethylsilyl (TMS) ether and ester derivatives. The analytical samples were prepared by first quenching the hydrogen peroxide with sodium bisulfite, then neutralizing with Amberlite IR-120, concentrating to dryness at pH 8, and silylating by the TRI-SIL/DMSO procedure of Verhaar and DeWilt [11]. For identification purposes, the products were first separated by gas chromatography using a 3% OV-17 on 100/120 mesh Chromosorb W column (13' x 1/8", SS) with the following operating conditions: helium carrier gas, 30 ml/min; injector temperature, 200°C; column temperature, 70-175°C at 3°C/min; and detector temperature, 260°C. Quantitative analysis of the reaction products was accomplished by assuming that the quantity of the acidic products was proportional to the areas on the chromatograms. The percent of each acid relative to the total quantity of acid detected by GLC could then be estimated as has been done by others [12]. Since the total quantity of glycoside, remaining glycoside and organic peroxide was known, the yield of the organic acids was estimated as follows:

$$\% \text{ Yield of product} = \frac{\text{Area on GLC of product}}{\text{Total area of all products}} [100 - (\% \text{ MBG remaining} + \% \text{ organic peroxide})]$$

This calculation does not take into account the production of acetic, formic, and carbonic acids. However, the discrepancy cannot be great since the bound methanol determined by methoxy analysis was identical within experimental error to the bound methanol calculated from the areas of the appropriate GLC peaks.

For mass spectrometry the separated TMS products were routed from the GC to a DuPont Instruments 21-491 mass spectrometer. The mass spectra for product identification were obtained at 70 ev.

The mass spectrum of methoxyacetic acid was identical to that of an authentic acid. The molecular weight of 162 is easily established from the strong peaks at m/e 162 (M), 147 (M-15), 131 (M-$CH_3O\cdot$), and 116 (M-15-$CH_3O\cdot$).

The mass spectrum of the 3-O-methyl-pentonic acid exhibited a parent ion at m/e 468 and associated fragments at 453 (M-15), 438 (M-30), 423 (M-45), and 378 (M-HOTMS). Fragments at m/e 249 and 263 result from cleavage between C-2 and C-3 and between C-3 and C-4, respectively, and indicate the methoxy group is at C-3.

The mass spectrum of the methyl β-D-hexopyranosuloside has been described previously [9].

The mass spectrum of 2-O-methyl-tetronic acid exhibited a parent ion at m/e 366 and fragments at m/e 351 (M-15), 321 (M-45), and 261 (M-15-HOTMS). A McLafferty-type rearrangement fragment [30] at m/e 234 established the position of the methoxy substituent.

Ericsson, et al. [4, 12] tentatively identified a methoxy tetronic acid in the oxygen-alkali and alkaline peroxide oxidations of MeMBG. The mass spectrum obtained by Ericsson lacked the molecular ion but otherwise was similar to the above data.

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Table 1

Products from the Oxidation of 0.01M Methyl β-D-Glucopyranoside (MBG) and 0.01M Methyl 4-O-Methyl (^{14}C)-β-D-Glucopyranoside with 0.2M H_2O_2 in 1.25M NaOH and 0.001M $MgSO_4$ at 60°C

T_r, min[a]	Compound	Product Number MBG	Product Number MeMBG	Identification Technique[b]
6.0	Methoxyacetic acid	1	1	MS, T_r
8.7	Lactic acid	2	2	MS (13), T_r
9.8	Glycolic acid	3	3	MS (13), T_r
12.6	3-Hydroxypropionic acid	4	4	MS (13), T_r
20.7	Glyceric acid	5	5	MS (13)
24.8	3,4-Dihydroxybutyric acid	--	15	MS (13)
25.2	2,4-Dihydroxybutyric acid	6	--	MS (13)
27.6	2-O-Methyl tetronic acid	--	16	MS (12)
29.1	Erythronic acid	7	--	MS (13)
30.1	Threonic acid	8	--	T_r (5)
34.8	3-O-Methyl pentono-1,4-lactone	--	17	T_r
36.2	Pentono-1,4-lactone	9	--	MS (13)
40.5	3-O-Methyl pentonic acid	--	18	MS
42.3	Pentonic acid	10	--	MS (13)
43.5	Methyl β-D-hexopyranosidulose	11	--	MS
49.2	Methyl 2-C-carboxy-3-deoxy-β-D-pentafuranosides	12	12	MS (12)
51.3	Methyl 2-C-carboxy-3-O-methyl-β-D-pentafuranosides	--	19	MS (12)
56.1	Dicarboxylic acids	13	--	MS, T_r (5, 12)
59.7	Dicarboxylic acids	14	--	MS, T_r (5, 12)

[a] Average GLC retention time. Analysis conditions were the same for reactions of MBG and MeMBG; see Experimental Section.

