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An Investigation of the Role of Sodium Sulfide in Cellulosic Chain Cleavage During Kraft Pulping

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AN INVESTIGATION OF THE ROLE OF SODIUM SULFIDE IN CELLULOSIC CHAIN CLEAVAGE DURING KRAFT PULPING

A thesis submitted by

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SUMMARY

During kraft pulping, sodium sulfide increases the rate of delignification relative to the soda process, but reportedly does not accelerate carbohydrate degradation. However, alkyl glycosides used as cellulose models undergo S_N2 reactions, especially in the presence of sulfur nucleophiles. In kraft pulping the sodium sulfide which is employed could potentially exist as a dianion (S^{-2}), or it could be hydrolyzed to hydrosulfide ion (SH^-). Either of these is expected to be a strong nucleophile.

Since the state of hydrolysis of sodium sulfide is uncertain under kraft pulping conditions, the oxygen-free kraft degradation (1.0M NaOH, 0.2M Na_2S) of 1,5-anhydro-4-O-(β-D-glucopyranosyl)-D-glucitol (1,5-anhydrocellobiitol) was compared to two soda controls. One control simulated the absence of hydrolysis (1.0M NaOH, 1.6 μ), while the other modeled the kraft cook if hydrolysis occurred (1.2M NaOH, 1.4 μ). The pseudo-first-order rate constant for the degradation of 1,5-anhydrocellobiitol under kraft conditions ($6.80 \pm 0.08 \times 10^{-6}$ sec^{-1}) was identical to that found for the latter control ($6.77 \pm 0.07 \times 10^{-6}$ sec^{-1}), and greater than that of the 1.0M NaOH control ($6.16 \pm 0.06 \times 10^{-6}$ sec^{-1}). The proportion of glycosyl-oxygen bond cleavage was the same in all three cases (ca. 87%). This indicates that the sodium sulfide is hydrolyzed under pulping conditions, and that the resulting hydrosulfide ion plays no role in the rate-determining steps of glycosidic bond cleavage in 1,5-anhydrocellobiitol. However, the yields of two products, 1,6-anhydro-β-D-glucopyranose and 1,5:3,6-dianhydro-D-galactitol were lower in the kraft cook than in the soda controls. This is due to the action of hydrosulfide ion during the product-determining steps of the reaction, where it diverts the reactive intermediates formed during bond cleavage toward other products.

In similar degradations of methyl α-D-glucopyranoside (known to degrade by an S_N2 mechanism) hydrosulfide ion was found to be 11 times as effective as hydroxide ion at cleavage of the oxygen-aglycone bond. Thus, it is proposed that hydrosulfide ion is a stronger nucleophile than hydroxide ion under pulping conditions, but 1,5-anhydrocellobiitol is not susceptible (for steric or electronic reasons) to an S_N2 attack.

This suggests that the hydrosulfide ion is also hindered from participating in an S_N2 attack on cellulose during the kraft pulping of wood. In light of the similarities between the hydrosulfide and hydroxide ions, it seems likely that glycosidic bond cleavage during pulping does not involve an S_N2 mechanism, but is the result of S_N1 and $S_N1cB(2)$ reactions.

INTRODUCTION

> "The first commercial mill for alkaline, or soda pulping was erected in America by Burgess in 1854. The method soon called for regeneration of the large quantities of alkali used, through evaporation and combustion of the waste liquors and caustization of the sodium carbonate formed. However, to cover the heavy losses of chemicals, sodium carbonate had to be added, and since that chemical was then made from sodium sulfate by the Leblanc process and was rather expensive, it was reasons of economy that caused Dahl in Danzig to modify the soda process in 1879 by direct introduction of sodium sulfate into the recovery system (1)."

Since then the sulfate, or kraft process has become the dominant method for the production of wood pulp. In 1982, the kraft process accounted for 73% of U.S. pulp production, while the soda process contributed only 0.5% (2). The addition of sodium sulfide (formed by reduction of sodium sulfate during combustion) to the cooking liquor results in a considerable improvement in both the rate of pulping and the strength of the pulp.

It is generally believed that these advantages result from an increase in the rate of delignification. This permits a shorter cook, which minimizes degradation of the carbohydrates by sodium hydroxide. Despite this, as much as 10% of the cellulose and 60% of the hemicellulose are lost during a kraft cook, and the degree of polymerization (DP) of the cellulose can be reduced to one-third of its original value (3,4).

Alkaline degradation of the wood polysaccharides involves several types of reactions, including swelling of the fiber, dissolution (and reprecipitation) of low DP polysaccharides, random cleavage of glycosidic bonds, and the sequential peeling of monomers from the reducing end of the polysaccharides. The peeling reaction is thought to be responsible for most of the yield losses associated with pulping (1). The reaction proceeds rapidly even at relatively low temperatures (under 100°C), so that much of the yield loss occurs during the heat-up period of the cook (3).

Peeling requires isomerization of the aldose end unit to a ketose, followed by elimination of the rest of the polymer chain from C-4 (creating a new reducing end unit on the polymer), and finally rearrangement of the original end unit to an isosaccharinic acid (5). This reaction sequence is repeated to peel an average of 65 units off the chain before it is stopped (6). The chemical stopping reaction begins with elimination of the C-3 hydroxyl group from the aldose end unit, followed by rearrangement of the end unit to a metasaccharinic acid (5). This leaves the polymer without a reducing end unit capable of peeling. Physical stopping of the peeling reaction is thought to occur when the polymer chain peels back to the edge of a crystallite and is no longer accessible to the hydroxide ion (7).

Random cleavage of glycosidic bonds is primarily responsible for decreasing the DP of the polysaccharides, but it also creates new reducing end groups which can subsequently peel (1,8). However, Matthews (3) has shown that this secondary peeling accounts for only one-fifth of the cellulose lost. While it is known that random chain cleavage requires much higher temperatures than peeling (over 150°C), the mechanisms are not well established. The reaction is not easily studied by using cellulose or whole wood, since cleavage cannot be separated from the other alkaline reactions. As a result, the starting material cannot be well defined, the hydroxide ion concentration and ionic strength are uncertain, and the products are not readily identified. Therefore much of what is thought to be known about chain cleavage has been derived from studies of model compounds.

KRAFT PULPING

The composition of a typical kraft pulping liquor is given in Table I. The white liquor has a pH of 14 at 25°C, but increasing the temperature has the effect of decreasing the pH. For example, at 170°C a 1M NaOH solution would have a pH of

about 11.8 (9). However, in a kraft cook the pH also decreases due to consumption of sodium hydroxide. Peeling is responsible for most of the alkali consumed, requiring about 1.5 hydroxide ions per monomer peeled (1,8). Thus, the pH of the liquor decreases most rapidly during the first stages of pulping (10). The final pH of the kraft cooking liquor is typically 10-12 at 25°C (1).

TABLE I

INITIAL COMPOSITION OF COOKING LIQUOR IN A NORMAL KRAFT COOK[a]

Compound	Composition, g L^{-1}
NaOH	38
Na_2S	15
Na_2CO_3	11
Na_2SO_4	0.2
Na_2SO_3	0.2
$Na_2S_2O_3$	0.4

[a]Sulfidity 30%, active alkali 50 g L^{-1} as NaOH, taken from Ref. (1).

The sodium sulfide is subject to hydrolysis in aqueous solutions according to the following equilibria:

$$S^{-2} + H_2O \rightleftharpoons SH^- + OH^- \quad (1)$$

$$SH^- + H_2O \rightleftharpoons H_2S + OH^- \quad (2)$$

The first dissociation constant of hydrogen sulfide (pK_a1) is about 7.0 at 25°C, and is thought to vary by only 0.5 up to 200°C (11). Therefore the equilibrium in Eq. (2) lies fully to the left in kraft cooking liquors, and virtually no hydrogen sulfide is present.

Unfortunately, the second dissociation constant of hydrogen sulfide (pK_a2) is not known with certainty (11,12). For example, Giggenbach (13) reported a value of

17.1 (at 25°C), while Zuman and Szafranski (14) reported 12.0 using the same spectroscopic technique. At 170°C, values between 11.0 and 12.5 have been proposed for pK_a2 (11). Thus, it is not readily apparent where the equilibrium in Eq. (1) might lie during kraft pulping. It is possible that the relative importance of the sulfide dianion and the hydrosulfide anion could change as the pH and temperature of the cooking liquor change.

Teder and Tormund (15) attempted to resolve this problem by pulping cotton linters at several levels of sulfide addition. The concentration of free hydroxide ions in the alkaline sulfide solutions was determined by comparing their ability to hydrolyze the cellulose with that of sodium hydroxide control solutions. They were able to show, at 170°C in 0.5M NaOH, that the sulfide dianion was completely hydrolyzed to hydroxide and hydrosulfide ions. Furthermore, they showed that the hydrosulfide ion does not accelerate chain cleavage, a result that is in agreement with previous research (16,17).

The hydrosulfide ion does participate in delignification, however, and much of the research into kraft pulping has focused on this area. Recently Gierer (18,19) has used model compounds to show that the hydrosulfide ion is responsible for cleavage of β-aryl ether linkages in free-phenolic lignin units (Fig. 1). Cleavage of these linkages is critical, since β-aryl ether bonds represent about 50% of the linkages between the phenylpropane monomers in native lignin (20).

As Fig. 1 shows, the most frequent reaction of free-phenolic lignin units (I) during soda pulping is elimination of formaldehyde. The β-aryl ether linkage is relatively stable (1,19). Kraft pulping, however, results in addition of the hydrosulfide ion to the α-carbon of the quinone methide (II). The sulfide anion then displaces the phenoxy anion, forming an episulfide (V) and cleaving the β-aryl ether

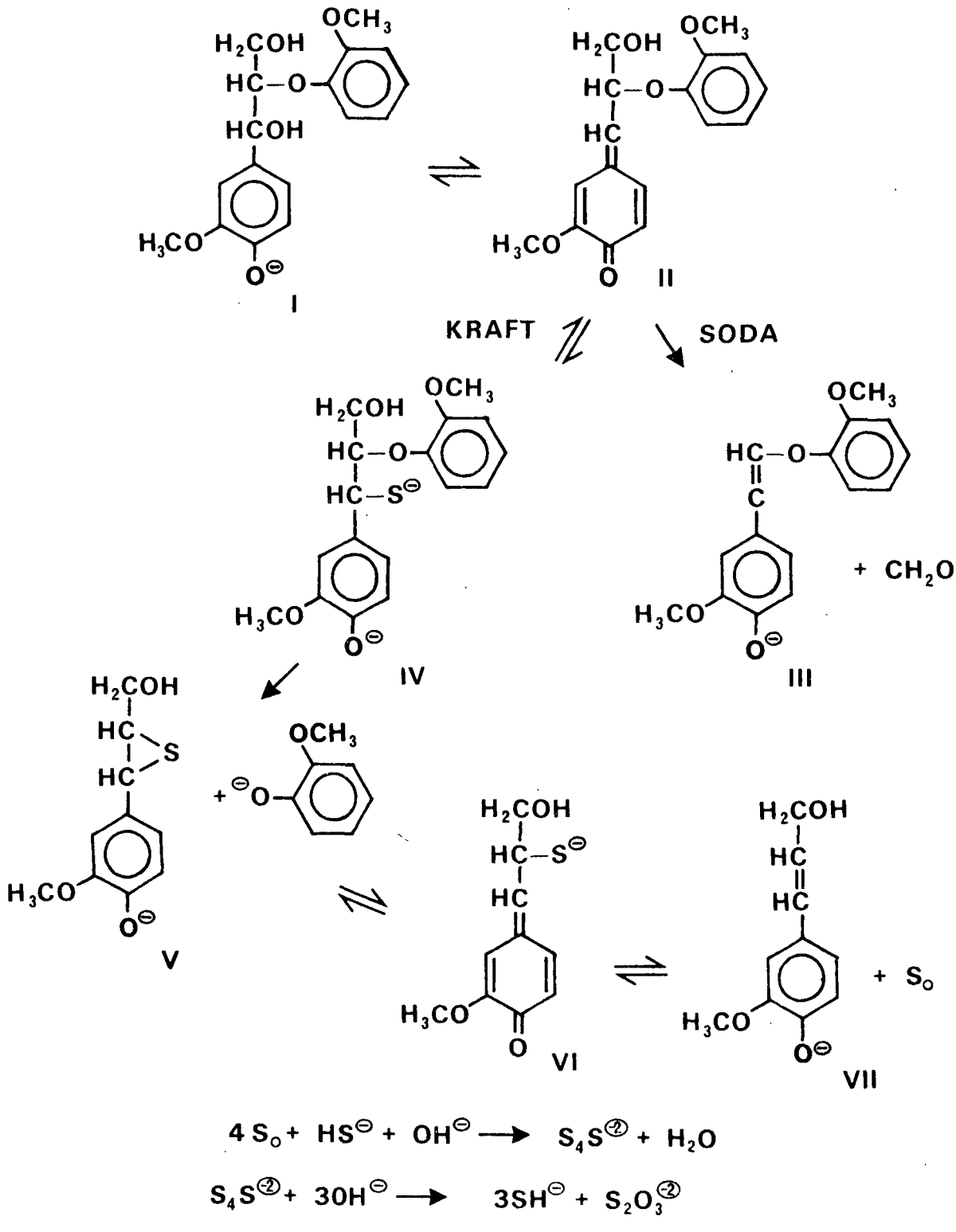


Figure 1. Typical reactions of free-phenolic arylpropane units during kraft and soda pulping (19,21).

bond. The episulfide eliminates elemental sulfur (21,22), which accounts for the fact that kraft lignin typically contains only small amounts of sulfur (1). The elemental sulfur is converted to hydrosulfide and thiosulfate ions (Fig. 1) (21,22).

The effectiveness of hydrosulfide ion at cleaving β-aryl ether bonds is presumably due to the nucleophilicity of the ion. Nucleophilicity is a relative term, defined by Swain and Scott (23) as:

$$\text{Log } k/k_o = sn \qquad (3)$$

where k = second-order rate constant for displacement on a substrate by a nucleophilic reagent

k_o = second-order rate constant for displacement on the substrate by water

s = susceptibility of the substrate to attack

n = nucleophilicity of the reagent

The standard reaction is the reaction of the substrate with water, which is assigned a nucleophilicity of zero. Methyl bromide is defined as having a susceptibility of 1. In this way nucleophilicity values for several reagents, including hydroxide ion ($n = 4.2$) and hydrosulfide ion ($n = 5.1$), were derived (23).

A substrate with a susceptibility of 1 will react 7.9 times more rapidly with hydrosulfide ion than with hydroxide ion (at 25°C). Unfortunately, susceptibility values are established for only a few substrates, and the nucleophilicity values are based on only a few reactions. Furthermore, inversions of nucleophilic order have been observed to result from changes in solvent (24), temperature (25), and substrate (26). Changing from a protic to an aprotic solvent is believed to result in a significant increase in the nucleophilicity of oxygen anions because they are no longer shielded by a solvent cage. This change has less of an effect on sulfur

nucleophiles since they have much weaker solvent interactions, even in protic solvents (24).

Recently, Smith and Dimmel (27) have shown that the hydroxide ion is a much stronger base at 170°C than it is at 25°C. One possible explanation for this is that the solvent cage does not exist at high temperatures. If so, it could be expected that the hydroxide ion would also become a better nucleophile as the temperature increases. The hydrosulfide ion would not be expected to benefit as much from this phenomenon. However, Gierer used a model compound similar to that shown in Fig. 1, and studied its degradation in soda and kraft systems at 130°C. He found that the β-aryl ether linkage was cleaved 200 times more rapidly by hydrosulfide ion than by hydroxide ion (18). This implies that hydrosulfide is still the better nucleophile at 130°C, and that the quinone methide substrate is more susceptible to nucleophilic attack than methyl bromide.

ALKALINE DEGRADATION OF CELLULOSE MODEL COMPOUNDS

In 1945, McCloskey and Coleman proposed a mechanism to explain the difference in reactivity between phenyl α-D-glucopyranoside and phenyl β-D-glucopyranoside (28). Table II shows that phenyl glycosides with a trans relationship between the C-2 hydroxyl group and the C-1 phenoxy substituent degrade much more rapidly in boiling potassium hydroxide solution than their cis analogues (29).

Figure 2 shows the mechanism McCloskey and Coleman proposed for the alkaline degradation of phenyl β-D-glucopyranoside (VIII). The first step is an $S_N1cB(2)$ reaction, in which the C-2 hydroxyl group is ionized ($VIII_a$), and the resultant trans oxyanion attacks C-1, displacing the phenoxy anion and forming the 1,2-anhydride (IX). Displacement of the phenoxy anion is the rate-determining step of the mechanism (30). The second step is an $S_N1cB(6)$ reaction, with the C-6 oxyanion (IX_a) attacking C-1 of the 1,2-anhydride to form 1,6-anhydro-β-D-glucopyranose

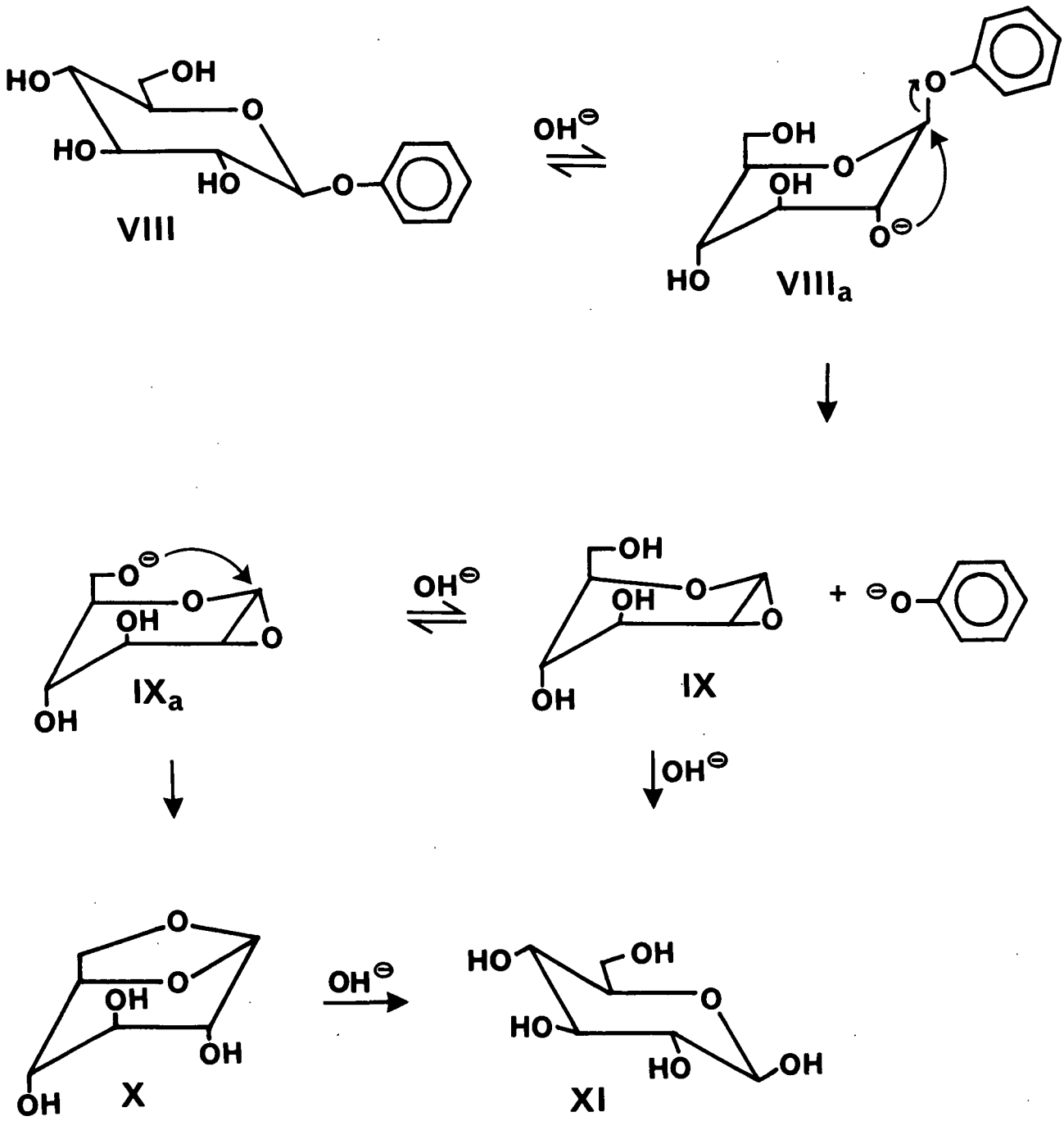


Figure 2. McCloskey-Coleman mechanism for the alkaline degradation of phenyl β-D-glucopyranoside (28).

(levoglucosan) (X) in 90% yield (29).*

TABLE II

ALKALINE HYDROLYSIS OF PHENYL GLYCOSIDES IN BOILING 1.3N POTASSIUM HYDROXIDE[a]

Phenyl Glycoside	C1 - C2 Configuration	Reaction Time, hour	Recovered Product
β-D-glucoside	trans	9	1,6-anhydride
α-D-glucoside	cis	336	glucoside
β-D-xyloside	trans	3	tar
α-D-xyloside	cis	48	xyloside
β-D-galactoside	trans	9	1,6-anhydride
α-D-galactoside	cis	2688	1,6-anhydride

[a]Data from Ref. (29).

Stereochemistry is a critical consideration for this mechanism. The C-1 and C-2 substituents must be able to achieve the trans-diaxial relationship shown in Fig. 2 ($VIII_a$) for the reaction to proceed. Phenyl β-D-glucopyranoside requires a change in conformation from C1 to 1C, but the energy barrier to this change is small. The cis-1,2 glycosides, however, cannot achieve the required stereochemistry, and the mechanism is blocked. The reaction can also be blocked by methylation of the C-2 hydroxyl group. Table III shows that this can result in a decrease in the rate of reaction by a factor of several hundred (31).