[b] Structural assignments are based on mass spectral (MS) or GLC retention time (T_r) data. Reference mass spectral data or chromatograms are in the indicated references.

Table 2

Products from the Reaction of 10 mM MBG with 1.25N NaOH and 1 mM $MgSO_4$ at 60°C

$[H_2O_2]$ mM	200			300			
Reaction time, h	6	10	29	1	9	20	44
Yield, %							
MBG	76	75	70	74	69	67	62
Methoxy acetic acid	2.4	3.5	4.2	3.6	7.7	5.0	7.2
Lactic acid	1.0	0.3	0.3	1.0	1.2	1.3	1.1
Glycolic acid	3.0	3.5	4.2	2.6	3.1	5.6	6.3
3-Hydroxypropionic acid	1.0	0.3	0.6	0.5	0.6	1.3	3.0
Glyceric acid	2.4	3.5	4.0	0.7	1.0	3.0	3.6
2,4-Dihydroxybutyric acid	1.2	1.0	1.2	1.5	1.8	2.2	0.5
Tetronic acids	2.5	3.0	4.2	2.6	3.1	4.3	3.0
Pentonic acids	3.4	3.0	3.3	3.4	3.9	1.9	1.6
Methyl 2-C-carboxy-3-deoxy-β-D-pantafuranoside	2.1	2.2	2.7	2.2	2.7	3.0	3.0
Dicarboxylic acids	5.0	5.0	5.4	7.5	9.0	8.6	4.6

Table 3

Products from the Reaction of 10 mM MBG with 1.25N NaOH and 1 mM $MgSO_4$ at 60°C

[$CrCl_3$] mM	0	0	10^{-3}
[H_2O_2] mM	200	300	200
Reaction time, h	10	9	10
Yield, %			
MBG	75	69	78
Methoxy acetic acid	3.5	7.7	1.32
Lactic acid	0.3	1.2	0.4
Glycolic acid	3.5	3.1	2.9
3-Hydroxypropionic acid	0.3	0.6	0.4
Glyceric acid	3.5	1.0	2.6
2,4-Dihydroxybutyric acid	1.0	1.8	0.4
Tetronic acids	3.0	3.1	2.4
Pentonic acids	3.0	3.9	5.5
Methyl 2-C-carboxy-3-deoxy-β-D-pentafuranoside	2.2	2.7	1.3
Dicarboxylic acids	5.0	9.0	5.3