TABLE III

SECOND-ORDER RATE CONSTANTS FOR THE DEGRADATION OF PHENYL GLYCOSIDES IN SODIUM HYDROXIDE AT 55°C[a]

p-Nitrophenyl Glycoside	C1 - C2 Configuration	$10^6 k_2$ L mol^{-1} sec^{-1}
β-D-galactoside	trans	416
2-O-methyl-β-D-galactoside	trans	1.26
α-D-mannoside	trans	3090
2-O-methyl-α-D-mannoside	trans	1.65

[a]Data from Ref. (31).

*In those sugars where the C-6 oxyanion is nonexistent or is cis to the epoxide, the 1,2-anhydride (IX) degrades to other products.

Methyl β-D-glucopyranoside, which has the trans-1,2 stereochemistry, requires significantly more rigorous conditions for glycosidic bond cleavage (2.5N NaOH, over 150°C) than does phenyl β-D-glucopyranoside. In 1956, Lindberg (32) proposed that it should also degrade via the McCloskey-Coleman mechanism, and Nault (33) has shown that levoglucosan is formed at 27% of the theoretical yield during the alkaline degradation of methyl β-D-glucopyranoside. However, Table IV shows that alkyl glycosides in which the McCloskey-Coleman mechanism is blocked (by methylation or by stereochemistry) do not exhibit the large decrease in reaction rate that is expected (34). Therefore a second reaction mechanism of only slightly higher free energy must exist.

TABLE IV

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF METHYL GLYCOSIDES IN 2.5N SODIUM HYDROXIDE AT 170°C[a]

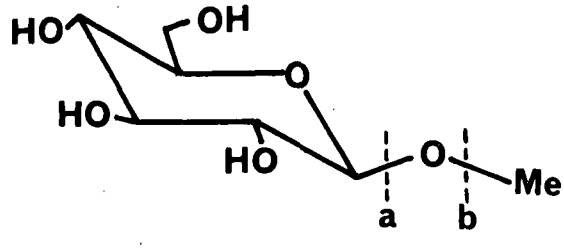
Methyl Glycoside	C1 - C2 Configuration	$10^3 k_r$ hr^{-1}
β-D-glucoside	trans	2.5
2-O-methyl-β-D-glucoside	trans	1.2
α-D-glucoside	cis	1.0
2-O-methyl-α-D-glucoside	cis	0.8

[a]Data from Ref. (34).

The 27% yield of levoglucosan seems to establish the minimum percentage of the alkaline degradation of methyl β-D-glucopyranoside that goes through the McCloskey-Coleman mechanism, but the total importance of the $S_N1cB(2)$ reaction is unknown, since the 1,2-anhydride intermediate (IX) can disappear by either of two pathways (see Fig. 2). It can undergo an $S_N1cB(6)$ reaction to give levoglucosan (X), or the epoxide can be opened through an S_N2 attack by hydroxide ion to give D-glucose (XI) (which degrades rapidly to various acids). The relative importance of these two reactions has not been established (33).

The other mechanism(s) by which methyl β-D-glucopyranoside degrades has not been positively identified (33). One possibility is an S_N2 reaction similar to that found for methyl α-D-glucopyranoside and methyl 2-O-methyl-β-D-glucopyranoside (Fig. 3) (25,33). Another possible mechanism for the degradation of these compounds is an S_N1 heterolysis of the bond (Fig. 4). This could theoretically result in the formation of levoglucosan (X), but the quantity generated should be quite small (35).

The glycosidic linkage consists of two carbon-oxygen bonds, the glycosyl-oxygen bond (bond a, below) and the oxygen-aglycone bond (bond b, below). While the McCloskey-Coleman mechanism must result in glycosyl-oxygen bond cleavage, the S_N1 and S_N2 mechanisms could cause cleavage at either bond. Alkaline degradation of methyl β-D-glucopyranoside in oxygen-18 enriched water has shown that the oxygen-aglycone bond is cleaved 5% of the time (33). When the McCloskey-Coleman mechanism is blocked, the rate of the overall reaction decreases by a factor of two (Table IV), but the rate of oxygen-aglycone bond cleavage might be expected to remain constant. Thus methyl 2-O-methyl-β-Dglucopyranoside shows 11% oxygen-aglycone bond cleavage. However, methyl α-D-glucopyranoside undergoes oxygen-aglycone bond cleavage more slowly than expected, cleaving only 5% of the time (33,36).



Methyl β-D-Glucopyranoside

1,5-Anhydro-4-O-(β-D-glucopyranosyl)-D-glucitol (1,5-anhydrocellobiitol) (below) has been proposed to be a better cellulose model than methyl β-D-glucopyranoside because the aglycone more nearly resembles that found in cellulose (37). Cleavage of the glycosyl-oxygen bond (bond a), by any mechanism, releases the agly-

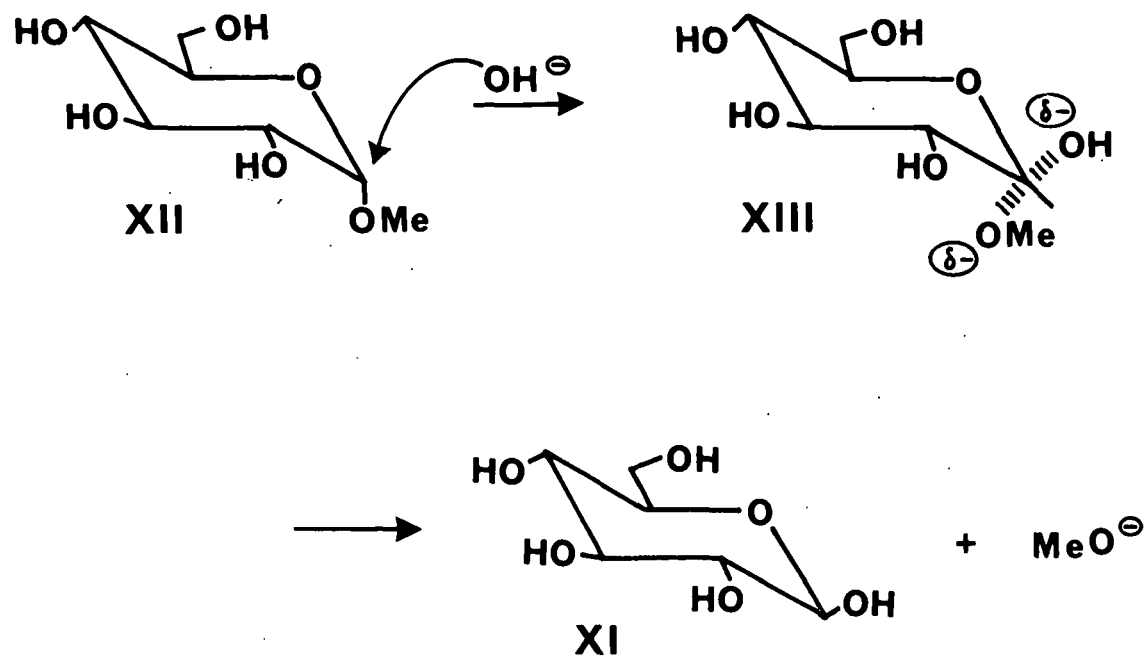


Figure 3. S_N2 cleavage proposed for the glycosyl-oxygen bond of methyl α-D-glucopyranoside (25).

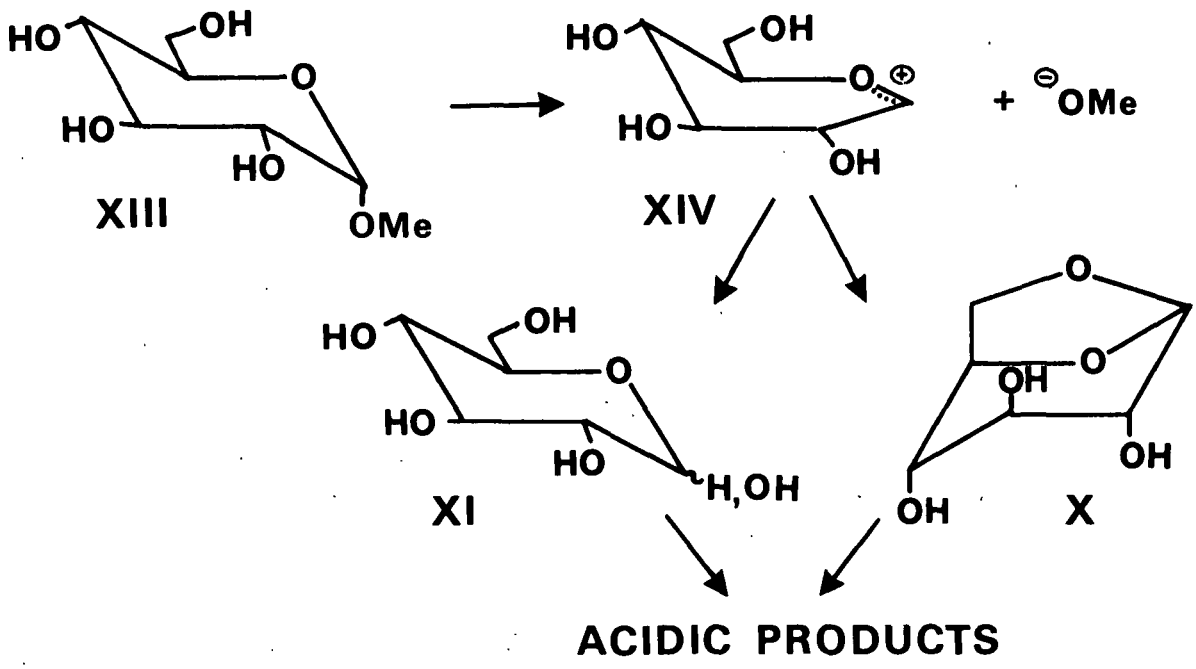
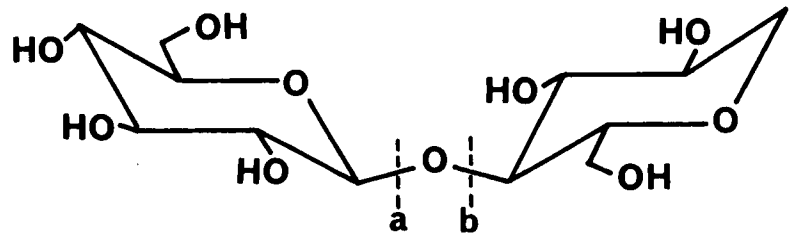


Figure 4. Potential S_N1 cleavage of the glycosyl-oxygen bond of methyl α-D-glucopyranoside (25).

cone as 1,5-anhydro-D-glucitol (XVI) (Fig. 5-7). By following the formation of this product Brandon, et al. (37) were able to show that the glycosyl-oxygen bond is cleaved 90% of the time (2.5N NaOH, 170°C). Cleavage occurs by a mixed mechanism and results in a 35% yield of levoglucosan. Therefore the McCloskey-Coleman mechanism is thought to be operative (Fig. 5) (37).



1,5-Anhydrocellobiitol

The importance of the McCloskey-Coleman mechanism was tested by studying the degradation of 1,5-anhydromaltitol. This α-linked analogue of 1,5-anhydrocellobiitol was found to degrade 5.8 times more slowly than 1,5-anhydrocellobiitol, and produced no levoglucosan (37). As was the case with methyl α-D-glucopyranoside, cleavage of the oxygen-aglycone bond occurred more slowly than expected, cleaving only 10% of the time. While this compound was studied only briefly, an S_N1 mechanism was suggested for its degradation based on the effect of ionic strength on the rate of reaction (37).

Brandon, et al. (37) proposed that the second mechanism responsible for glycosyl-oxygen bond cleavage in 1,5-anhydrocellobiitol is an S_N1 reaction (Fig. 6). Unfortunately, rejection of the S_N2 mechanism (Fig. 7) was based primarily on the results of a faulty experiment. The rate of an S_N2 reaction should increase with the strength of the attacking nucleophile. Iodide ion, which is a stronger nucleophile than hydroxide ion at 25°C (23), failed to increase the rate of degradation of 1,5-anhydrocellobiitol (37). However, Gilbert (25) added iodide ion to an

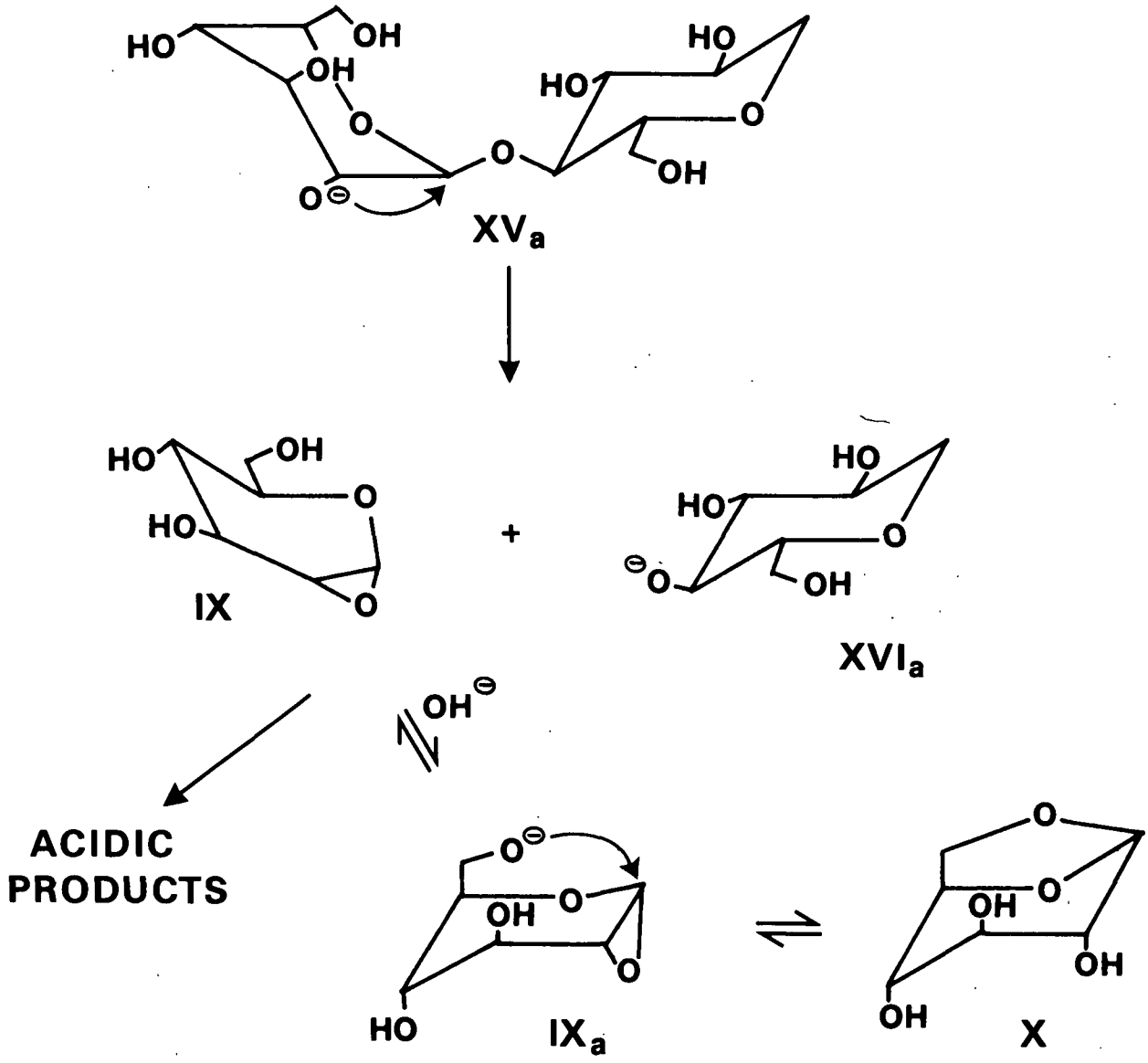


Figure 5. $S_N1cB(2)$ cleavage proposed for the glycosyl-oxygen bond of 1,5-anhydrocellobiitol (37).

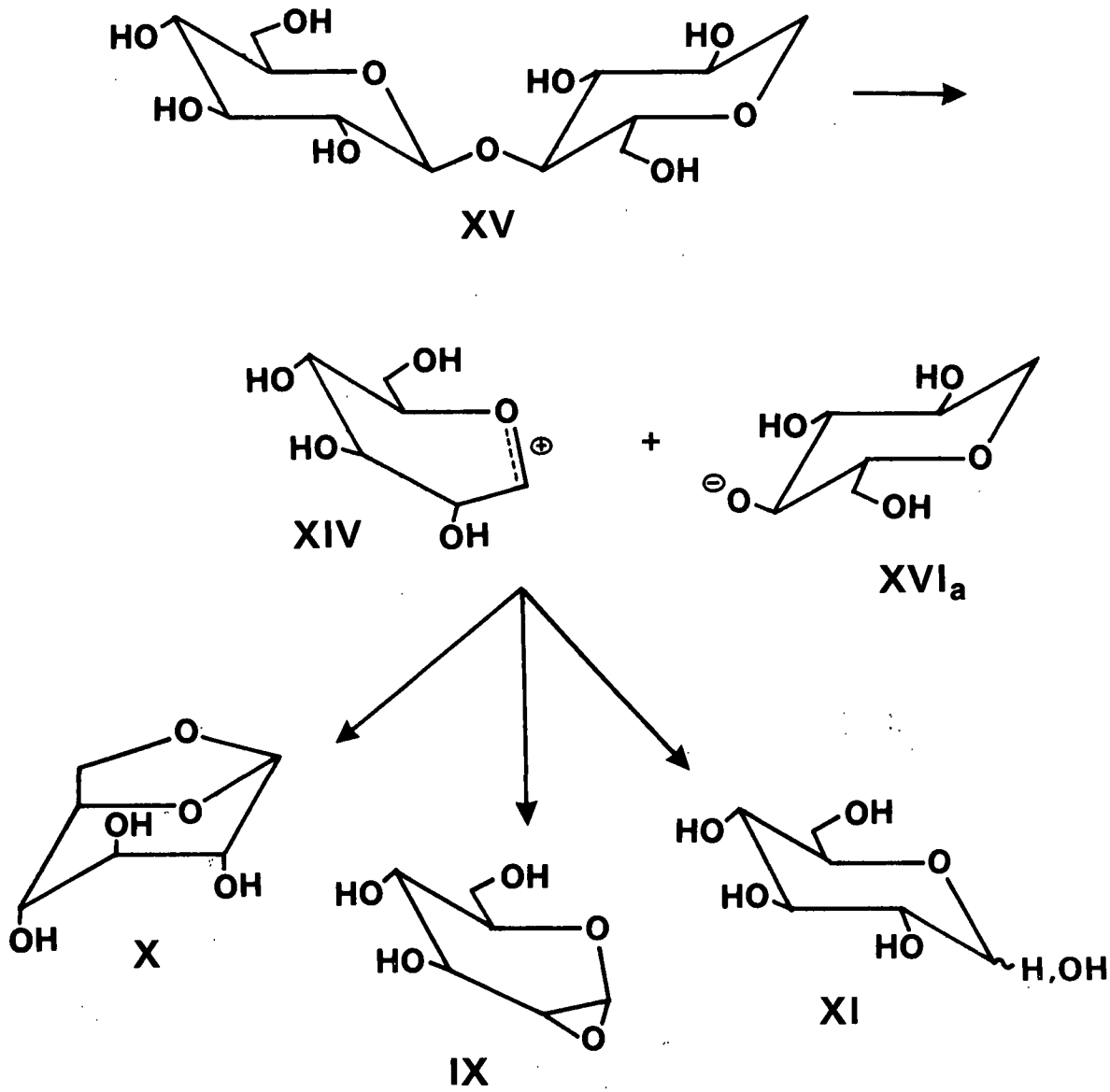


Figure 6. S_N1 cleavage proposed for the glycosyl-oxygen bond of 1,5-anhydrocellobiitol (37).

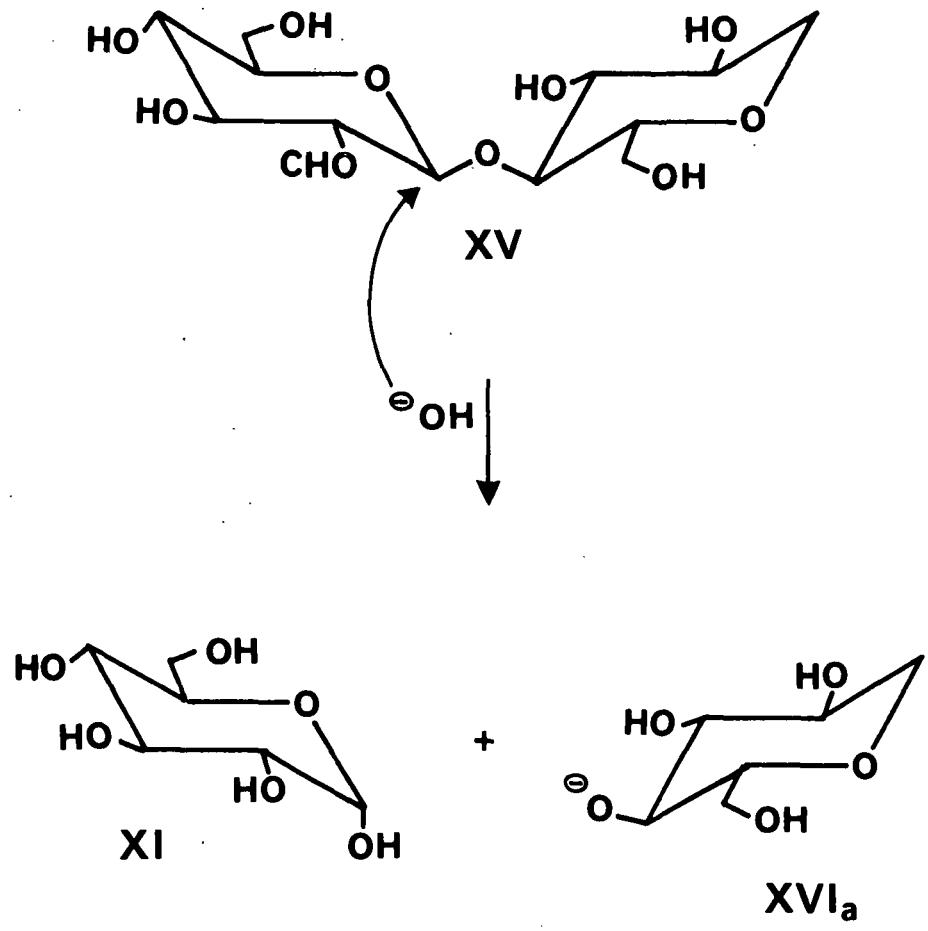
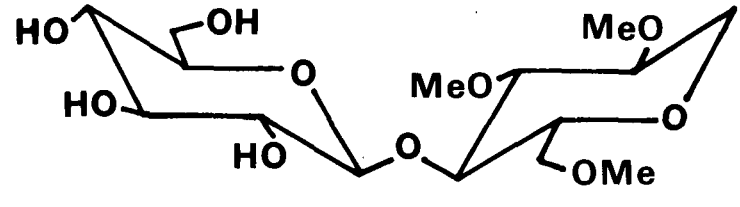


Figure 7. Potential S_N2 cleavage of the glycosyl-oxygen bond of 1,5-anhydrocellobiitol (37).

alkaline degradation of methyl α-D-glucopyranoside (known to degrade by an S_N2 mechanism), and found that it is an extremely weak nucleophile, relative to hydroxide ion, at 170°C.

Brandon, et al. (37) were able to show, based on product analysis, that cleavage of the oxygen-aglycone bond of 1,5-anhydrocellobiitol proceeds through an S_N1 mechanism (Fig. 8). Heterolysis of this bond results in the formation of a 1,5-anhydro-4-deoxy-D-xylo-hexitol-4-cation (XVII) from the aglycone. Direct addition of hydroxide ion to this cation would give 1,5-anhydro-D-glucitol (XVI) and 1,5-anhydro-D-galactitol (XVIII) (Fig. 8). However, only traces of 1,5-anhydro-D-galactitol were found. Therefore it was concluded that hydroxide ion does not add to the cation, validating the assumption that all of the 1,5-anhydro-D-glucitol (XVI) observed must result from glycosyl-oxygen bond cleavage. The dianhydride (XXII) was isolated from the reaction solution, and a pathway was proposed by which this product could be formed from the 4-cation (Fig. 8) (37).

An S_N2 cleavage of the oxygen-aglycone bond (Fig. 9) was rejected since 1,5-anhydro-D-galactitol (XVIII) would be a necessary product of the reaction. Cleavage by an intramolecular conjugate base mechanism was ruled out by methylating the three hydroxyl groups on the aglycone. Oxygen-aglycone bond cleavage in 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol (below) occurred at about the same rate as in 1,5-anhydrocellobiitol (37,38).



1,5-Anhydro-2,3,6-tri-O-methyl-cellobiitol

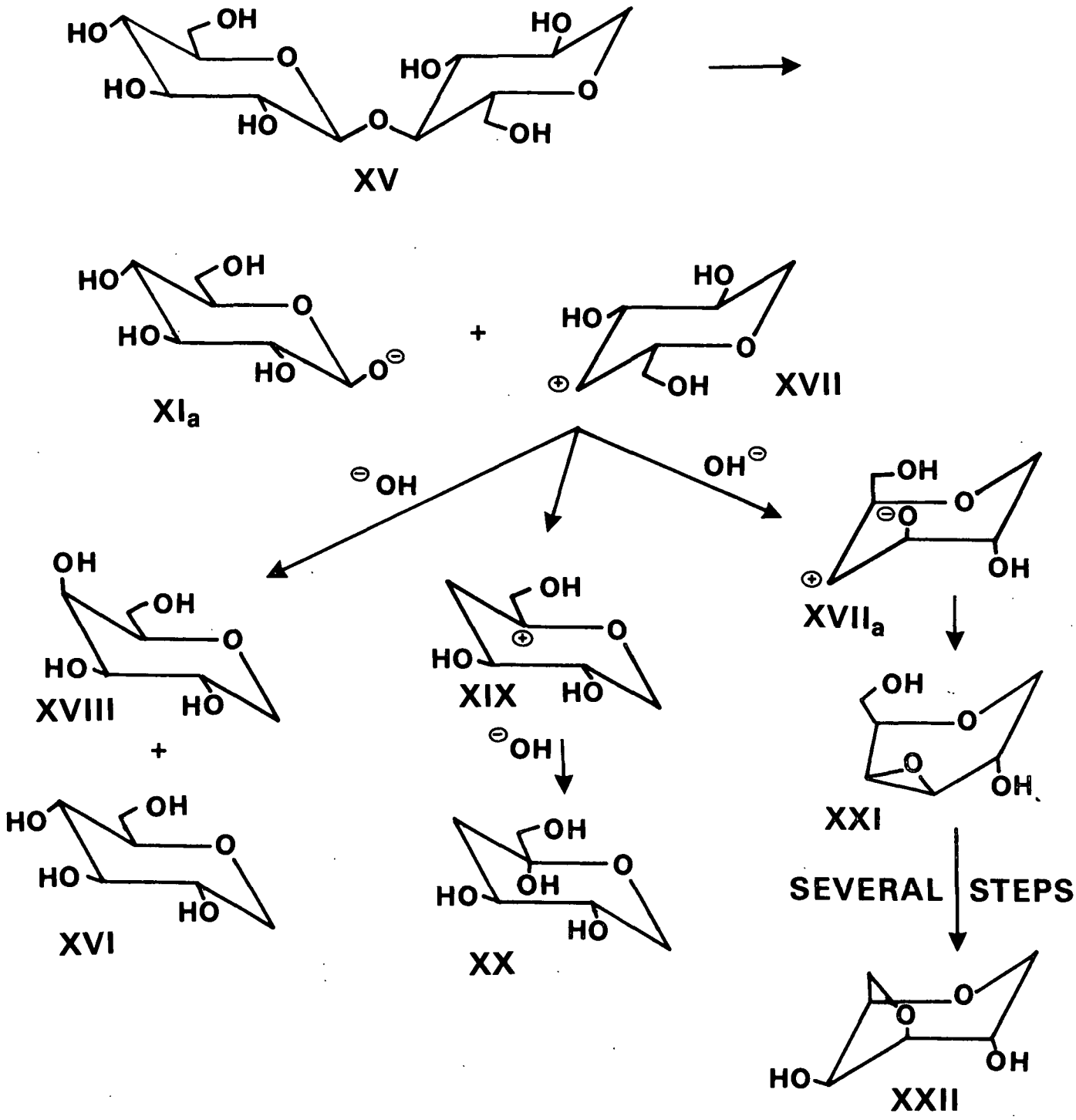


Figure 8. S_N1 cleavage proposed for the oxygen-aglycone bond of 1,5-anhydrocellobiitol (37).

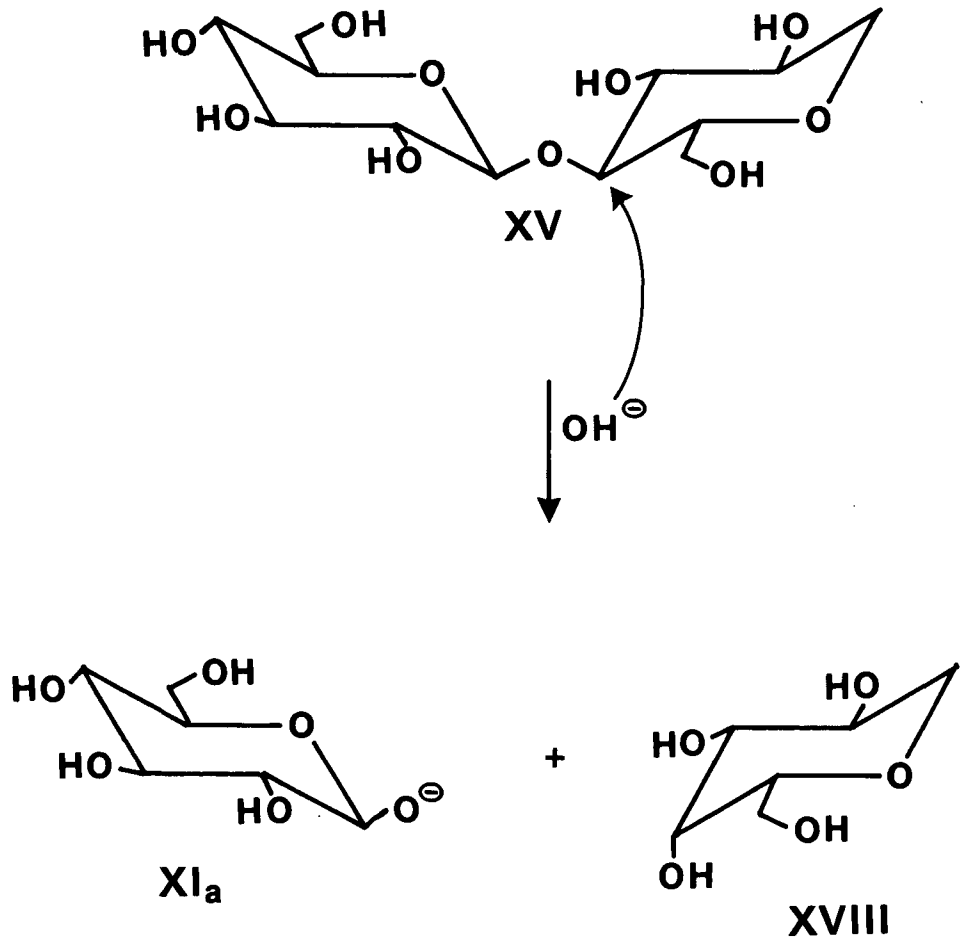


Figure 9. Potential S_N2 cleavage of the oxygen-aglycone bond of 1,5-anhydrocellobiitol (37).

However, the alkaline degradation of 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol did provide a surprise. The overall rate of degradation was 10-40% faster than that of 1,5-anhydrocellobiitol, and produced a 55-75% yield of levoglucosan (37,38). Blocking the McCloskey-Coleman mechanism by methylation of the C-2' hydroxyl group resulted in a decrease in the overall reaction rate by a factor of 12, while the rate of oxygen-aglycone cleavage was unaffected (38). It appears that 1,5-anhydro-2,3,6-tri-O-methyl-cellobiitol degrades primarily via the McCloskey-Coleman mechanism.

In summary, it is apparent that alkaline cleavage of the glycosidic linkage is not thoroughly understood. For most glycosides there are a number of nucleophilic substitution reactions of similar free energy functioning, including S_N1, S_N2, and $S_N1cB(i)$ mechanisms. Furthermore, Nault (33) has recently shown that the addition of a strong nucleophile (such as thiophenoxide or thiosulfate) can result in new S_N2 reactions which must also be considered.

THESIS OBJECTIVES

Random chain cleavage results in a significant decrease in the degree of polymerization of cellulose during alkaline pulping. An understanding of the reaction mechanisms involved may come from studies on the high temperature alkaline degradation of simpler glycosides. Previous studies have shown that simple glycosides may be subject to S_N2 reactions, especially in the presence of a strong nucleophile.

Kraft pulping utilizes aqueous alkaline solutions of sodium sulfide. While the state of hydrolysis of the sodium sulfide is uncertain under pulping conditions, both the sulfide dianion and its hydrolysis product, the hydrosulfide anion, are expected to be good nucleophiles. The presence of a strong sulfur nucleophile during kraft pulping may promote S_N2 reactions, thereby altering the rate-determining and/or the product-determining steps of glycosidic bond cleavage.

The objective of this thesis was to determine whether sodium sulfide affects the alkaline degradation of a nonreducing cellulose model compound. 1,5-Anhydrocellobiitol was chosen as the cellulose model because it resembles cellulose closely, does not suffer from competing reactions (such as peeling), and offers relatively easy product analysis.

RESULTS AND DISCUSSION

1,5-Anhydrocellobiitol was degraded under conditions similar to those used for the commercial pulping of wood. Pseudo-first-order rate constants were determined for the disappearance of reactant and for the appearance of neutral products. The first part of this section of the thesis describes the methods used to obtain these rate constants.

In the second part of this section, rate constants for the kraft degradation of 1,5-anhydrocellobiitol are compared to the appropriate controls. It was found that the sodium sulfide is hydrolyzed to sodium hydrosulfide and sodium hydroxide. Furthermore, the hydrosulfide ion did not increase the rate of glycosidic bond cleavage. These results could be explained in two ways. Either the hydrosulfide ion is a weak nucleophile, or it is hindered from participating in an S_N2 attack on 1,5-anhydrocellobiitol.

To resolve this uncertainty, kraft degradations of methyl α-D-glucopyranoside (which is known to degrade by an S_N2 mechanism) were performed. They showed that the hydrosulfide ion is a stronger nucleophile than hydroxide ion. While the data supporting this conclusion are given in the third part of this section, the result must be presented earlier to permit a complete analysis of the disaccharide work.

Finally, in the fourth part of this section, the results of several degradations of 1,6-anhydro-β-D-glucopyranose are given. These experiments were required, as explained below, in order to calculate the rate of formation of 1,6-anhydro-β-D-glucopyranose during degradations of 1,5-anhydrocellobiitol.

KINETIC STUDIES

DISAPPEARANCE OF REACTANT

The general rate expression for the disappearance of the reactant during a kraft cook is given by:

$$d\underline{R}/dt = -k\, f[\underline{R}]^a\, f[\underline{OH^-}]\, f[\underline{SH^-}] \qquad (4)$$

where $\underline{R}$ = reactant activity, mol L^{-1}

t = time, sec

k = specific rate constant, sec^{-1}

$f[\underline{R}]$ = unknown function of reactant activity, mol L^{-1}

$f[\underline{OH^-}]$ = unknown function of hydroxide ion activity, mol L^{-1}

$f[\underline{SH^-}]$ = unknown function of hydrosulfide ion activity, mol L^{-1}

a = constant

Assuming that the activity coefficient of $\underline{R}$ is constant and unity, permits the use of reactant concentration as an estimate of activity. Equation (4) can be further simplified by assuming that the reaction is first order with respect to the reactant, i.e., $a = 1.0$.

The activities of the hydroxide and hydrosulfide ions will be constant if their activity coefficients and concentrations are constant. The activity coefficients depend on temperature, pressure, and ionic strength, all of which were held constant. Furthermore, the concentrations of sodium hydroxide and sodium sulfide were sufficiently large that they, too, remained essentially constant throughout the reaction.

These assumptions lead to the pseudo-first-order rate expression (39):

$$dR/dt = -k_r R \qquad (5)$$

where R = reactant concentration, mol L^{-1}

k_r = pseudo-first-order rate constant for the disappearance of reactant, sec^{-1}

Integration and rearrangement gives:

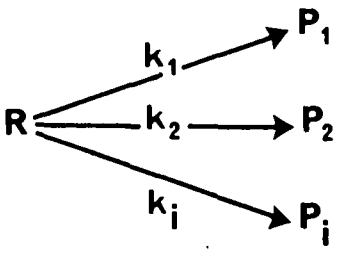
$$\ln R = -k_r t + \ln R_o \qquad (6)$$

where R_o = initial reactant concentration, mol L^{-1}

Pseudo-first-order rate constants for the disappearance of reactant were generated from Eq. (6) using a least squares regression technique (Computer Program 1, Appendix I). The validity of the use of pseudo-first-order kinetics was shown in two ways (39). First, the data plotted according to Eq. (6) was linear over two half-lives of the reaction (Fig. 10). Second, duplicate reactions with different initial reactant concentrations (0.01 and 0.02M) generated the same pseudo-first-order rate constants.

FORMATION OF STABLE PRODUCTS

When a reactant can undergo two or more reactions independently, the reactions are called parallel reactions. Frost and Pearson (39) have mathematically described parallel kinetics for the case where each reaction pathway leads to a unique product.



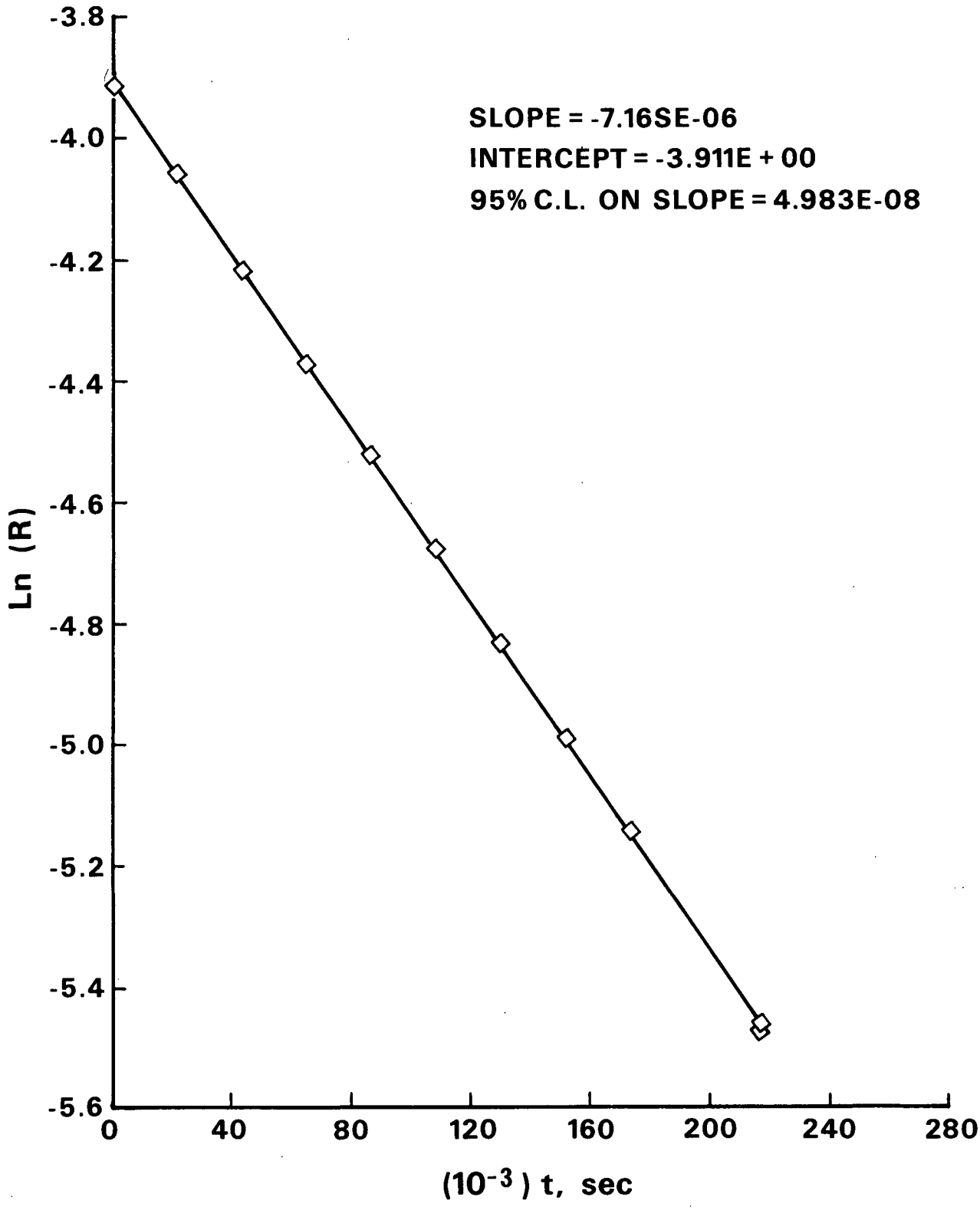


Figure 10. Disappearance of 1,5-anhydrocellobiitol under kraft conditions at 170°C.

The general rate expression is given by:

$$dP_i/dt = k_i\, f[R]^a\, f[OH^-]\, f[SH^-] \tag{7}$$

where P_i = activity of product i, mol L^{-1}

k_i = specific rate constant, sec^{-1}

The pseudo-first-order assumptions reduce this to:

$$dP_i/dt = k_i R \tag{8}$$

where P_i = concentration of product i, mol L^{-1}

k_i = pseudo-first-order rate constant for the appearance of product i, sec^{-1}

Equation (6) can be expressed in the exponential form as:

$$R = R_o \exp(-k_r t) \tag{9}$$

Substitution for R in Eq. (8) yields:

$$dP_i/dt = k_i R_o \exp(-k_r t) \tag{10}$$

Integration produces:

$$P_i = -(k_i R_o/k_r)\, \exp(-k_r t) + C \tag{11}$$

The constant of integration, C, can be evaluated by setting $P_i = P_{i,o}$ at $t = 0$ in Eq. (11):

$$C = P_{i,o} + (k_i R_o/k_r)\, \exp(-k_r t) \tag{12}$$

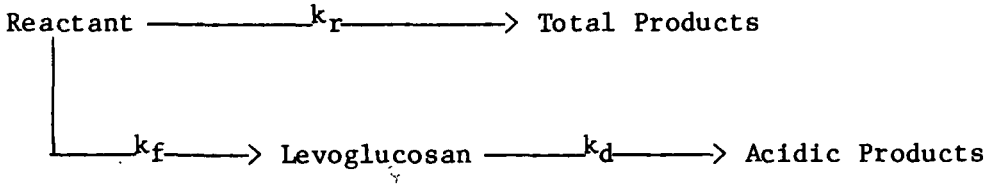
Substituting Eq. (12) into Eq. (11) gives the parallel pseudo-first-order rate expression (39):

$$(P_i - P_{i,o}) = k_i(R_o/k_r)\ [1 - \exp(-k_r t)] \qquad (13)$$

Pseudo-first-order rate constants for the formation of stable products were given by a least squares regression analysis (Program 2, Appendix I) on the data plotted according to Eq. (13). The initial product concentration, $P_{i,o}$, may be non-zero since the first sample (t = 0) was taken a short time after the reactor system had reached the desired temperature. Typical data for the appearance of 1,5-anhydro-D-glucitol and 1,5:3,6-dianhydro-D-galactitol during a kraft degradation of 1,5-anhydrocellobiitol are shown in Fig. 11. The formation of methanol and methyl mercaptan during a kraft degradation of methyl α-D-glucopyranoside are displayed in Fig. 12.

FORMATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE

1,6-Anhydro-β-D-glucopyranose (levoglucosan) is a labile product of the degradation of 1,5-anhydrocellobiitol. A mathematical method for determining the pseudo-first-order rate constant for the formation of levoglucosan was reported by Brandon, et al. (37). The reaction sequence is envisioned as:



Thus, the change in levoglucosan concentration as a function of time can be written:

$$dL/dt = k_f R - k_d L \qquad (14)$$

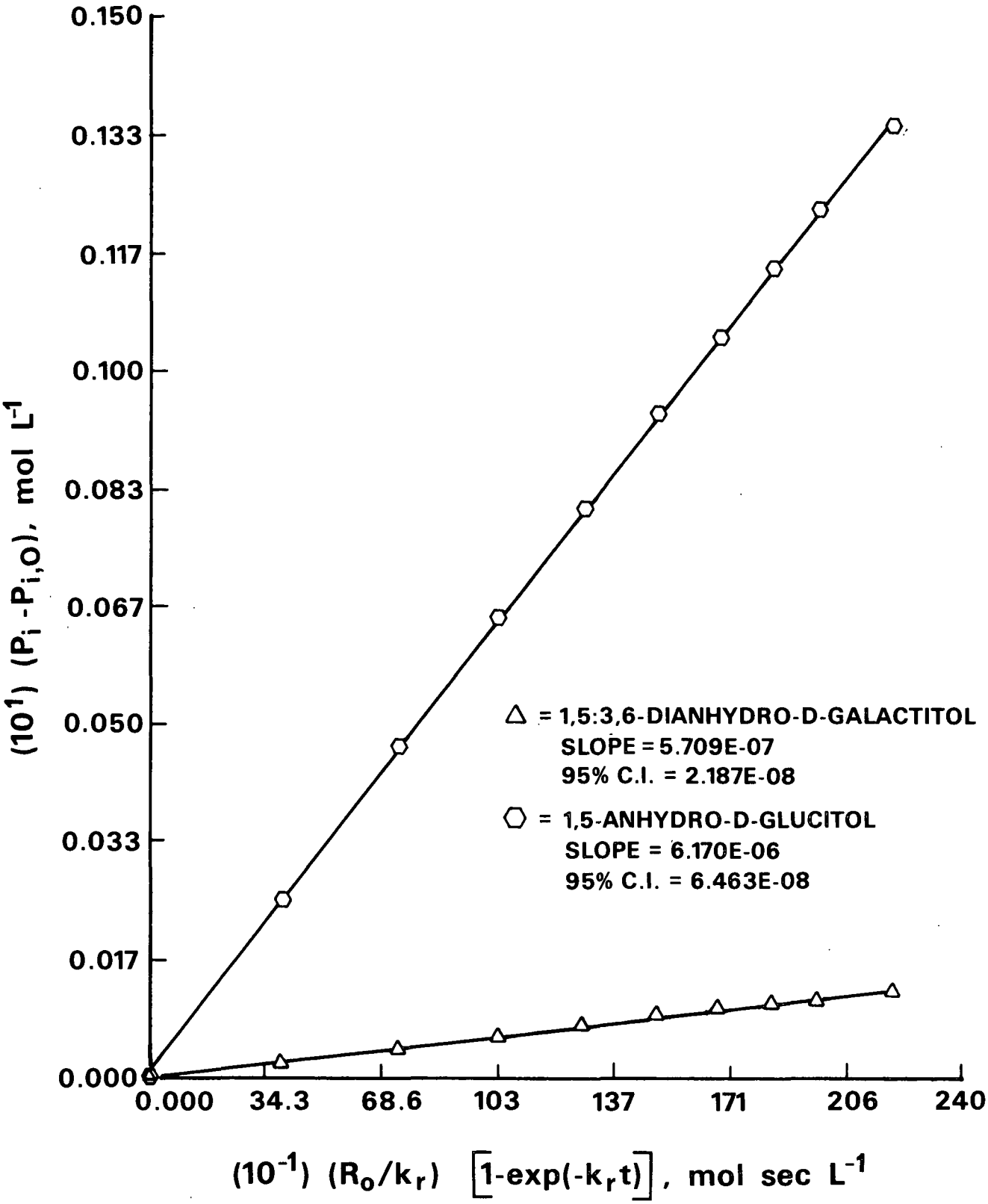


Figure 11. Formation of stable products during the kraft degradation of 1,5-anhydrocellobiitol at 170°C.

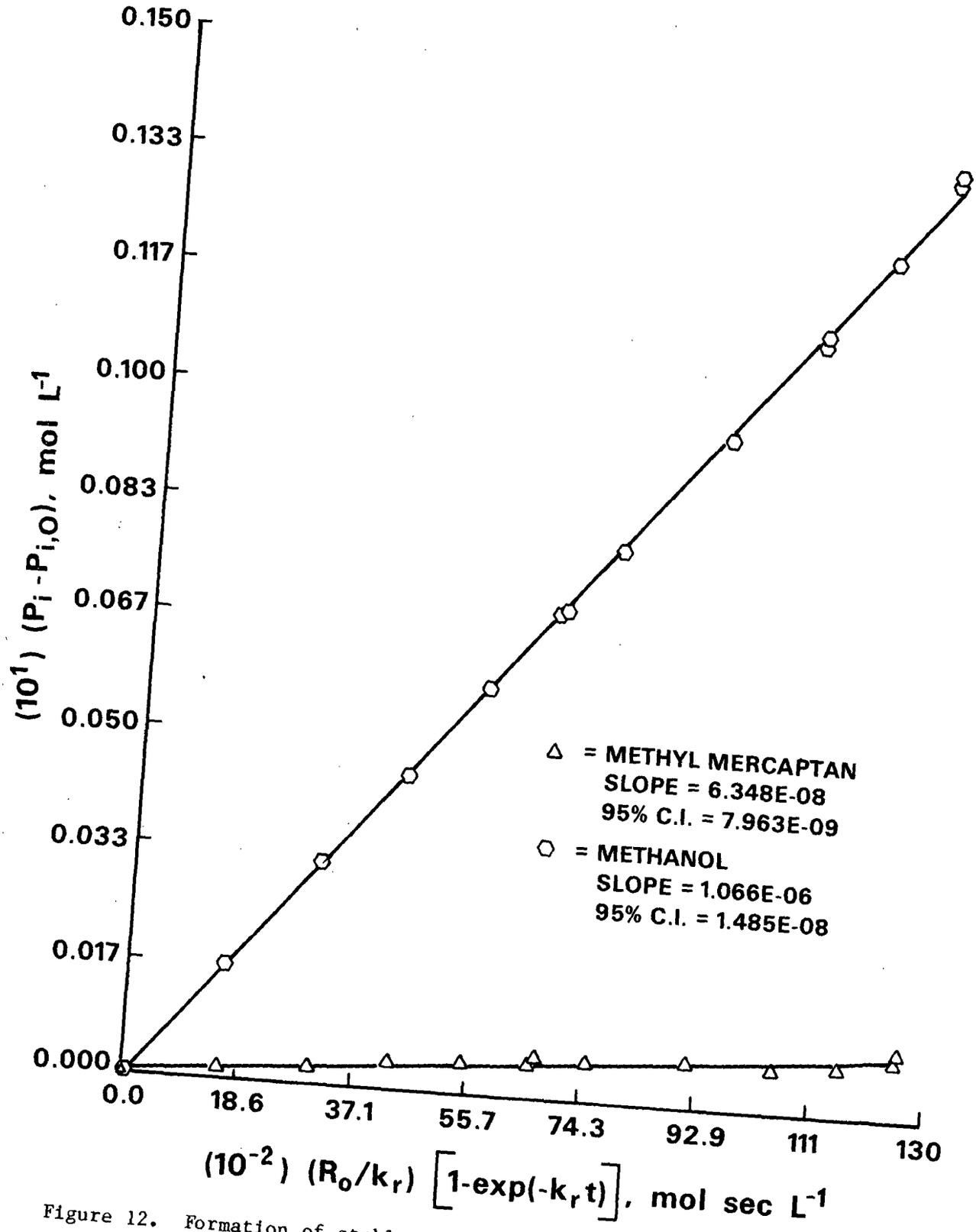


Figure 12. Formation of stable products during the kraft degradation of methyl α-D-glucopyranoside at 180°C.

where L = levoglucosan concentration, mol L^{-1}

k_f = pseudo-first-order rate constant for the formation of levoglucosan, sec^{-1}

k_d = pseudo-first-order rate constant for the degradation of levoglucosan, sec^{-1}

The quantity R was defined by Eq. (9), and substitution into Eq. (14) gives:

$$dL/dt = k_f R_o \exp(-k_r t) - k_d L \tag{15}$$

Rearrangement produces:

$$k_d L dt - k_f R_o \exp(-k_r t) dt + dL = 0 \tag{16}$$

This is a linear first order differential equation, and can be solved through the use of an integrating factor. Let

$$V(x) = \exp \int k_d dt \tag{17}$$

$$V(x) = \exp (k_d t) \tag{18}$$

Multiplying Eq. (16) by V(x) gives:

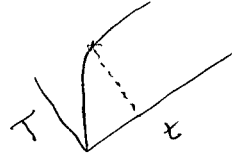
$$k_d L \exp(k_d t) dt - k_f R_o \exp(k_d - k_r) t \, dt + dL \exp(k_d t) = 0 \tag{19}$$

Integrating with respect to t:

$$L \exp(k_d t) - [k_f R_o/(k_d - k_r)] \exp(k_d - k_r) t = C \tag{20}$$

Letting $L = L_o$ at $t = 0$:

$$L_o - k_f R_o/(k_d - k_r) = C \tag{21}$$



Substitution of Eq. (21) into Eq. (20), followed by rearrangement gives the rate expression (37):

$$L - L_o \exp(-k_d t) = k_f[R_o/(k_d-k_r)]\,[\exp(-k_r t) - \exp(-k_d t)] \qquad (22)$$

Pseudo-first-order rate constants for the formation of levoglucosan were generated using Eq. (22) and a least squares regression technique (Program 3, Appendix I). To solve this equation, it was necessary to know k_d, the pseudo-first-order rate constant for the degradation of levoglucosan. Thus, k_d was determined according to Eq. (6) for each set of reaction conditions under which k_f was to be measured. Figure 13 presents a typical determination of k_f from the data plotted according to Eq. (22).

APPARENT THERMODYNAMIC FUNCTIONS OF ACTIVATION

The transition state theory of chemical kinetics leads to Eq. (23) relating the observed reaction rate to the entropy and enthalpy of activation (39).

$$k_r = (\mathbf{k}\ T/h) \exp(\Delta S^{\ddagger}/\mathbf{R}) \exp(-\Delta H^{\ddagger}/\mathbf{R}T) \qquad (23)$$

where $\mathbf{k}$ = Boltzmann's constant, 1.380×10^{-6} erg $°K^{-1}$

T = absolute temperature, °K

h = Planck's constant, 6.625×10^{-27} erg sec

$\Delta S^{\ddagger}$ = entropy of activation, cal mol^{-1}

$\mathbf{R}$ = Universal gas constant, 1.987 cal mol^{-1} $°K^{-1}$

$\Delta H^{\ddagger}$ = enthalpy of activation, cal mol^{-1}

Equation (23) can be rearranged to:

$$\ln(k_r/T) = \ln(\mathbf{k}/h) + \Delta S^{\ddagger}/\mathbf{R} - \Delta H^{\ddagger}/\mathbf{R}T \qquad (24)$$

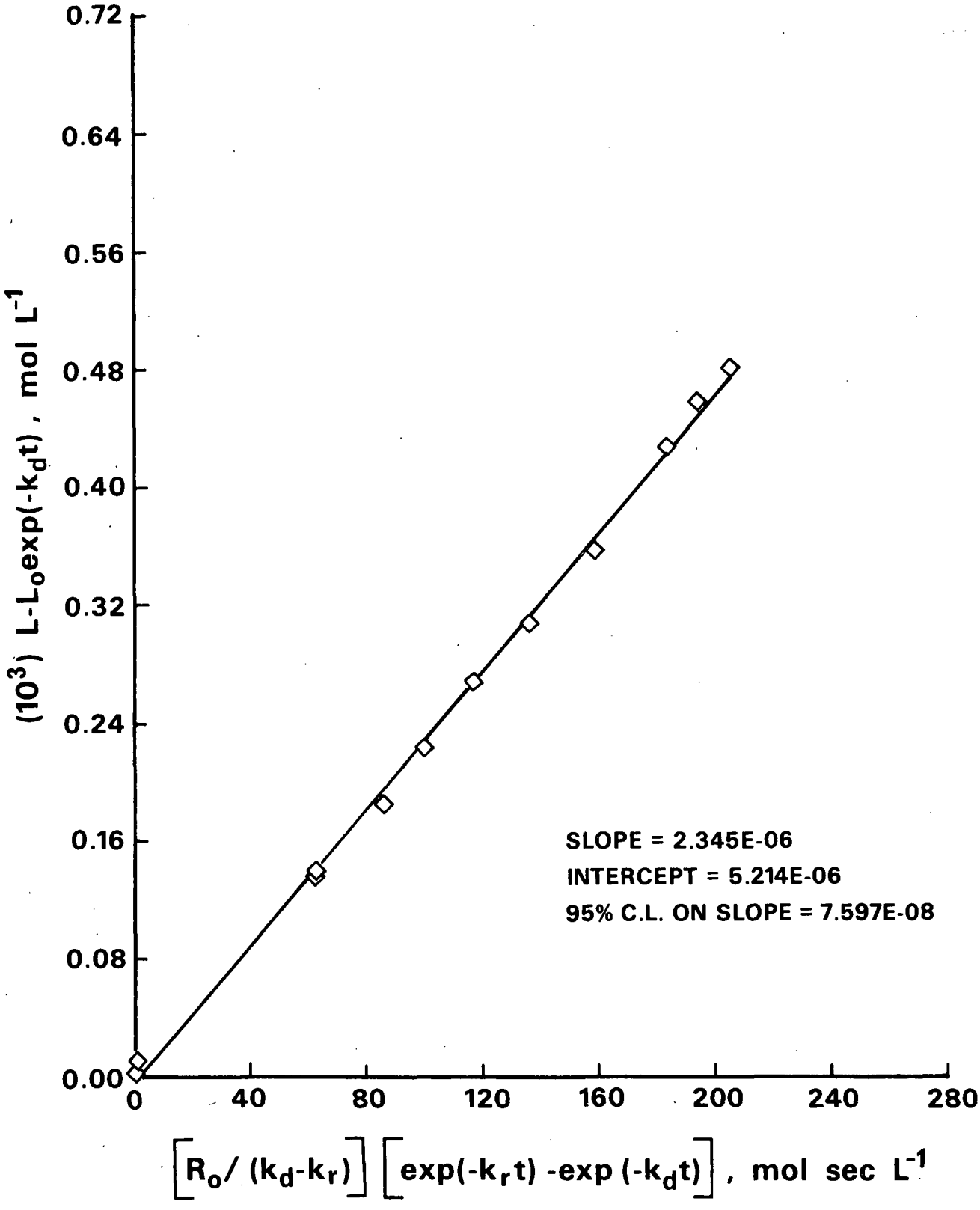


Figure 13. Formation of 1,6-anhydro-β-D-glucopyranose during the kraft degradation of 1,5-anhydrocellobiitol at 170°C.

The kinetic data were plotted according to Eq. (24) (Fig. 14), and analyzed using a least squares regression technique (Program 4, Appendix I). The enthalpy and entropy of activation were calculated from the slope and intercept, respectively, of the regression line. The Arrhenius activation energy, E_a, was calculated from Eq. (25) (39).

$$E_a = \Delta H^{\ddagger} + RT \tag{25}$$

It is often necessary to compare the rate constants of two reactions that were performed at slightly different temperatures. In this case the rate of one, or both, was adjusted to a common temperature using Eq. (26).

$$k_{T2} = \exp\ [\ln k_{T1} - (E_a/R)(1/T2 - 1/T1)] \tag{26}$$

where k_{T2} = pseudo-first-order rate constant at the common temperature, sec^{-1}

k_{T1} = pseudo-first-order rate constant at the reaction temperature, sec^{-1}

E_a = Arrhenius activation energy, cal mol^{-1}

T1 = absolute reaction temperature, °K

T2 = absolute common temperature, °K

This form of the Arrhenius Equation was incorporated into a computer program (Program 5, Appendix I). These rate-temperature adjustments rarely exceeded 1°C and are noted in the tables where they were applied.

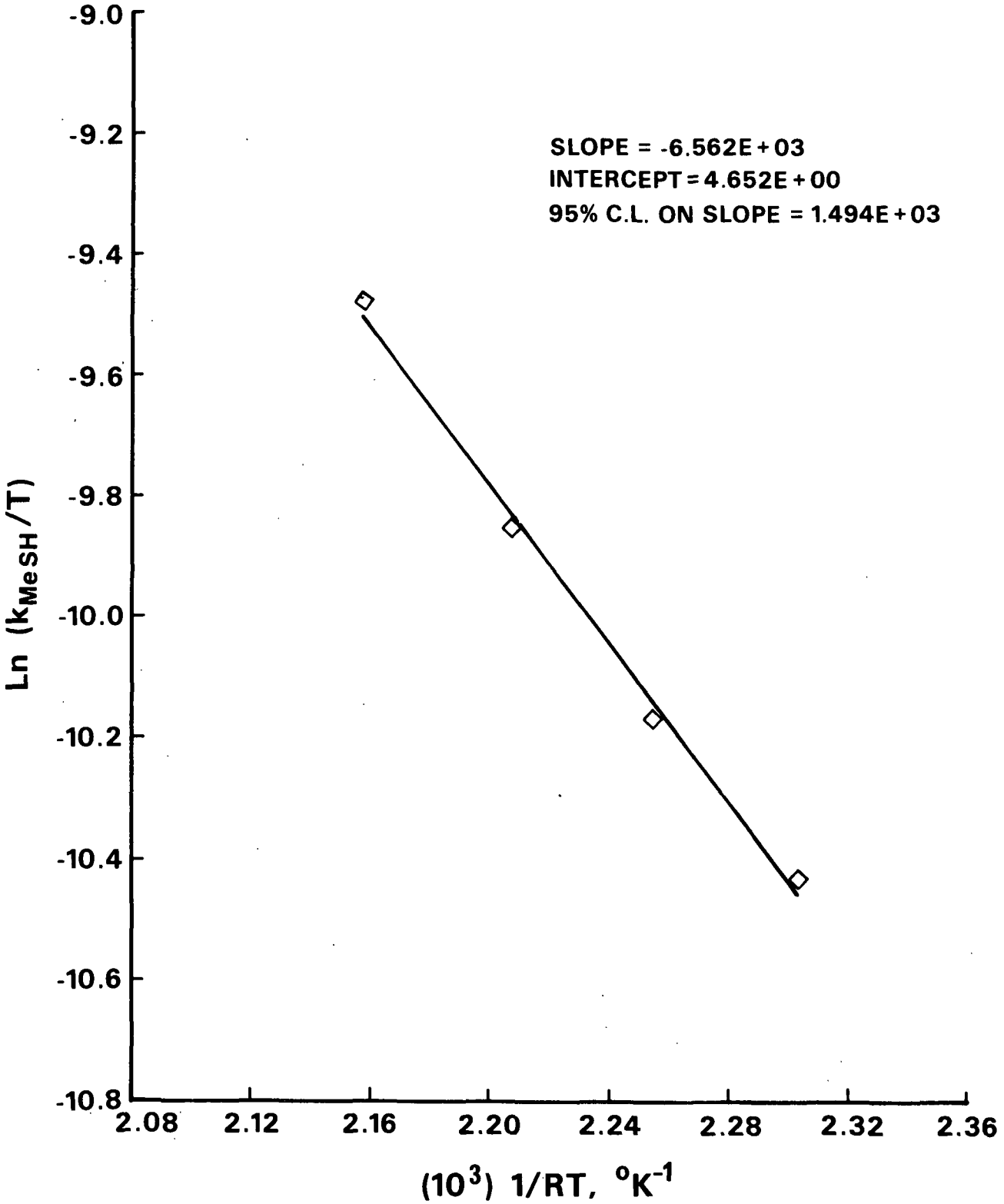


Figure 14. Temperature dependence of the rate constant for the formation of methyl mercaptan during the kraft degradation of methyl α-D-glucopyranoside.

KRAFT DEGRADATION OF 1,5-ANHYDROCELLOBIITOL

Oxygen-free kraft degradations of 1,5-anhydrocellobiitol were carried out at 170°C in a solution containing 1.0M NaOH and 0.2M Na_2S. Because the rate of degradation of 1,5-anhydrocellobiitol depends on the hydroxide ion concentration (37), and the state of hydrolysis of sodium sulfide was uncertain, two control reactions were required. One contained 1.0M NaOH, with the ionic strength adjusted to a μ of 1.6 by the addition of sodium p-toluenesulfonate. The ionic strength is important, since it also affects the rate of reaction (through the activity coefficients and the "salt effect") (37). This soda degradation modeled the kraft system if the sulfide was not hydrolyzed. The other control contained 1.2M NaOH at a μ of 1.4, and corresponded to complete hydrolysis of the 0.2M sodium sulfide in the kraft reaction to 0.2M sodium hydrosulfide and 0.2M sodium hydroxide.