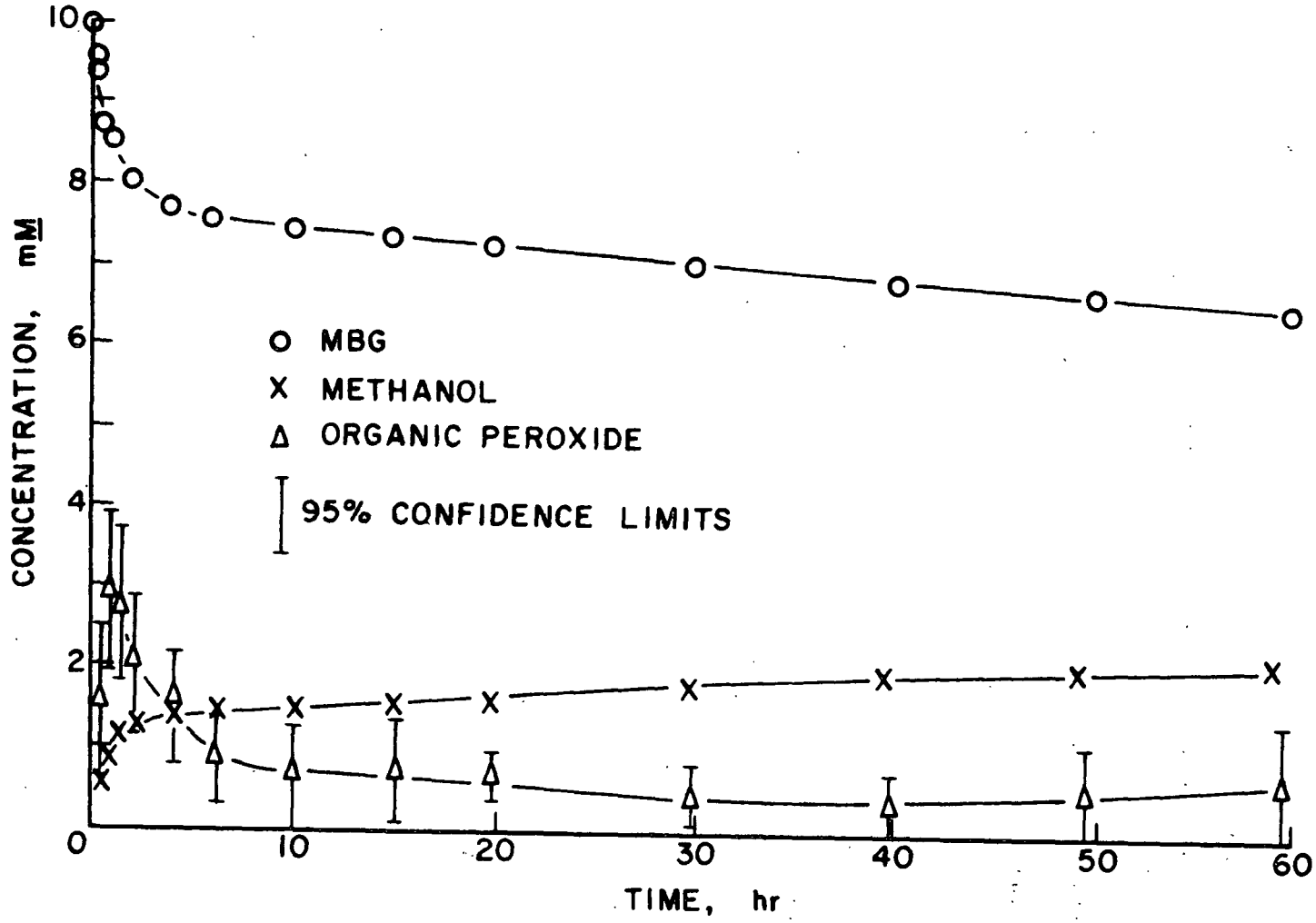

Fig. 1. Oxidation of 0.01M Methyl β-D-Glucopyranoside with 0.2M H_2O_2 in 1.25N NaOH and 0.001M $MgSO_4$ at 60°C.