The rate of disappearance of 1,5-anhydrocellobiitol under kraft conditions was identical to that found for the control representing total hydrolysis of the sulfide (Table V). In addition, 1,5-anhydro-D-glucitol was formed to the extent of ca. 88% of the theoretical yield in both the kraft and soda cooks (Table VI). Since this product results exclusively from glycosyl-oxygen bond cleavage (37), the rate of glycosyl-oxygen bond cleavage (and of oxygen-aglycone bond cleavage) must be the same in the kraft and 1.2M NaOH reactions. Therefore the same reaction mechanisms are thought to be operating at the same relative rates in both the kraft and soda systems. This leads to the conclusion that the sodium sulfide is hydrolyzed under pulping conditions (1.0M NaOH, 170°C), and the resulting hydrosulfide ion plays no role in the rate-determining steps of the reaction.

It should be noted that the data in Tables V and VI do not specifically exclude the possibility that the sodium sulfide is not hydrolyzed. However, if this were the case, the sulfide dianion would have to react with 1,5-anhydrocellobiitol at the

same rate as the hydroxide ion, and with the same reaction site specificity. This explanation of the data seems far less plausible than total hydrolysis of the sodium sulfide and an inability of the hydrosulfide ion to accelerate chain cleavage.

The failure of the hydrosulfide ion to participate in an S_N2 attack on 1,5-anhydrocellobiitol could indicate that the hydrosulfide ion is a weak nucleophile at 170°C. However, in a subsequent section of this thesis it will be shown that cleavage of the oxygen-aglycone bond of methyl α-D-glucopyranoside (which occurs by an S_N2 mechanism) proceeds 11 times more rapidly with hydrosulfide ion than with hydroxide ion. This shows that hydrosulfide ion is a stronger nucleophile than hydroxide ion at 170°C. Therefore, it is believed that the inability of hydrosulfide ion to cleave the glycosidic linkage of 1,5-anhydrocellobiitol is the result of either steric or electronic hindrance.

TABLE V

RATE CONSTANTS FOR THE DEGRADATION OF 1,5-ANHYDROCELLOBIITOL AT 170°C[a]

	Kraft 1.0M NaOH 0.2M Na_2S (1.4/1.6 μ)[b,d]	Soda 1.2M NaOH 0.2M NaOTs 1.4 μ[b]	Soda 1.0M NaOH 0.6M NaOTs 1.6 μ[c]
Disappearance of 1,5-anhydrocellobiitol (10^{-6} k_r sec^{-1})	6.80 ± 0.08	6.77 ± 0.07	6.16 ± 0.06
Formation of 1,5-anhydro-D-glucitol (10^{-6} k_{ag} sec^{-1})	5.95 ± 0.08	5.97 ± 0.07	5.40 ± 0.08
Formation of 1,6-anhydro-β-D-glucose (10^{-6} k_f sec^{-1})	2.24 ± 0.10	2.50 ± 0.11	2.38 ± 0.17
Formation of 1,5:3,6-dianhydro-D-galactitol (10^{-7} k_{dag} sec^{-1})	5.71 ± 0.26	6.91 ± 0.18	6.38 ± 0.29

[a]Pseudo-first-order rate constants adjusted to 170°C.
[b]Average of three reactions.
[c]Average of two reactions.
[d]Ionic strength of 1.4 if Na_2S is hydrolyzed, or 1.6 if it is not hydrolyzed.

TABLE VI

KINETIC ANALYSIS OF THE DEGRADATION OF 1,5-ANHYDROCELLOBIITOL AT 170°C[a]

	Kraft 1.0M NaOH 0.2M Na_2S (1.4/1.6 μ)[b,d]	Soda 1.2M NaOH 0.2M NaOTs 1.4 μ[b]	Soda 1.0M NaOH 0.6M NaOTs 1.6 μ[c]
Formation of 1,5-anhydro-D-glucitol (k_{ag}/k_r)	0.875	0.881	0.876
Formation of 1,6-anhydro-β-D-glucose (k_f/k_{ag})	0.376	0.419	0.441
Formation of 1,5:3,6-dianhydro-D-galactitol (k_{dag}/k_r)	0.084	0.102	0.104

[a]Ratios of pseudo-first-order rate constants.
[b]Average of three reactions.
[c]Average of two reactions.
[d]Ionic strength of 1.4 if Na_2S is hydrolyzed, or 1.6 if it is not hydrolyzed.

Cleavage of the glycosyl-oxygen bond is very likely due in part to an $S_N1cB(2)$ reaction (Fig. 5) (37). The product of the rate-determining step is 1,2-anhydro-α-D-glucopyranose (IX). This epoxide can follow two different reaction pathways in the product-determining step of the reaction. It could undergo nucleophilic attack by hydroxide or hydrosulfide ions to open the 1,2-epoxide (IX), generating reducing sugars which would rapidly degrade to acidic products. Alternatively, an $S_N1cB(6)$ reaction could generate 1,6-anhydro-β-D-glucopyranose (X). The yield of 1,6-anhydro-β-D-glucopyranose from the degradation of 1,5-anhydrocellobiitol was found to decrease as the concentration of hydroxide and hydrosulfide ions in the system increased (Table VI). This probably results from an increase in the rate of S_N2 attack by these two nucleophiles on the 1,2-epoxide in the product-determining step of the reaction.

Cleavage of the oxygen-aglycone bond of 1,5-anhydrocellobiitol occurs about 12% of the time, as the result of an S_N1 mechanism (37) (Fig. 8). A C-4 cation (XVII) is produced in the rate-determining step. While several product-determining reactions can be envisioned, the one leading to 1,5:3,6-dianhydro-D-galactitol (XXII) dominates. Thus, 98% of the aglycone is accounted for in the control reactions (Table VI).

In the kraft system the yield of 1,5:3,6-dianhydro-D-galactitol was lower than in the controls. This could be due to attack by the hydrosulfide ion on the epoxide intermediates (XXI) leading from the C-4 cation (XVII) to the 1,5:3,6-dianhydride (XXII), forming various thio-anhydro-alditols. Attack by hydrosulfide ion directly on the C-4 cation is also possible, although Brandon, et al. (37) did not observe an analogous attack on the cation by hydroxide ion. Such a reaction would generate the 1,5-anhydro-4-deoxy-4-thio-D-glucitol and -D-galactitol epimers, with the latter predominating due to shielding of the C-4 cation by the departing anion.

No evidence of the thio-anhydro-alditols could be found in the gas-liquid chromatograms from kraft degradations of 1,5-anhydrocellobiitol. It was not clear whether these sugars were failing to survive the reaction conditions, or if they were being lost during the sample workup procedure. Therefore, a thio-anhydro-alditol was synthesized to distinguish between these two possibilities. The synthesis of 1,5-anhydro-4-deoxy-4-thio-D-glucitol could not be effected (see Appendix II), but 1,5-anhydro-6-deoxy-6-thio-D-glucitol was successfully synthesized (see Experimental). This compound was shown to be stable in kraft liquor at 170°C over a period of time equal to four half-lives of 1,5-anhydrocellobiitol. However, it was retained on the mixed bed (H^+, OH^-) ion exchange resin normally used to deionize reaction samples in the analytical procedure.

To resolve this problem, samples from the kraft degradation of 1,5-anhydro-cellobiitol were prepared for GLC by passage through acidic (H^+) resin only prior to acetylation. This caused unidentified products of the reaction (probably organic acids) to appear in the gas-liquid chromatograms. These masked the region of the GLC trace where the thio compounds were expected to appear, complicating both flame-ionization and specific ion mass spectrometric detection. Elemental sulfur, resulting from the action of the acidic resin on the sodium sulfide, interfered with flame-photometric detection. Therefore, the anticipated formation of the thio-anhydro-alditol products could not be verified. This is not considered to be of critical importance, however, since it has been shown that the sulfur is introduced during the product-determining, and not the rate-determining, steps of the reaction.

KRAFT DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE

The failure of hydrosulfide ion to participate in an S_N2 cleavage of 1,5-anhydro-cellobiitol raised questions about its nucleophilicity. Hydrosulfide ion is a better nucleophile than hydroxide ion at room temperature (23). However, iodide ion is also a better nucleophile than hydroxide ion at 25°C (23), but much weaker than hydroxide at 170°C (25). This was shown by adding sodium iodide to a high temperature alkaline degradation of methyl α-D-glucopyranoside, which is known to degrade by an S_N2 mechanism. The addition of iodide ion resulted in an increase in the reaction rate that was only 20% of the rate increase caused by an equal amount of hydroxide ion.

The same approach was used in this work. Oxygen-free degradations of methyl α-D-glucopyranoside were performed at about 181°C. The control reaction contained 1.2M NaOH at a μ of 1.4. The kraft degradation (1.0M NaOH, 0.2M Na_2S) had the same hydroxide ion concentration as the control but also contained 0.2M hydrosulfide ion. A 1.4M NaOH reaction was used to measure the effect of adding 0.2M hydroxide ion.

The rate constant for the kraft degradation of methyl α-D-glucopyranoside was 13.11 x 10^{-7} sec^{-1}, or 2.68 x 10^{-7} sec^{-1} greater than that of the 1.2M NaOH control (Table VII). However, each of the rate constants in Table VII are the result of several different reactions. By assuming that the competing reactions were additive, it was possible to partition each of the observed overall rate constants for the disappearance of reactant into its substituent parts. For example, the 1.2M NaOH control had a rate constant of 10.43 x 10^{-7} sec^{-1} (Table VII). Of this, 5%, or 0.52 x 10^{-7} sec^{-1}, represents oxygen-aglycone bond cleavage (25), and the remaining 9.91 x 10^{-7} sec^{-1} corresponds to an S_N2 cleavage of the glycosyl-oxygen bond (Fig. 3) (Table VIII).

TABLE VII

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE AT 181.5°C[a]

NaOH, M	NaOTs, M	Na_2S, M	10^7k_r, sec^{-1}	10^7k_{MeSH}, sec^{-1}
1.2	0.2	-	10.43 ± 0.11	--
1.0	-	0.2	13.11 ± 0.60	0.71 ± 0.08
1.4	-	-	11.72 ± 0.18	--

[a]Pseudo-first-order rate constants adjusted to 181.5°C.

TABLE VIII

PARTITIONED RATE CONSTANTS FOR THE DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE

	Degradation Due to 1.2M NaOH		Degradation Due to 0.2M Nucleophile	
Conditions	10^7k_{g-o}[a]	10^7k_{o-a}[b]	10^7k_{g-o}[a]	10^7k_{o-a}[b]
1.2M NaOH[c]	9.91	0.52	--	--
Kraft[d]	9.91	0.52	1.97	0.71
1.4M NaOH	9.91	0.52	1.23	0.065

[a]Pseudo-first-order rate constants for glycosyl-oxygen bond cleavage.
[b]Pseudo-first-order rate constants for oxygen-aglycone bond cleavage.
[c]1.2M NaOH, 0.2M NaOTs.
[d]1.0M NaOH, 0.2M Na_2S.

Similarly, the kraft rate constant can be partitioned into the reactions of hydroxide ion and those of hydrosulfide ion. The 2.68 x 10^{-7} sec^{-1} increase in the rate constant for the kraft reaction (relative to the 1.2M NaOH control) was attributed to the degradative reactions of hydrosulfide ion (Table VIII). While an S_N2 cleavage of the glycosyl-oxygen bond by hydrosulfide ion (Fig. 15) would result in a rate increase, it would not generate any unique stable products. However, a rate increase due to an S_N2 cleavage of the oxygen-aglycone bond by hydrosulfide ion (Fig. 16) must be accompanied by the formation of methyl mercaptan. Therefore, the rate constant for the formation of methyl mercaptan, 0.71 x 10^{-7} sec^{-1} (Table VII) defines the rate constant for cleavage of the oxygen-aglycone bond by hydrosulfide ion. The remainder of the rate increase, or 1.97 x 10^{-7} sec^{-1}, corresponds to the rate constant for hydrosulfide ion cleavage of the glycosyl-oxygen bond (Table VIII).

The rate constant for the 1.4M NaOH degradation was partitioned in a similar manner. The rate increase (relative to the 1.2M NaOH control) was attributed to 0.2M hydroxide ion, and 5% of the rate increase was assigned to accelerated oxygen-aglycone bond cleavage (25) (Table VIII).

In order to estimate the relative nucleophilicities of the hydroxide and hydrosulfide ions, it is necessary to compare the rate constants for S_N2 attack by the two nucleophiles on the same substrate. Table VIII shows that the rate constant for cleavage of the oxygen-aglycone bond by 0.2M hydrosulfide ion (0.71 x 10^{-7} sec^{-1}) is 11 times as great as that for 0.2M hydroxide ion (0.065 x 10^{-7} sec^{-1}). This indicates that the hydrosulfide ion is the stronger nucleophile at 180°C.

By comparison, sodium thiophenoxide was found to be about 80 times as effective as sodium hydroxide at cleaving the oxygen-aglycone bond of methyl α-D-glucopyranoside (33). This result is directly comparable, since the increase in the rate constant

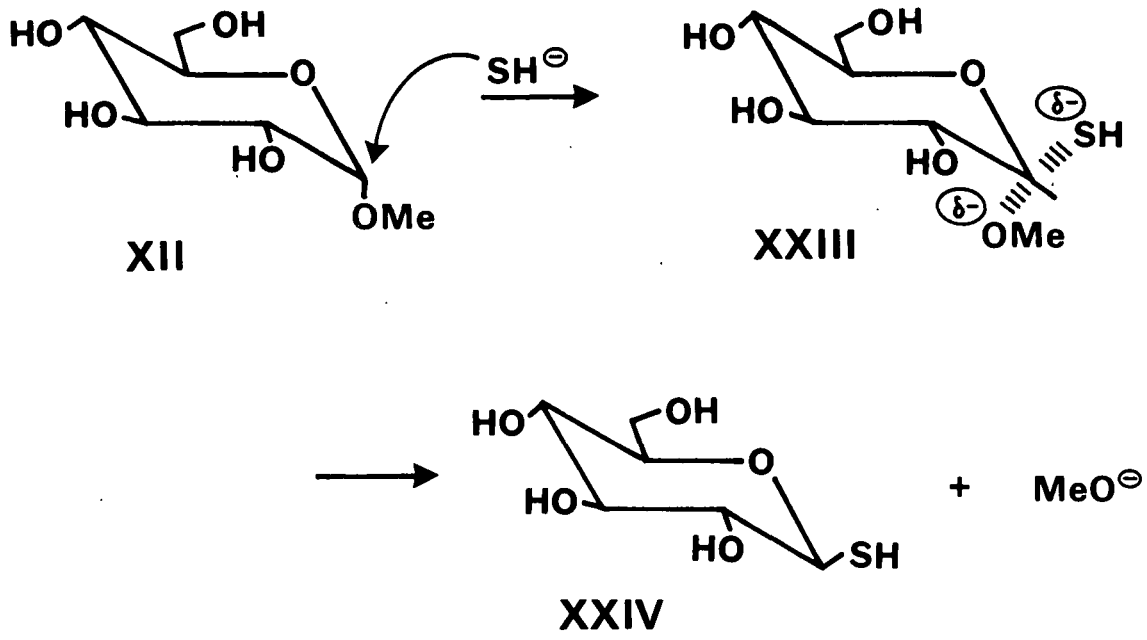


Figure 15. Potential S_N2 cleavage of the glycosyl-oxygen bond of methyl α-D-glucopyranoside by hydrosulfide ion.

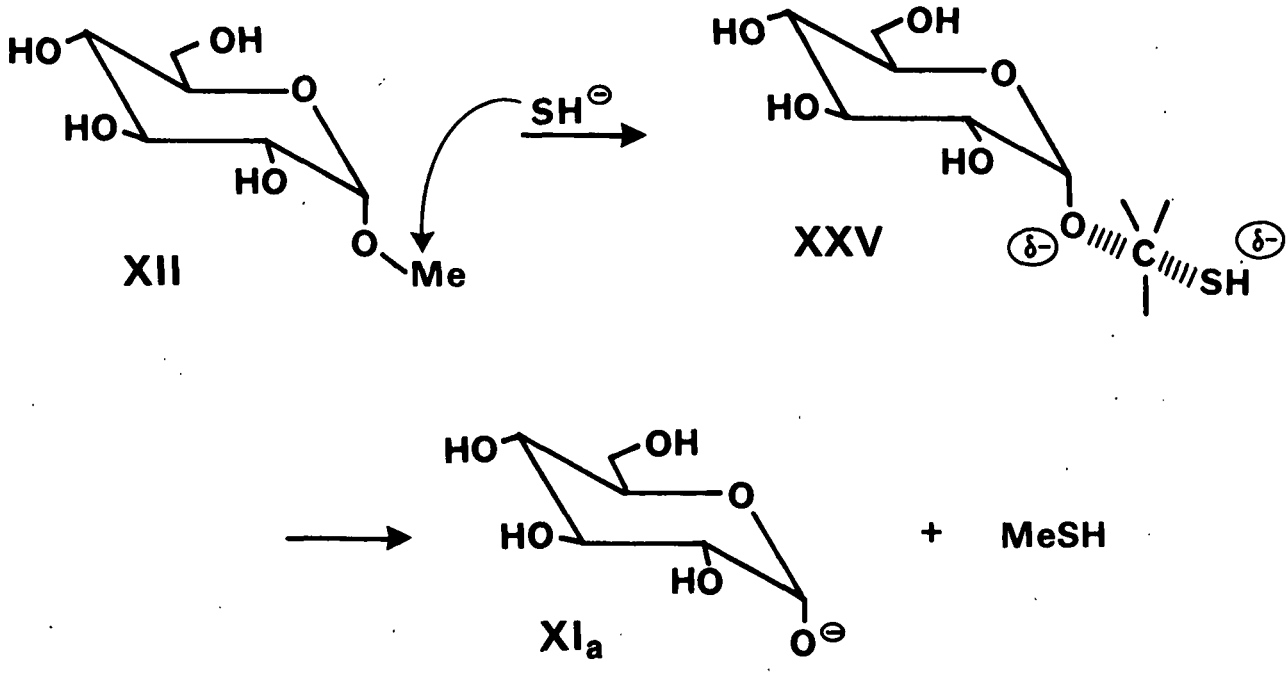


Figure 16. Potential S_N2 cleavage of the oxygen-aglycone bond of methyl α-D-glucopyranoside by hydrosulfide ion.

due to the addition of hydroxide ion was the same as that found in this work (on a molar basis, 6.0 vs. 6.4 x 10^{-7} sec^{-1} mol^{-1}). Thiophenoxide did not cleave the glycosyl-oxygen bond, probably due to the size of the nucleophile.

The rate constant for cleavage of the glycosyl-oxygen bond in methyl α-D-glucopyranoside was enhanced by 1.97 x 10^{-7} sec^{-1} in the kraft system, and 1.23 x 10^{7} sec^{-1} in the 1.4M NaOH case (Table VIII). Therefore the hydrosulfide ion was only 1.6 times as effective as the hydroxide ion at cleavage of this bond. Why this should be less than at the oxygen-aglycone bond is not clear. Certainly the difference in the electronic nature of the carbon atom under attack is a factor. Another possibility is the degree of steric hindrance, but there is not a large difference in the size of these two ions (1.5 vs. 1.85Å) (40,41).

The attack by hydrosulfide ion on the aglycone carbon of methyl α-D-glucopyranoside to generate methyl mercaptan is interesting in that it represents a well-defined S_N2 mechanism which leads to a unique product. A study of the characteristics of this reaction would permit it to be used as a reference for systems of unknown mechanism. Therefore, kraft and 1.2M NaOH degradations of methyl α-D-glucopyranoside were carried out between 160-180°C in order to obtain the apparent thermodynamic functions of activation for this reaction (Table IX).

Table X compares the apparent thermodynamic functions of activation for the formation of methyl mercaptan with those of other "known" mechanisms. As expected, the S_N2 mechanism has a lower enthalpy and more negative entropy of activation than the S_N1 mechanism. Similar energy is required to cleave the carbon-oxygen bond in both mechanisms. However, part of the energy is regained from the concurrent formation of a second bond in the transition state of the S_N2 mechanism. This results in a lower enthalpy of activation. A new bond is also being formed in the $S_N1cB(2)$

transition state, but it is a higher energy strained bond, so the enthalpy of activation is not quite as low as that of the S_N2 reaction.

TABLE IX

RATE CONSTANTS FOR THE DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE AND THE FORMATION OF REACTION PRODUCTS

Temp., °C	Conditions	$10^7 k_r$, sec^{-1}	$10^7 k_{MeOH}$, sec^{-1}	$10^7 k_{MeSH}$, sec^{-1}
170.5	1.2M NaOH[a]	3.60 ± 0.02	3.69 ± 0.02	--
180.6	1.2M NaOH[a]	9.72 ± 0.18	10.21 ± 0.06	--
180.9	1.2M NaOH[a]	9.75 ± 0.04	10.21 ± 0.15	--
191.4	1.2M NaOH[a]	24.68 ± 0.23	25.93 ± 0.16	--
161.2	Kraft[b]	2.06 ± 0.24	1.89 ± 0.24	0.16 ± 0.06
170.5	Kraft[b]	4.40 ± 0.10	3.81 ± 0.04	0.30 ± 0.02
180.1	Kraft[b]	11.62 ± 0.42	10.66 ± 0.15	0.63 ± 0.08
181.9	Kraft[b]	13.55 ± 0.80	--	--
190.5	Kraft[b]	26.78 ± 0.26	24.19 ± 0.30	1.54 ± 0.09

[a] 1.2M NaOH and 0.2M NaOTs.
[b] 1.0M NaOH and 0.2M Na_2S.

TABLE X

APPARENT THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR SEVERAL REACTIONS

Compound and Mechanism	E_a Kcal mol^{-1}	$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.
1,6-Anhydro-β-D-glucopyranose, $S_N1cB(2)$, (25)	32.7	31.8	-6.0
1,5-Anhydrocellobiitol, oxygen-aglycone bond, S_N1, (37)	42.6	41.7	+6.9
Methyl α-D-glucopyranoside, 2.5M NaOH degradation, S_N2, (25)	31.7	30.8	-18.2
Methyl α-D-glucopyranoside, kraft degradation, mercaptan formation, S_N2	31.1	30.3	-25.4

The entropy of an S_N1 system increases in the transition state due to an increase in the vibrational and rotational degrees of freedom, whereas an S_N2 system initially involves two distinct species which lose degrees of freedom, including translational freedom, as they are brought together in the transition state. The result is a more negative entropy of activation for a reaction proceeding by an S_N2 mechanism. The new bond being formed in the $S_N1cB(2)$ transition state dictates a loss of vibrational and rotational degrees of freedom, but there is no loss of translational freedom, so the decrease in entropy is not as great as in the S_N2 case.

The apparent thermodynamic functions of activation for the disappearance of methyl α-D-glucopyranoside in 1.2M NaOH are given in Table XI. Since the glycosyl-oxygen bond is cleaved 95% of the time in alkali (25), these values primarily reflect the cleavage of that bond. In addition, the apparent thermodynamic functions of activation are reported for the formation of methanol, but the values will resemble those for the disappearance of the reactant, since methanol is generated by any cleavage of the glycosidic linkage, regardless of the mechanism.

The apparent thermodynamic functions of activation for the 1.2M NaOH degradation of methyl α-D-glucopyranoside (Table XI) are intermediate between those of the "known" S_N1 and S_N2 mechanisms (Table X). However, an $S_N1cB(i)$ mechanism does not occur during the alkaline degradation of this sugar (25). Therefore the data indicate that both the S_N1 and S_N2 mechanisms are operating, at least at low hydroxide ion concentrations. There is no good way to determine the relative importance of these two mechanisms, but the evidence of Gilbert (25) suggests that the S_N2 dominates. The apparent thermodynamic functions of activation for the kraft degradation of methyl α-D-glucopyranoside are similar to those of the soda reaction, but show some bias toward the S_N2 "known" because of the presence of the S_N2 reactions of hydrosulfide ion (Table XI).

TABLE XI

APPARENT THERMODYNAMIC FUNCTIONS OF ACTIVATION FOR THE DISAPPEARANCE OF METHYL α-D-GLUCOPYRANOSIDE AND THE APPEARANCE OF REACTION PRODUCTS UNDER VARIOUS CONDITIONS

Conditions and Compound	E_a Kcal mol^{-1}	$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.
1.2M NaOH[a]			
Disappearance of methyl α-D-glucopyranoside	37.7	36.8	-5.9
Formation of methanol	38.2	37.3	-4.7
Kraft[b]			
Disappearance of methyl α-D-glucopyranoside	35.7	34.8	-9.8
Formation of methanol	35.6	34.7	-10.3
Formation of methyl mercaptan	31.1	30.3	-25.4

[a] 1.2M NaOH and 0.2M NaOTs.
[b] 1.0M NaOH and 0.2M Na_2S.

The hydrosulfide ion was shown to be 11 times as effective as hydroxide ion at cleaving the oxygen-aglycone bond, but only 1.6 times as effective on the glycosyl-oxygen bond. The presence of an S_N1 component in the alkaline cleavage of the glycosyl-oxygen bond may provide a partial explanation of this difference, since the calculation assumed that the increase in the rate constant upon the addition of hydroxide ion was the result of an S_N2 mechanism only. Any portion due to an S_N1 mechanism would have to be subtracted before calculating the effectiveness of the hydrosulfide ion relative to the hydroxide ion.

KRAFT DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE

1,6-Anhydro-β-D-glucopyranose degrades by an $S_N1cB(2)$ mechanism (Fig. 17) (25). The rate-determining step is attack by the C-2 oxyanion on the anomeric carbon.

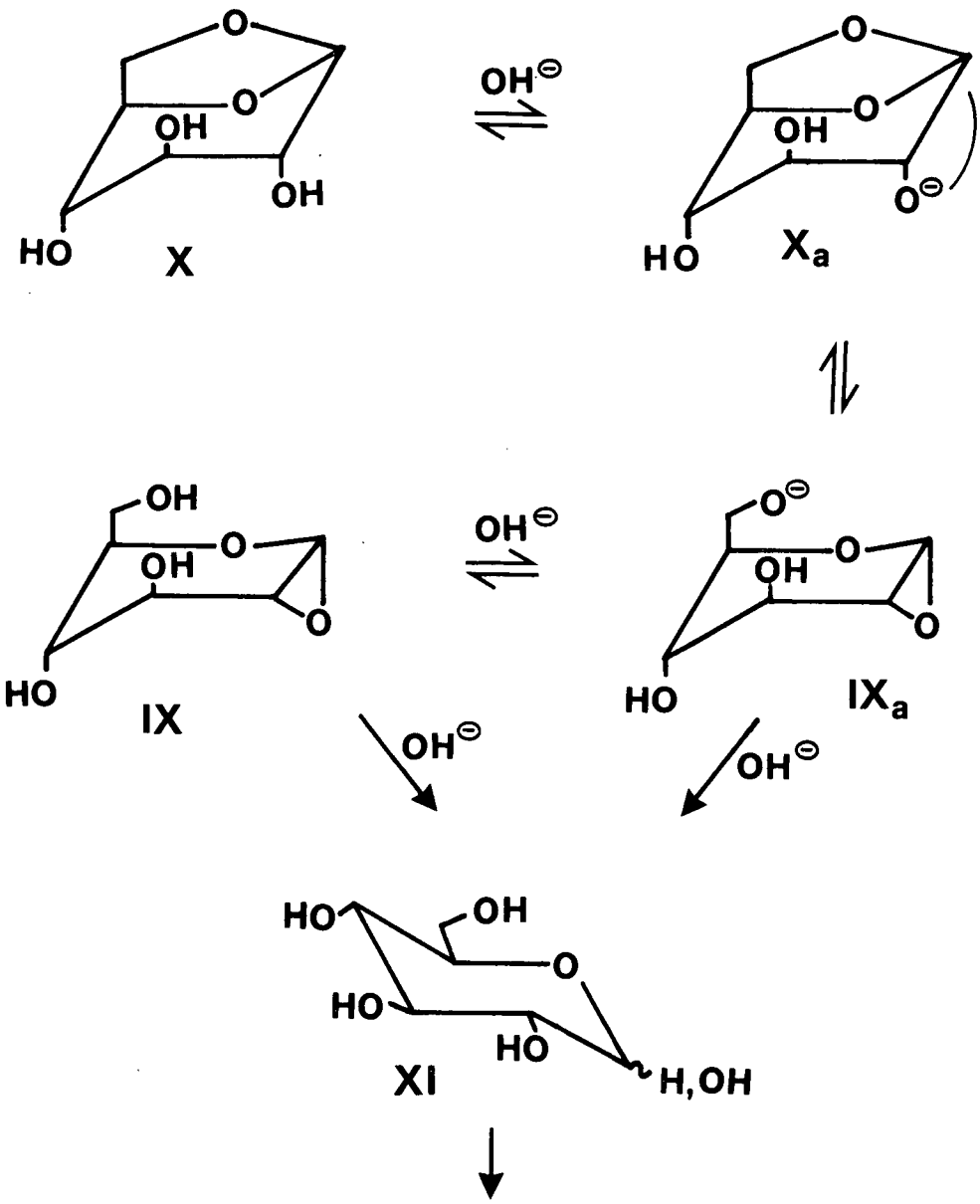


Figure 17. $S_N1cB(2)$ mechanism proposed for the degradation of 1,6-anhydro-β-D-glucopyranose under alkaline conditions (25).

Methylation of the C-2 hydroxyl group resulted in a decrease in the rate constant to about 3% of that for the unetherified substrate (25).

Several degradations of 1,6-anhydro-β-D-glucopyranose were carried out at 170°C in order to obtain degradation rate constants (k_d) for analysis of the formation of 1,6-anhydro-β-D-glucopyranose from 1,5-anhydrocellobiitol. In those cases where the temperature of this measurement differed from the temperature of the 1,5-anhydrocellobiitol degradation, the rate constants were adjusted using the Arrhenius Equation as described earlier.

An analysis of the data obtained from the degradation of 1,6-anhydro-β-D-glucopyranose (Table XII) revealed that the addition of 0.2M hydrosulfide ion caused the rate constant to increase to the same extent as did the addition of 0.2M hydroxide ion. No explanation for this observation is readily apparent.

TABLE XII

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE AT 170°C[a]

NaOH, M	NaOTs, M	Na_2S, M	$10^5 k_r$, sec^{-1}
1.0	0.6	--	5.64 ± 0.24
1.2	0.2	--	6.30 ± 0.13
1.4	--	--	7.09 ± 0.11
1.0	--	0.2	7.16 ± 0.24

[a]Pseudo-first-order rate constants adjusted to 170°C.

CONCLUSIONS

Sodium sulfide was found to be completely hydrolyzed under kraft pulping conditions (1.0M NaOH, 160-190°C). The resulting hydrosulfide ion was shown to be a stronger nucleophile than the hydroxide ion, yet it did not accelerate glycosidic bond cleavage in 1,5-anhydrocellobiitol. This indicates that the hydrosulfide ion does not cause a decrease in the DP of cellulose during kraft pulping.

Under alkaline conditions the oxygen-aglycone bond of 1,5-anhydrocellobiitol is cleaved by an S_N1 mechanism. Glycosyl-oxygen bond cleavage occurs by a mixed mechanism, one part of which has been identified as an $S_N1cB(2)$ reaction. Based on the data obtained in this investigation, it is proposed that hydrosulfide ion is hindered (by steric or electronic factors) from participating in an S_N2 attack on the glycosidic linkage of 1,5-anhydrocellobiitol. The similarity of the hydrosulfide and hydroxide ions suggests that hydroxide may also be incapable of an S_N2 attack. Therefore, glycosyl-oxygen bond cleavage in 1,5-anhydrocellobiitol is probably the result of $S_N1cB(2)$ and S_N1 mechanisms. This is consistent with other data obtained by Brandon, et al. (37).

The results of this study suggest that random chain cleavage in cellulose may not occur by an S_N2 mechanism at all, but rather by $S_N1cB(2)$ and S_N1 mechanisms. To the extent that the $S_N1cB(2)$ mechanism is hindered in cellulose by the need to change conformations, the S_N1 mechanism would be relatively more important in cellulose than in the disaccharide model compound.

EXPERIMENTAL

GENERAL ANALYTICAL PROCEDURES

Melting points were determined on a Thomas Hoover capillary melting point apparatus calibrated against known compounds.

Optical rotations were determined at room temperature on a Perkin-Elmer 141MC polarimeter.

^{13}C-Nuclear magnetic resonance (NMR) spectra (Appendix III) were obtained on a Jeol FX100 Fourier transform spectrometer at normal probe temperature. All chemical shifts were referenced to external tetramethylsilane.

Infrared (IR) spectra were obtained from potassium bromide pellets on a Nicolet 7199C Fourier transform spectrophotometer.

Thin layer chromatography (TLC) was performed on microscope slides coated with silica gel (Merck Kieselgel D-5). The solvent systems used for development are described in the appropriate sections. The components were detected by spraying the developed chromatograms with methanol:sulfuric acid (4:1, vol.), followed by charring.

Elemental analyses were performed by Micro-Tech Laboratories, Inc. (4117 Oakton St., Skokie, Ill. 60076).

Sodium sulfide concentrations were determined by titration with 0.1M mercuric chloride (42) followed with an Orion silver/sulfide specific ion electrode and an Orion 901 ionalyzer. The fixed increment method of addition was used, and the inflection in the mv vs. mL plot was identified by the second derivative method (43). The active alkali of kraft liquors was determined by titration with 1.0M

hydrochloric acid in the presence of formaldehyde to the phenolphthalein endpoint. The sodium hydroxide concentration was then calculated by subtracting the sodium sulfide concentration from the active alkali (44).

Gas-liquid chromatography (GLC) was performed on a Perkin-Elmer Sigma 2 instrument equipped with both flame-ionization and flame-photometric detectors, and interfaced with a Sigma 10 data station. Nitrogen was used as the carrier gas at a rate of 30 mL/min. The following columns and conditions were used:

(A) Alltech Super Q (80-100 mesh) in Teflon tubing (4 ft x 0.125 inch) rigged for off-column injection. The operating conditions were: injector, 275°C; detector, 300°C; and column, 65°C for 1 minute, 3° min^{-1} to 95°C, and held at 95°C. The injector insert was replaced after every other injection. Table XIII gives retention times and response factors for these analyses.

(B) OV-101 (3%) on Supelcoport (80-100 mesh) in stainless steel tubing (5 ft x 0.125 inch) rigged for on-column injection. The operating conditions were: injector, 275°C; detector, 300°C; and column, 140°C to 250°C at 7° min^{-1}. Table XIII gives retention times and response factors for these analyses.

(C) OV-101 (3%) on Supelcoport (80-100 mesh) in stainless steel tubing (5 ft x 0.125 inch) rigged for on-column injection. The operating conditions were: injector, 275°C; detector, 300°C; and column, 130°C for 1 minute, 7° min^{-1} to 275°C, and held at 275°C. Table XIII gives retention times and response factors for these analyses.

Quantitative GLC utilized internal standards. Molar response factors were calculated according to Eq. (27):

$$F_x = A_r M_r \qquad (27)$$

where F_x = response factor for compound X relative to the internal standard

A_r = ratio of the internal standard peak area to the peak area of compound X

M_r = mole ratio of compound X to the internal standard

Response factors were determined by subjecting a series of known solutions of varying mole ratios to the appropriate work-up procedure. The response factors were calculated as the average of the values obtained.

TABLE XIII

GAS CHROMATOGRAPHIC RETENTION TIMES (T_r) AND RESPONSE FACTORS (F_x)

Conditions	Compound	T_r, min	F_x
A	Methyl alcohol	2.3	2.96[a]
A	Methyl mercaptan	5.0	2.84[a]
A	Isopropyl alcohol	12.2	1.00[a]
B	1,6-Anhydro-β-D-glucopyranose	4.7	1.64[b]
B	Methyl α-D-glucopyranoside	7.6	1.22[b]
B	2-Hydroxyethyl 1-thio-β-D-glucopyranoside	13.7	1.00[b]
C	1,5:3,6-Dianhydro-D-galactitol	3.8	1.22[b]
C	1,6-Anhydro-β-D-glucopyranose	6.5	1.90[b]
C	1,5-Anhydro-D-glucitol	8.8	1.25[b]
C	1,5-Anhydro-6-deoxy-6-thio-D-glucitol	12.1	--
C	2-Hydroxyethyl 1-thio-β-D-glucopyranoside	16.0	1.00[b]
C	1,5-Anhydrocellobiitol	22.5	0.69[b]

[a]Calculated relative to isopropyl alcohol.
[b]As the acetate derivative, calculated relative to 2-hydroxyethyl 1-thio-β-D-glucopyranoside.

A Hewlett-Packard 5985 instrument was used for GLC-mass spectroscopy (GLC-MS). GLC was performed on OV-101 (3%) on Supelcoport (80-100 mesh) in a glass column (6 ft x 0.125 inch) rigged for off-column injection. The GLC conditions were similar to those described earlier. The GLC-MS interface was maintained at 250°C. Electron impact (EI) MS utilized helium as the carrier gas, a source temperature of 200°C,

and an ionizing voltage of 70 Ev. Chemical ionization (CI) and negative chemical ionization (NCI) MS utilized methane as the carrier gas, a source temperature of 200°C, and an ionizing voltage of 230 Ev. Mass spectra are given in Appendix III.

SOLUTIONS, REAGENTS AND CATALYSTS

ACETIC ANHYDRIDE

Reagent grade acetic anhydride (1 L) was fractionally distilled. The first 100 mL was discarded, and the next 700 mL was collected and stored in dark bottles.

CHLOROFORM

Reagent grade chloroform (1.5 L) was fractionally distilled. The first 50 mL was discarded, and the next 1300 mL was collected. The distilled chloroform was stabilized with 1% (w/w) ethanol and stored in dark bottles. Absolute chloroform was only required for use with GLC samples.

ANHYDROUS DIMETHYLFORMAMIDE

Reagent grade dimethylformamide (DMF)(1 L) was shaken with molecular sieves (Davison 4Å, ca. 150 mL) for five hours (45). The sieves were filtered off and replaced with fresh ones. After twelve hours the sieves were filtered off and the DMF was fractionally distilled under reduced pressure (ca. 25 mm Hg). The first 100 mL was discarded, and the next 750 mL was collected and stored in dark bottles.

ANHYDROUS ETHYL ACETATE

Reagent grade ethyl acetate (500 mL) was shaken with aqueous sodium carbonate (5%, 500 mL) and then saturated calcium chloride (500 mL), dried over potassium carbonate, and fractionally distilled (45). The first 150 mL was discarded, and the next 250 mL was collected and stored in dark bottles.

HYDROGEN BROMIDE IN ACETIC ACID

Hydrogen bromide (HBr) gas was bubbled through a known amount of glacial acetic acid in tared 1 L reagent bottles. When the solution reached about 20% (w/w) HBr, the bottles were placed in ice baths. The addition was terminated at 42-44% HBr. The bottles were sealed, wrapped in aluminum foil, and refrigerated.

ANHYDROUS METHANOL

Magnesium turnings (10 g) were covered with reagent grade methanol, and iodine (0.25 g) was added (45). As the reaction subsided, methanol (2 L) was slowly added. The mixture was refluxed for two hours, and then fractionally distilled. The first 100 mL of distillate was discarded, and the next 1700 mL was collected and stored in tightly-sealed bottles.

POTASSIUM ACID PHTHALATE

Reagent grade potassium acid phthalate was dried under vacuum at 105°C overnight and then stored under vacuum.

POTASSIUM THIOCYANATE

Reagent grade potassium thiocyanate was powdered with a mortar and pestle, and dried under vacuum at 105°C for twelve hours immediately before use.

ANHYDROUS PYRIDINE

Reagent grade pyridine (1 L) was refluxed over potassium hydroxide for four hours, and then fractionally distilled (45). The first 50 mL was discarded, and the next 750 mL was collected and stored in dark bottles.

SODIUM METHOXIDE

A 1M solution of sodium methoxide was prepared from sodium metal (23 g). The sodium was cut into small pieces, rinsed in methanol, and slowly added to anhydrous methanol (1 L). After the solution cooled, it was stored in tightly-sealed, dark bottles.

SODIUM p-TOLUENESULFONATE

Technical grade sodium p-toluenesulfonate (NaOTs), recrystallized from an ethanol-water mixture (5:2, v/v) (37), was supplied by M. Bovee.

OXYGEN-FREE WATER

Organic-free, triply-distilled water (ca. 1.6 L) (46) was boiled for about 30 minutes, transferred to a 1 L reagent bottle, and purged with nitrogen while cooling in an ice bath. The bottle was tightly sealed and stored for no more than 24 hours before use.

STANDARD ALCOHOL SOLUTIONS

Standard aqueous solutions of methanol and isopropanol were prepared by taking the alcohol up in a syringe, taring it, injecting the alcohol into a half-filled volumetric flask, and reweighing the syringe. The flask was then filled and tightly sealed.

STANDARD HYDROCHLORIC ACID SOLUTION

Concentrated hydrochloric acid was diluted to ca. 1M and standardized by titration with a standard 2M sodium hydroxide solution to the phenolphthalein endpoint.

STANDARD MERCURIC CHLORIDE SOLUTION

Reagent grade mercuric chloride was dried under vacuum at room temperature overnight. A 0.100M solution was prepared by dissolving mercuric chloride (27.1520 g) in water (1 L).

STANDARD METHYL MERCAPTAN SOLUTION

A gas absorption bottle containing 1M sodium hydroxide solution (300 mL) was tared with the dispersion stone in place. Methyl mercaptan gas was bubbled through the solution for ten seconds, and the system was reweighed. The concentration was calculated from the weight gain, and the solution was diluted with 1M sodium hydroxide to the desired concentration. The bottle was tightly sealed and used within 4 hours.

STOCK SODIUM HYDROXIDE SOLUTION

Reagent grade sodium hydroxide (500 g) was stirred with triply-distilled water (500 g) in a covered beaker. After cooling, the solution was transfered to a paraffin-lined bottle which was flushed with nitrogen and tightly stoppered. The density of the solution was determined by filling two tared 10-mL volumetric flasks. The concentration of the solution was found by combining the two flasks, diluting to 100 mL, and titrating against potassium acid phthalate.

STOCK SODIUM SULFIDE SOLUTION

Reagent grade sodium sulfide nonahydrate was rinsed in a Buchner funnel (without filter paper) with distilled water to remove all discoloration. The ice-like crystals (400 g) were stirred in triply-distilled, oxygen-free water (600 g) under a nitrogen atmosphere. The dissolution is quite endothermic and requires several

hours. The solution was stored in a tightly-stoppered, paraffin-lined bottle. The density of the solution was determined by filling two tared 10-mL volumetric flasks. The concentration of the solution was found by diluting each flask to 100 mL with oxygen-free water, and titrating against 0.1M mercuric chloride (42).

PALLADIUM ON CHARCOAL CATALYST (10%)

The catalyst was obtained from Dr. Schroeder.

RANEY NICKEL, TYPE W-5

Nickel-aluminum alloy (50/50, 100 g) was added to a stirred sodium hydroxide solution (6.4M, 520 mL) at such a rate that the temperature remained at 48-52°C (47). Cooling in an ice bath permitted faster addition of the alloy. The slurry was then held at 50°C for fifty minutes. The nickel was washed with water by decantation (3 x 100 mL), and then in a continuous extractor (a 1 L graduated cylinder fitted with an overhead stirrer and a gravity-feed water supply) until the effluent was neutral. It was solvent exchanged with tetrahydrofuran (THF) by decantation (3 x 100 mL), and by centrifugation and decantation (3 x 100 mL).

To double the preparation, all of the volumes were doubled, but the final digestion at 50°C was cut to thirty minutes since the time required for the addition of the alloy to the sodium hydroxide solution was longer. The nickel was stored under tetrahydrofuran, and was found to be active after two weeks. The average yield (calculated as the difference between the slurry weight and the weight of an equal volume of the solvent) was 96.5% for nine reactions.