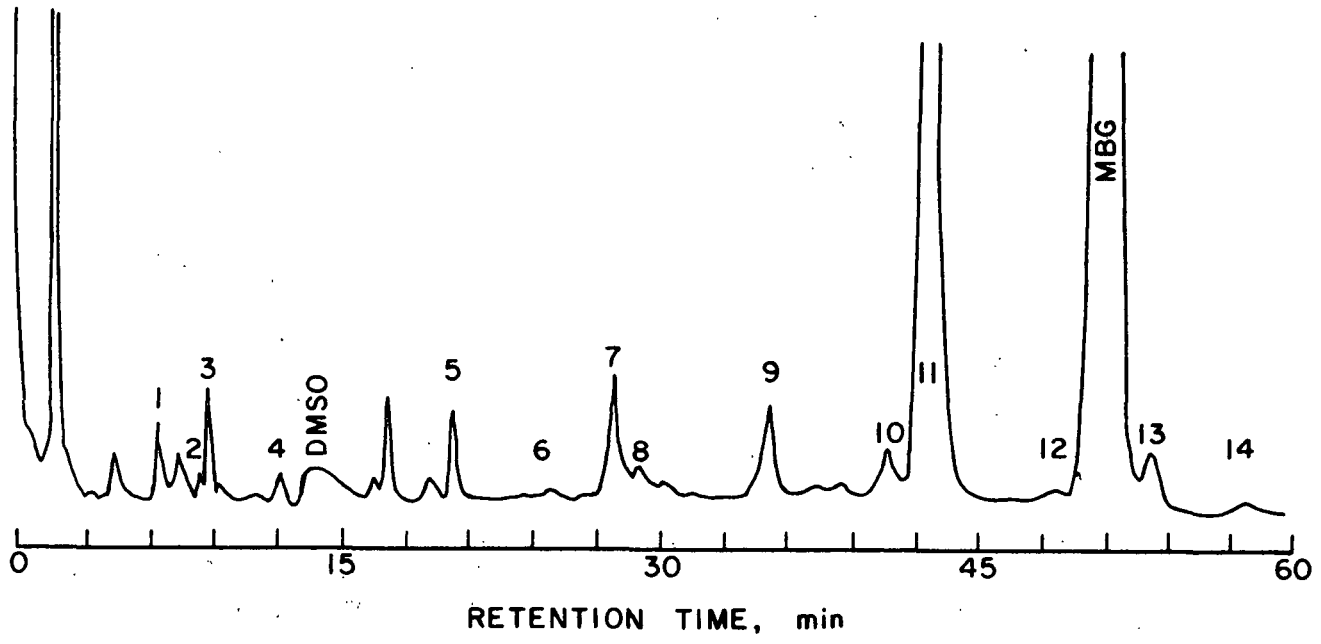

Fig. 3. GLC Analysis of Products Formed After 0.5 h Reaction of 0.1M Methyl β-D-Glucopyranoside with 0.3M H_2O_2 in 1.25N NaOH and 0.001M $MgSO_4$ at 60°C: Methoxyacetic Acid (1), Lactic Acid (2), Glycolic Acid (3), 3-Hydroxypropanoic Acid (4), Glyceric Acid (5), 2,4-Dihydroxybutanoic Acid (6), Erythronic Acid (7), Threonic Acid (8), Pentono-1,4-lactone (9), Pentonic Acid (10), Methyl β-D-Hexopyranosidulose (11), Methyl 2-C-Carboxy-3-deoxy-β-D-pentafuranoside (12), and Dicarboxylic Acids (13 and 14).

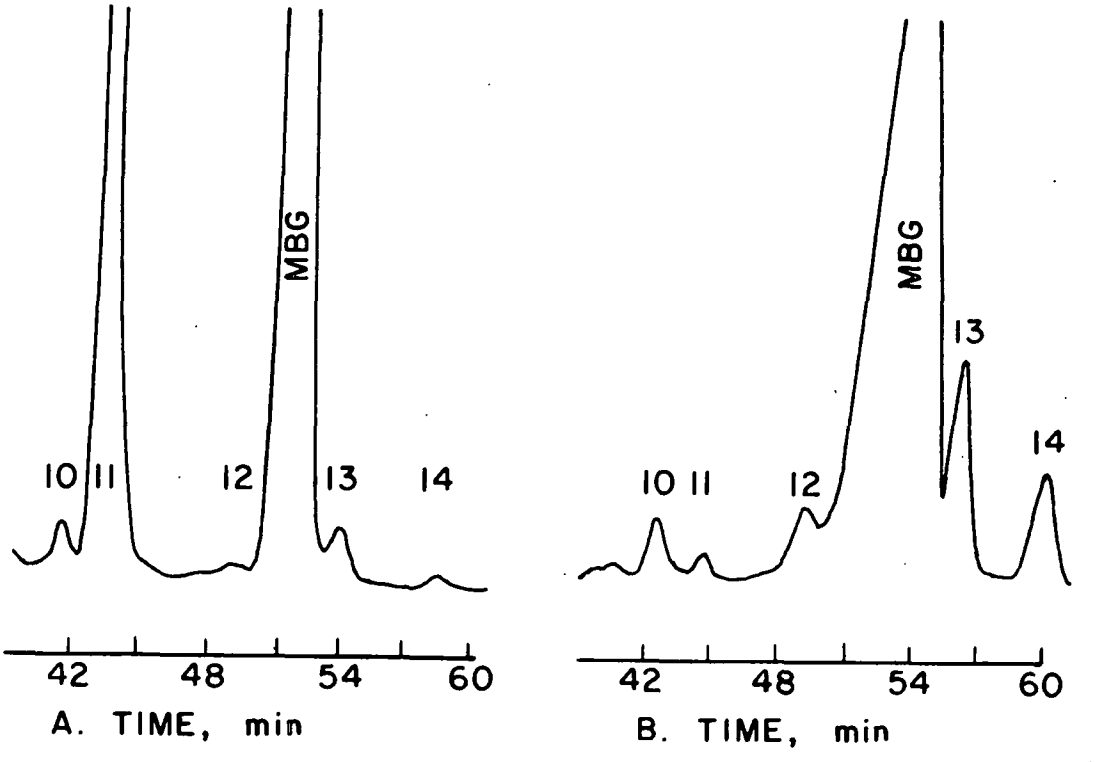

Fig. 4. GLC Analyses of MBG Degradation Products (TMS-Derivatives). A, 1/2 h Reaction; B, 9 h Reaction.