SYNTHESIS OF COMPOUNDS

α-CELLOBIOSE OCTAACETATE

Acetic anhydride (400 mL) was held below 20°C as sulfuric acid (35 mL) was added. Cellulose powder (100 g) was slowly added to the stirred solution so that the temperature remained below 40°C (48). The mixture was stirred for one hour, covered, and held at 30°C for ten days. The highly colored product mixture was poured into stirred ice water (3 L). The water was decanted from the crude product and the product was dissolved in chloroform (1 L). The chloroform solution was extracted with water (500 mL), saturated sodium bicarbonate (2 x 500 mL), and water (500 mL); dried over calcium chloride; and reduced *in vacuo* to about 300 mL. Addition of boiling methanol (600 mL) gave crystals (34.9 g, 16.9%) which on recrystallization from absolute ethanol had: m.p. 227-229°C, $[\alpha]_D$ +40.8° (*c* 1.5, $CHCl_3$). Literature: m.p. 225-226°C, $[\alpha]_D$ +42.5° ($CHCl_3$) (48).

HEPTA-O-ACETYL-α-CELLOBIOSYL BROMIDE

α-Cellobiose octaacetate (130 g) was powdered and slurried in 1,2-dichloroethane (400 mL) (49). Hydrogen bromide in acetic acid (42%, 135 mL) was added, and the mixture stirred for two hours. Chloroform (800 mL) was added, and the solution was stirred with ice water (2 L) for a half hour. The organic layer was washed with water (1 L), aqueous sodium bicarbonate (to neutrality, 1 L), and water (1 L); dried over calcium chloride; and concentrated in vacuo to about 450 mL. Crystals formed upon the addition of petroleum ether (100 mL). Four preparations gave an average yield of 75%. Product recrystallized from ethyl ether by addition of petroleum ether had: m.p. 182°C (decomp.), $[\alpha]_D$ +94.7° (*c* 1.5, $CHCl_3$). Literature: m.p. 180°C (decomp.), $[\alpha]_D$ +96.3° (*c* 7.3, $CHCl_3$) (49).

PHENYL HEPTA-O-ACETYL-1-THIO-β-CELLOBIOSIDE

Hepta-O-acetyl-α-cellobiosyl bromide (75 g) dissolved in chloroform (300 mL) was refluxed with methanolic potassium hydroxide (0.5M, 400 mL) containing thiophenol (25 mL) for two hours (50). The reaction was followed by TLC (chloroform). The solution was allowed to cool, washed with water (500 mL) and sodium hydroxide (2.5M, 3 x 400 mL); dried over calcium chloride; and concentrated to dryness in vacuo. Crystallization from absolute ethanol gave an average yield of 73% for three reactions. Product recrystallized from ethanol had: m.p. 221.5-223.5°C, $[\alpha]_D$ -28.7° (c 1.5, $CHCl_3$). Literature: m.p. 225-226°C, $[\alpha]_D$ -28.7° (c 1.36, $CHCl_3$) (51).

1,5-ANHYDRO-2,3,6-TRI-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-GLUCITOL

Hepta-O-acetyl-α-cellobiosyl bromide (14 g) was placed in a modified Parr bomb with 10% palladium-on-carbon (0.5 g), anhydrous ethyl acetate (150 mL), and triethylamine (3 mL) (52). The reaction was stirred under hydrogen at 45 psig, and monitored by TLC (chloroform:ethyl acetate, 1:1, vol.). After five days, the reaction slurry was filtered through Celite, and the filter was rinsed with ethyl acetate. Chloroform (150 mL) was added to the filtrate, and the organic phase was extracted with saturated sodium bicarbonate (2 x 300 mL), water (300 mL), and silver nitrate (3% in aqueous acetone, 5 mL); and reduced in vacuo to a solid. The crude 1,5-anhydro-2,3,6-tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-glucitol (1,5-anhydrocellobiitol heptaacetate) was crystallized from ethanol, decolorized with carbon, and recrystallized to give 8.2 g (66%): m.p. 191.5-192°C, $[\alpha]_D$ +4.6° (c 1.5, $CHCl_3$). Literature: m.p. 193.5-194°C, $[\alpha]_D$ +4.1° (c 2.9, $CHCl_3$) (37).

The title compound was also prepared by reduction of phenyl hepta-O-acetyl-1-thio-β-cellobioside (63 g) in THF (250 mL) with W-5 Raney nickel (75 g, or 1700 g

alloy/mole sugar). The slurry was stirred at 48°C for three hours, and then refluxed for three hours. The reaction was followed by TLC (chloroform:ethyl acetate, 2:1, vol.). If it failed to reach completion, it was cooled to room temperature and more Raney nickel was added (25 g, or 2300 g total alloy/mole sugar). Upon completion, the slurry was cautiously filtered, and the nickel carefully washed with THF (3 x 50 mL). The filtrate was reduced *in vacuo* to a solid, which was crystallized from absolute ethanol. GLC (conditions C) showed this product to be contaminated with at least two by-products. Repeated recrystallization at the rate of 10 g of sugar in 200 mL of absolute ethanol gave pure compound: m.p. 193.8-194.8°C, $[\alpha]_D$ +3.9° (*c* 1.5, $CHCl_3$). Literature: m.p. 193.5-194.0°C, $[\alpha]_D$ +4.1° (*c* 2.9, $CHCl_3$) (37). The mass spectra (Tables XIV-XVI, Appendix III) gave the correct molecular weight, and included peaks at 331 for the glycone and 273 for the aglycone.

1,5-ANHYDRO-4-*O*-(β-D-GLUCOPYRANOSYL)-D-GLUCITOL

1,5-Anhydrocellobiitol heptaacetate (50 g) was dissolved in anhydrous methanol (500 mL) with heating and sodium methoxide (1M, 5 mL) was added (53). The reaction was monitored with TLC (chloroform:ethyl acetate, 1:1, vol.). The resulting precipitate (20.9 g, 80%), on recrystallization from 95% ethanol, had: m.p. 206-207°C, $[\alpha]_D$ +28.5° (*c* 1.5, H_2O). Literature: m.p. 204.5-205.5°C, $[\alpha]_D$ +28.2 (*c* 2.2, H_2O) (37). The ^{13}C-NMR spectrum (Fig. 21, Appendix III) was consistent with the literature (54).

Anal. Calc. for $C_{12}H_{22}O_{10}$: C, 44.17; H, 6.75. Found: C, 43.92; H, 6.79.

1,5-ANHYDRO-2-DEOXY-3,6-DI-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-ARABINO-HEXITOL

1,5-Anhydro-2-deoxy-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-arabino-hexitol (5 g) was isolated from mixture with 1,5-anhydrocellobiitol heptaacetate by fractional crystallization from absolute ethanol, and had: m.p. 132.5-133.5°C; $[\alpha]_D$ +6.1° (c 1.5, $CHCl_3$). The mass spectra (Tables XVII-XVIII, Appendix III) featured peaks at 331 for the glycone and 215 for the aglycone, and were consistent with the molecular weight of 546.

Mass spectral evidence was also found for a 1,5-anhydro-dideoxy-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-hexitol, but the compound was not isolated. The mass spectra (Tables XIX-XX, Appendix III) show a molecular weight of 488, with peaks at 331 for the glycone and at 157 for the aglycone.

1,5-ANHYDRO-2-DEOXY-4-O-(β-D-GLUCOPYRANOSYL)-D-ARABINO-HEXITOL

1,5-Anhydro-2-deoxy-3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-arabino-hexitol (1 g) was dissolved in hot methanol (15 mL). Sodium methoxide (1M, 0.5 mL) was added (53), and the solution was stirred until the product precipitated to give 0.4 g (72%). Recrystallization from 95% ethanol gave pure compound: m.p. 209-211°C, $[\alpha]_D$ +3.7° (c 1.5, H_2O). The ^{13}C-NMR spectrum showed a shift in the C-2 resonance from 70.3 ppm in 1,5-anhydrocellobiitol to 33.4 ppm in this compound (Fig. 22, Appendix III).

Anal. Calc. for $C_{12}H_{22}O_9$: C, 46.45; H, 7.10. Found: C, 46.24, H, 7.22.

2,3,4,6-TETRA-O-ACETYL-α-D-GLUCOPYRANOSYL BROMIDE

α,β-D-Glucose pentaacetate (200 g) was slurried in hydrogen bromide in acetic acid (42%, 130 mL) and allowed to stand for two hours (55). Chloroform (800 mL) was added, and the solution was stirred with ice water (3 L) for thirty minutes. The organic phase was washed with water (1 L), saturated sodium bicarbonate (to neutrality, 2 x 500 mL), and water (500 mL); dried over calcium chloride; and reduced *in vacuo* to a thin oil. The oil was dissolved in ethyl ether (500 mL), and crystals formed upon the addition of petroleum ether (250 mL) and refrigeration. Four preparations gave an average yield of 77%. Recrystallization from ethyl ether by addition of petroleum ether gave pure compound: m.p. 89-90°C, $[\alpha]_D$ +197.3° (*c* 1.5, $CHCl_3$). Literature: m.p. 88-89°C, $[\alpha]_D$ +197.8° ($CHCl_3$) (55).

PHENYL 2,3,4,6-TETRA-O-ACETYL-1-THIO-β-D-GLUCOPYRANOSIDE

2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide (200 g) in chloroform (400 mL), was refluxed with ethanolic potassium hydroxide (1M, 750 mL) containing thiophenol (75 mL) for three hours (50). The reaction was followed by TLC (chloroform:ethyl acetate, 1:1, vol.) of silver nitrate (3% in aqueous acetone) treated samples. Upon completion, the reaction solution was washed with water (500 mL), sodium hydroxide (2.5M, 3 x 500 mL), and water (500 mL); dried over calcium chloride; and reduced *in vacuo* to a thick oil. Crystallization from absolute ethanol gave an average yield of 50% for three reactions. Recrystallization from ethanol gave pure compound: m.p. 117.5-118.0°C, $[\alpha]_D$ -17.3° (*c* 1.5, $CHCl_3$). Literature: m.p. 117°C, $[\alpha]_D$ -17.5° (*c* 2.5, $CHCl_3$) (50).

1,5-ANHYDRO-2,3,4,6-TETRA-O-ACETYL-D-GLUCITOL

Phenyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (20.9 g) was dissolved in THF (150 mL), and Raney nickel (42.9 g, or 1800 g alloy/mole sugar) was added. The slurry was stirred at 48°C for two hours, and then refluxed for three hours. The reaction was followed by TLC (ethyl acetate). If it failed to reach completion, it was cooled to room temperature and more Raney nickel was added (7.1 g, or 2100 g total alloy/mole sugar). Upon completion, the reaction mixture was cautiously filtered, and the nickel residue was carefully washed with THF (3 x 50 mL). The filtrate was reduced in vacuo to a thick oil which was crystallized from hot absolute ethanol (30 mL) by addition of petroleum ether (30 mL) and refrigeration. GLC showed this product to be contaminated with at least two by-products. Repeated recrystallization from absolute ethanol gave pure compound: m.p. 72.5-74.0°C, $[\alpha]_D$ +38.7° (c 1.5, $CHCl_3$). Literature: m.p. 73.6-74.8°C, $[\alpha]_D$ +38.9° (c 2.9, $CHCl_3$) (56). The mass spectra (Tables XXI-XXIII, Appendix III) indicate the correct molecular weight. The CI-MS shows peaks at 333 for M+1 and 273 for M-59. The ^{13}C-NMR spectrum (Fig. 23, Appendix III) was also consistent with the desired product.

Mass spectral evidence was found for a 1,5-anhydro-deoxy-tri-O-acetyl-D-hexitol (Tables XXIV-XXVI, Appendix III). The CI-MS had peaks at 275 for M+1 and 215 for M-59. A 1,5-anhydro-dideoxy-di-O-acetyl-D-hexitol was also indicated (Tables XXVII-XXVIII, Appendix III). Peaks occurred at 217 for M+1 and 157 for M-59 in the CI-MS. Neither compound was isolated.

1,5-ANHYDRO-D-GLUCITOL

1,5-Anhydro-2,3,4,6-tetra-O-acetyl-D-glucitol (44.4 g) was dissolved in anhydrous methanol (400 mL), and sodium methoxide (1M, 5 mL) was added (53).

After six hours, TLC (chloroform:ethyl acetate, 1:1, vol.) showed the reaction to be complete. The solution was deionized with MB-3 ion exchange resin (15 g) and reduced *in vacuo* to a syrup which crystallized on standing. Product recrystallized from a large quantity of absolute ethanol had: m.p. 140-141°C, $[\alpha]_D$ +41.6° (*c* 1.5, H_2O). Literature: m.p. 142-143°C, $[\alpha]_D$ +42.8° (*c* 1.4, H_2O) (37). The ^{13}C-NMR spectrum (Fig. 24, Appendix III) was consistent with the literature (57).

METHYL α-D-GLUCOPYRANOSIDE

Reagent grade methyl α-D-glucopyranoside purified (25) by M. Bovee was used: m.p. 166-167.5°C, $[\alpha]_D$ +159.1° (*c* 1.5, H_2O). Literature: m.p. 167-168°C, $[\alpha]_D$ +159.0° (*c* 2.0, H_2O) (25).

1,6-ANHYDRO-2,3,4-TRI-*O*-ACETYL-β-D-GLUCOPYRANOSE

Crude 1,6-anhydro-β-D-glucopyranose (200 g) (58) was dissolved in pyridine (1250 mL), and acetic anhydride (1050 mL) was added (59). After forty-eight hours, TLC (chloroform:ethyl acetate, 1:1, vol.) showed that the reaction had reached completion. The solution was stirred in ice water (4.5 L) for thirty minutes and then extracted with chloroform (3 x 500 mL). The chloroform was washed with water (1 L), sulfuric acid (5%, to neutrality, 1 L), and water (1 L); dried over sodium sulfate; reduced *in vacuo* to a thin syrup; decolorized with carbon; and crystallized from ethanol to give 235 g (66%): m.p. 109-110°C, $[\alpha]_D$ -63.1° (*c* 1.5, $CHCl_3$). Literature: m.p. 109-110°C, $[\alpha]_D$ -62.0° ($CHCl_3$) (60).

1,6-ANHYDRO-β-D-GLUCOPYRANOSE

1,6-Anhydro-2,3,4-tri-*O*-acetyl-β-D-glucopyranose (190 g) was dissolved in anhydrous methanol (1.5 L), and sodium methoxide (1M, 40 mL) was added (53). After thirty minutes, TLC (chloroform:ethyl acetate, 1:1, vol.) showed the reaction to be

complete. The solution was treated with IR-120 (H^+) resin (100 g), decolorized with carbon, and reduced *in vacuo* to a solid. Recrystallization from absolute ethanol gave 85 g (80%): m.p. 180-181°C, $[\alpha]_D$ -67.2° (*c* 1.5, H_2O). Literature: m.p. 178-180°C, $[\alpha]_D$ -66.3° (H_2O) (60).

2-ACETOXYETHYL 2,3,4,6-TETRA-*O*-ACETYL-1-THIO-β-D-GLUCOPYRANOSIDE

2-Mercaptoethanol (10 mL) was dissolved in anhydrous methanol (100 mL), and potassium hydroxide (5.5 g) was added. Tetra-*O*-acetyl-α-D-glucosyl bromide (20 g) in chloroform (50 mL) was added dropwise over thirty minutes to the stirred alcohol solution. After four hours, sodium methoxide (1*M*, 5 mL) was added to ensure complete deacetylation. The reaction was followed by TLC (chloroform:ethyl acetate, 4:1, vol.). The reaction slurry was filtered and the filtrate was neutralized with aqueous acetic acid (1*N*) and reduced *in vacuo* to a solid. The solid was extracted with hot pyridine (2 x 50 mL), and the pyridine was filtered and cooled before acetic anhydride (50 mL) was added (59). After twelve hours, the acetylation solution was poured into ice water (200 mL), and the resultant mixture was extracted with chloroform (3 x 75 mL). The organic phase was washed with hydrocloric acid (1*N*, to neutrality, 4 x 300 mL) and water (1 x 300 mL), and reduced *in vacuo* to a thick syrup. Crystallization from absolute ethanol gave an average yield of 30% for four reactions. Product recrystallized from ethanol had: m.p. 106.0-106.5°C, $[\alpha]_D$ -32.0° (*c* 1.5, $CHCl_3$). Literature: m.p. 108.0-108.5°C, $[\alpha]_D$ -31.5° ($CHCl_3$) (61). The ^{13}C-NMR spectrum (Fig. 25, Appendix III) and mass spectra (Tables XXIX-XXXI, Appendix III) were consistent with the desired product.

2-HYDROXYETHYL 1-THIO-β-D-GLUCOPYRANOSIDE

2-Acetoxyethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (9.6 g) was dissolved in anhydrous methanol (50 mL), and sodium methoxide (1*M*, 5 mL) was added (53).

After twelve hours TLC (chloroform:ethyl acetate, 1:1, vol.) showed the deacetylation to be complete. The solution was deionized with MB-3 ion exchange resin (10 g), filtered, and reduced *in vacuo* to a thick syrup. Crystallization from absolute ethanol gave 4.5 g (87%): m.p. 115.5-116.5°C, $[\alpha]_D$ -54.9° (*c* 1.5, H_2O). Literature: m.p. 114-116°C, $[\alpha]_D$ -61.8° (H_2O) (61). The IR spectrum showed no absorbance in the 2600-2500 cm^{-1} region characteristic of S-H stretching (62). The ^{13}C-NMR spectrum (Fig. 26, Appendix III) was consistent with the desired product.

Anal. Calc. for $C_8H_{16}O_6S$: C, 40.00; H, 6.67; S, 13.33. Found: C, 40.03; H 6.62; S, 13.20.

SYNTHESIS OF 1,5-ANHYDRO-6-DEOXY-6-THIO-D-GLUCITOL

The synthetic route to 1,5-anhydro-6-deoxy-6-thio-D-glucitol (XXIX) is shown in Fig. 18. Compounds XXIX and XXX have been previously reported as by-products in the synthesis of 1,6-thioanhydro-D-glucitol (63). Unfortunately, the physical constants given in the literature differ significantly from those obtained in this study. Although the formation of the disulfide (XXVIII) was entirely unexpected, that was the only difficulty encountered during the synthesis. All of the intermediates have been thoroughly characterized, and the identity of the final product is believed to be well established.

1,5-Anhydro-2,3,4-tri-*O*-benzoyl-6-*O*-methanesulfonyl-D-glucitol

1,5-Anhydro-D-glucitol (5 g) was dissolved in anhydrous pyridine (100 mL). The solution was stirred at 0°C for thirty minutes, then methanesulfonyl chloride (2.4 mL, 1.0 equiv.) was added dropwise. This was allowed to warm to room temperature and stirred for three hours. Benzoyl chloride (16 mL, 4.5 equiv.) was added

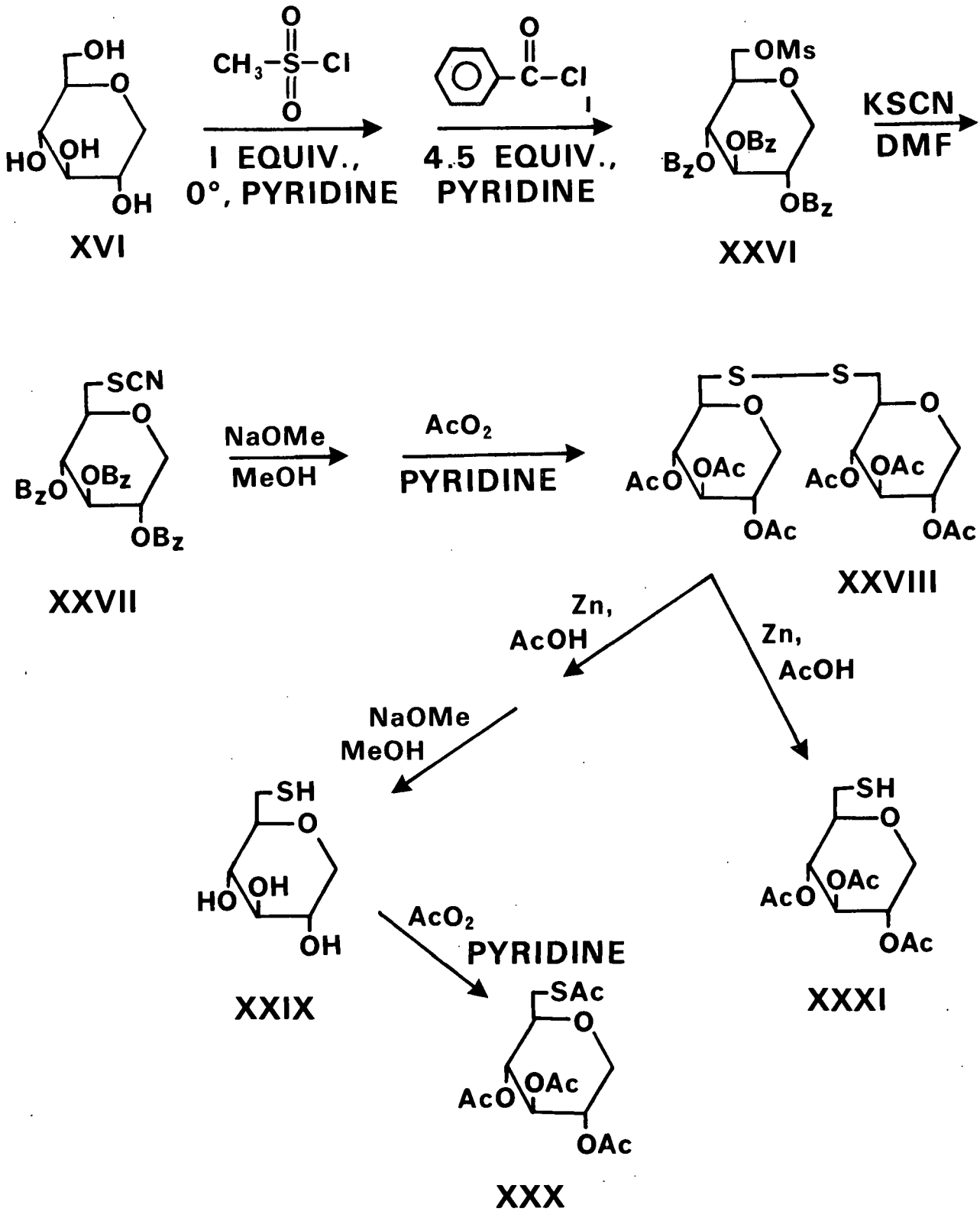


Figure 18. Synthetic route to 1,5-anhydro-6-deoxy-6-thio-D-glucitol.

dropwise, and the slurry was stirred for twelve hours. The reaction was followed by TLC (chloroform:ethyl acetate, 4:1, vol.). Chloroform (50 mL) was added, and the mixture was poured into ice water (300 mL). The aqueous phase was extracted with chloroform (2 x 50 mL), and the organic phase was washed with hydrochloric acid (1N, to neutrality, 6 x 150 mL), saturated sodium bicarbonate (1 x 150 mL), and water (1 x 150 mL); and reduced *in vacuo* to a thick syrup. Crystallization from absolute ethanol gave 10.8 g (64%). Product recrystallized from ethanol had: m.p. 127-127.5°C, $[\alpha]_D$ +12.6° (*c* 1.5, $CHCl_3$). The ^{13}C-NMR spectrum (Fig. 27, Appendix III) shows the C-6 peak at 68.7 ppm, compared to 62.1 ppm in 1,5-anhydro-D-glucitol (Fig. 24, Appendix III) and 63.0 ppm in 1,5-anhydro-2,3,4,6-tetra-*O*-benzoyl-D-glucitol (Fig. 28, Appendix III).

Anal. Calc for $C_{28}H_{26}O_{10}$ S: C, 60.65; H, 4.69, S, 5.78. Found: C, 60.93; H, 4.64; S, 5.87.

1,5-Anhydro-2,3,4-tri-*O*-benzoyl-6-deoxy-6-*S*-thiocyano-D-glucitol

1,5-Anhydro-2,3,4-tri-*O*-benzoyl-6-*O*-methanesulfonyl-D-glucitol (4 g) was dissolved in anhydrous DMF (50 mL), and dry potassium thiocyanate (3.5 g, 5 equiv.) was added. The reaction was stirred at 90°C for forty-eight hours, and followed by TLC (chloroform:ethyl acetate, 4:1, vol.). Upon completion, the reaction was stirred with ice water (200 mL). The resulting solid was recovered by filtration, washed with water (50 mL), and dissolved in chloroform (50 mL). The chloroform solution was washed with water (3 x 200 mL) and reduced *in vacuo* to a syrup. Crystals (3.2 g, 86%) were obtained with difficulty from methanol: m.p. 63-65°C, $[\alpha]_D$ +30.1° (*c* 1.5, $CHCl_3$). The IR spectrum showed an absorbance at 2157 cm^{-1} characteristic of the thiocyanate C≡N stretch (62). The ^{13}C-NMR spectrum (Fig. 29, Appendix III) shows the C-6 resonance shifted to 37.0 ppm.

Anal. Calc. for $C_{28}H_{23}O_7NS$: C, 64.99; H, 4.45; N, 2.71; S, 6.19. Found: C, 64.95; H, 4.55; N, 2.57; S, 5.94.

Di-1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol 6,6'-Disulfide

1,5-Anhydro-2,3,4-tri-O-benzoyl-6-deoxy-6-S-thiocyano-D-glucitol (3 g) was dissolved in methanol (100 mL), and sodium methoxide (1M, 1 mL) was added (53). The reaction was followed by TLC (chloroform:ethyl acetate, 1:1, vol.). After twenty-four hours the solution was deionized with MB-3 ion exchange resin (12 g), reduced in vacuo to a syrup, and purified by column chromatography (Merck Kieselgel 60, 70-230 mesh; 2.5 x 90 cm; eluent ethyl acetate:ethanol, 5:1, vol.). The desired fractions were combined, reduced in vacuo to a syrup, and dissolved in pyridine (30 mL) with acetic anhydride (15 mL) (59). After six hours the solution was stirred with ice water (100 mL) and extracted with chloroform (3 x 25 mL). The combined organics were washed with hydrochloric acid (1N, to neutrality, 3 x 100 mL) and water (100 mL), reduced in vacuo to a syrup, and crystallized from absolute ethanol to give 1.75 g (87%): m.p. 160.0-160.5°C, $[\alpha]_D$ +112.3° (c 1.5, $CHCl_3$). The mass spectra (Tables XXXII-XXXIV, Appendix III) were consistent with this product, the CI-MS showing peaks at 611 for M+1 and 551 for M-59, and the NCI-MS having a large peak at 304 for the monomer-1. The IR spectrum showed no absorbance characteristic of thiols at 2600-2500 cm^{-1} (62). The ^{13}C-NMR spectrum (Fig. 30, Appendix III) had the C-6 peak at 42.9 ppm.

Anal. Calc. for $C_{24}H_{34}O_{10}S$: C, 47.21; H, 5.57; S, 10.49. Found: C, 47.09; H, 5.61; S, 10.41.

1,5-Anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol

Di-1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol 6,6'-disulfide (1.5 g) was dissolved in glacial acetic acid (60 mL) at 75°C. Zinc dust (3 g) was added, and the reaction was stirred for three hours and followed by GLC (conditions C). After cooling, the reaction mixture was poured into water (300 mL) and extracted with chloroform (4 x 25 mL). The organics were washed with water (3 x 100 mL), reduced in vacuo to a syrup, and crystallized from absolute ethanol to give 0.6 g (80%): m.p. 94.5-96.5°C, $[\alpha]_D$ +65.1° (c 1.5, $CHCl_3$). The mass spectra (Tables XXXV-XXXVII, Appendix III) indicate the correct molecular weight. The CI-MS had peaks at 307 for M+1 and 247 for M-59. The ^{13}C-NMR spectrum (Fig. 31, Appendix III) showed the C-6 resonance at 27.3 ppm.

1,5-Anhydro-6-deoxy-6-thio-D-glucitol

Di-1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol 6,6'-disulfide (4.5 g) was dissolved in glacial acetic acid (150 mL) and zinc dust (3 g) was added. The slurry was stirred at 75°C for 8 hours, more zinc dust was added (3.0 g), and it stirred for 16 hours. The reaction mixture was cooled, poured into water (350 mL), and extracted with chloroform (3 x 75 mL). The combined organics were washed with saturated sodium bicarbonate (to neutrality, 3 x 100 mL) and water (2 x 100 mL); reduced in vacuo to a syrup; dissolved in anhydrous methanol (150 mL); and sodium methoxide (1M, 25 mL) was added (53). After 5 hours TLC (chloroform, ethyl acetate, 10:1, vol.) showed the deacetylation to be complete. The solution was deionized with IR-120 (H^+) resin (25 g); filtered; reduced in vacuo to a syrup; and purified by column chromatography (Merck Kieselgel 60, 70-230 mesh; 2.5 x 90 cm; eluent ethyl acetate:chloroform, 5:1, vol.). The desired fractions were combined, reduced in vacuo to a solid, and crystallized from a small amount of absolute ethanol (5 mL) to give 0.75 g (56%): m.p. 99.5-101.0°C, $[\alpha]_D$ +53.7° (c 1.5, H_2O). Literature:

(Syrup); $[\alpha]_D$ -15° (c 1, CH_3OH) (63). The infrared spectrum showed an absorbance at 2536 cm^{-1} characteristic of thiols (62). The ^{13}C-NMR spectrum (Fig. 32, Appendix III) showed the C-6 peak at 26.5 ppm.

Anal. Calc. for $C_6H_{12}O_4S$: C, 40.00; H, 6.67; S, 17.78. Found: C, 40.07; H, 6.78; S, 17.26.

1,5-Anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-S-acetyl-D-glucitol

The mother liquor from the crystallization of 1,5-anhydro-6-deoxy-6-thio-D-glucitol was reduced in vacuo to dryness, and dissolved in pyridine (10 mL) with acetic anhydride (5 mL) (59). After 12 hours the solution was stirred with ice water (50 mL) and extracted with chloroform (3 x 20 mL). The combined organics were washed with hydrochloric acid (1N, to neutrality, 3 x 25 mL) and water (25 mL); reduced in vacuo to a syrup; and crystallized from absolute ethanol to give 0.8 g: m.p. 87.5-88.5°C, $[\alpha]_D$ +29.9° (c 1.5, $CHCl_3$). Literature: (Syrup); $[\alpha]_D$ +60° (c 1, $CHCl_3$) (63). The infrared spectrum showed an absorbance at 1694 cm^{-1} characteristic of the C=O stretch in an S-acetyl linkage (62). The mass spectra (Tables XXXVIII-XL, Appendix III) gave the correct molecular weight. The CI-MS featured peaks at 349 for M+1 and 289 for M-59. The ^{13}C-NMR spectrum is included in Appendix III (Fig. 33).

Anal. Calc. for $C_{14}H_{20}O_8S$: C, 48.28; H, 5.75; S, 9.20. Found: C, 48.10; H, 5.81; S, 9.06.

PROCEDURES FOR KINETIC ANALYSIS

THE REACTOR SYSTEM

The degradation experiments were carried out in a reactor system developed by Brandon, et al. (37). The reactor was a 316 stainless steel bomb with an internal volume of 140 mL (Fig. 19). The removable top was fitted with two Gyrolok connectors (replaced every fourth run), permitting a sample line and a thermocouple to enter the reactor. A pressure seal was obtained by compressing a Teflon sealing ring (replaced every other run) with heat-treated retaining bolts (tightened to about 7 ft-lb, replaced every fourth run).

Whereas samples from soda cooks were colorless, those from kraft cooks were blue-green in color, and formed a blue-gray precipitate on standing. The precipitate was identified by Energy Dispersive X-ray Analysis as ferric sulfide. Sarkanen, et al., (64) studied sulfide corrosion of stainless steel, and his data suggested that the amount of sulfide consumed should be less than 0.5% in this system. Measurements were made of ferric sulfide formation by heating kraft liquors, without carbohydrates, to 170 and 180°C. Substantially less ferric sulfide than expected was formed, probably due to "pickling" of the reactor surfaces during previous reactions. Sodium sulfide analyses before and after the cooks showed no measurable change in the concentration. Therefore, ferric sulfide formation is thought not to affect the reaction kinetics.

The sealed reactor was attached to a movable rack on the oil bath (ca. 3.5 gal, HTF-100 high temperature fluid, Curtin Matheson Scientific). Lowering the rack positioned the reactor in the fluid and over a mechanically driven magnetic stirrer. The bath was heated by three 500 watt knife heaters. Two were constantly heating, while the third was switched by a fixed point thermostat (J. L. Stortz TH-606A)

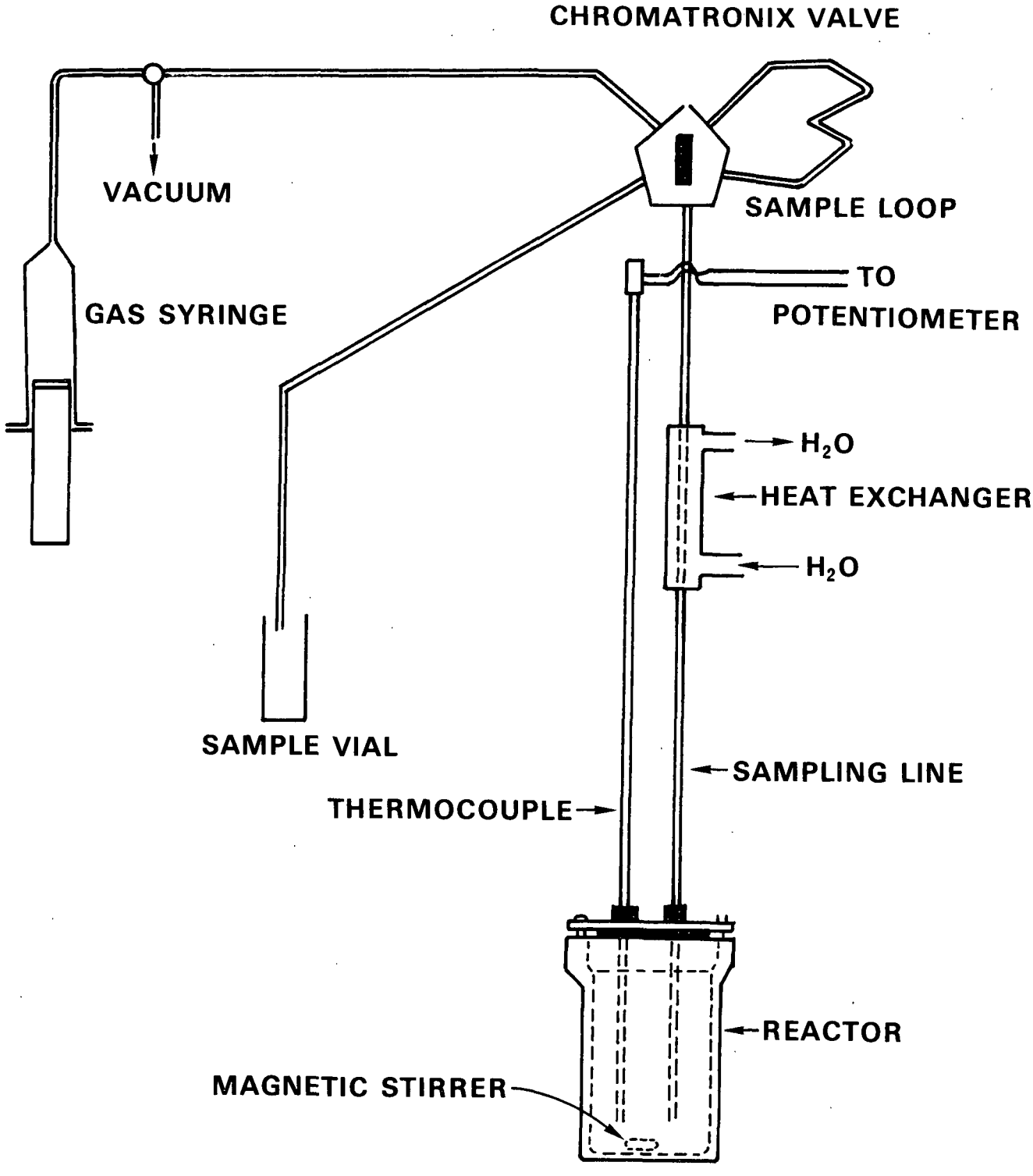


Figure 19. The reactor and its sampling system (37).

operating through an electronic relay. The power to all three heaters was supplied through an Over-Temp Guard (Instruments for Industry and Research). An overhead stirrer circulated the fluid.

The temperature of the reaction solution was measured with an Inconel clad iron-constantan thermocouple (Omega ICIN-18G-12) connected through an electronic cold junction compensator (Omega CJ-J) to a precision potentiometer (Leeds and Northrup 8691-2). To obtain a continuous record of the temperature, the thermocouple was connected to a strip chart recorder (1 mv range) using an adjustable bucking circuit (37) to reduce the thermocouple output to match the recorder's range.

The reactor sample line was a 1/8 inch 304 stainless steel capillary tube (0.025 inch ID), which passed through a small heat exchanger (3 x 0.5 inch) and connected to a Chromatronix eight port, two position sampling valve (Laboratory Data Control) (see Fig. 19). The valve was connected so that in one position the reactor was isolated, and the gas syringe, sample loop, and the line to the sample vial were contiguous. In the other valve position, the reactor and the sample loop were connected, but isolated from the rest of the system. The sample loop then filled until the pressure at the head of the loop was equal to the pressure in the reactor. When the valve was returned to its original position, the syringe could be used to push the sample into a tared vial.

PREPARATION OF SOLUTIONS

Solutions used for the kinetic experiments were prepared in a glove bag in which the air had been replaced with nitrogen using a deflation-inflation cycle repeated three times. The solutions were used the same day they were made.

Standard solutions of 2.0M sodium hydroxide (250 mL) and 0.9M sodium sulfide (for kraft cooks only, 100 mL) were prepared from their respective stock solutions according to Eq. (28):

$$X = M_S V_S \rho / M \tag{28}$$

where X = weight of stock solution required, g

M_S = desired molarity of standard solution, mol L^{-1}

V_S = desired volume of standard solution, mL

ρ = density of stock solution, g mL^{-1}

M = molarity of stock solution, mol L^{-1}

The desired amount of stock solution was weighed into the tared volumetric flask and diluted with oxygen-free water. The flask was weighed, and the density of the standard solution calculated. The molarity of the sodium hydroxide solution was determined by titration against potassium acid phthalate using phenolphthalein indicator. The concentration of the sodium sulfide solution was found by diluting each of two 10 mL samples to 100 mL with oxygen-free water. These samples were titrated with 0.100M mercuric chloride (42).

The reaction solutions were prepared in a similar manner, except that the thermal expansion of the solvent had to be accounted for. The volume expansivity factor, F_V, was defined as the ratio of the volume of water at reaction temperature to its volume at room temperature:

$$F_V = V_T / V_{RT} \tag{29}$$

This definition assumes that a solution will show the same expansivity as a pure solvent. The expansivity factor was calculated from the steam tables (65) based on the observed oil bath temperature and room temperature. Thus, Eq. (28) becomes:

$$X_S = M_R V_R \rho_S / M_S \quad (30)$$

where X_S = weight of standard solution required, g

M_R = desired molarity of reaction solution, mol L^{-1}

V_R = volume of reaction solution at temperature, mL

ρ_S = density of standard solution, g mL^{-1}

M_S = molarity of standard solution, mol L^{-1}

and the analagous equation for solid additives is:

$$Y = M_R V_R W_M \quad (31)$$

where Y = weight of compound required, g

W_M = molecular weight of compound

Soda reaction solutions were prepared by weighing the desired amount of sodium tosylate into a tared 100 mL volumetric flask outside of the glove bag, and purging it with nitrogen in a vacuum oven. In the glove bag, sodium hydroxide was added and the solution was diluted with oxygen-free water. The flask was weighed and the density calculated, but it was not possible to titrate sodium tosylate solutions.

Kraft reaction solutions were prepared in the glove bag by taring a 250 mL volumetric flask, and weighing in the desired amounts of standard sodium hydroxide and standard sodium sulfide [Eq. (30)]. The solution was diluted with oxygen-free water, the flask was weighed, and the density calculated. The sodium sulfide concentration was determined by titrating 10 mL aliquots of the reaction solution with 0.100M mercuric chloride (42). The sodium hydroxide concentration was found by titrating 10 mL aliquots with 1.0M hydrochloric acid in the presence of formaldehyde (44) to the phenolphthalein endpoint.

LOADING THE REACTOR

The reactor parts were buffed with steel wool, rinsed in acetone, and washed with soapy water. They were thoroughly rinsed with distilled water and allowed to dry. All of the parts except the thermocouple and the sample line were placed in a desiccator and heated under vacuum at 105°C for twelve hours to desorb oxygen (37). In the glove bag, the reactor was removed from the desiccator and the reaction solution (100 mL, determined gravimetrically) and the desired amount of carbohydrate [sufficient for 0.01 or 0.02M solutions, Eq. (31)] were added to it. The reactor was then sealed, and removed to the oil bath.

SAMPLING THE REACTOR

Ten sampling times were scheduled over two half-lives of the reaction. After the reactor had come to temperature (ca. 20 min), the sampling system was purged by drawing two samples which were discarded. At each sampling time, the system was purged (one sample) and the desired number of samples were collected in tared 4-mL vials. The vials were weighed to determine the exact amount of sample. The sample loop was then washed with water and dried by applying a vacuum to one end (Fig. 19).

Samples of about 1 mL were taken from reactions with an initial sugar concentration of 0.01M. These reactions were analyzed for neutral carbohydrates only. Reactions with an initial concentration of 0.02M were subject to both carbohydrate and methanol analysis. In this case, samples of about 0.5 mL in size were taken. At each sampling time, duplicate samples were taken for carbohydrate analysis, but only one sample was taken for methanol analysis at any time.

Calculations showed that 30 mL could be withdrawn from the reactor without changing the concentration of nonvolatiles by more than 0.2%. The concentrations

of volatile products could also have been affected by changes in the reactor headspace. However, an experiment at 180°C involving 100 mL of a kraft solution containing methanol and methyl mercaptan showed no change in the observed concentrations as 50 mL of liquor was removed (Table XLII, Appendix IV). In practice, no more than 30 mL was withdrawn during a kinetic experiment.

GLC ANALYSIS

Isopropanol (0.1M, 1 drop, ca. 0.05 g) was added to each sample destined for methanol analysis, and the vial was weighed to determine the exact amount of internal standard added. The sample was immediately analyzed by GLC as described earlier.

2-Hydroxyethyl 1-thio-β-D-glucopyranoside (0.005M, 1 mL, ca. 1 g) was added to one of the duplicate carbohydrate samples, and the vial was weighed to determine the amount of internal standard added. Both samples were then stored in a refrigerator.

The carbohydrate samples containing internal standard were deionized by passing them through a column of MB-3 mixed bed ion exchange resin (5 mL, 1.5 x 3 cm) and eluting with water (10 mL). If the reaction solution contained sodium tosylate, the thymolphthalein indicator tended to wash off the MB-3 resin. This interfered with the 1,5-anhydrocellobiitol peak in the GLC. Therefore, the eluent was passed through the same resin bed again to remove the dye, and was eluted with water (10 mL).

The choice of ion exchange resin is critical, since some resins (Amberlite MB-1, Baker M-614) were found to contain sufficiently strong base functionalities to ionize the weakly acidic carbohydrates. This makes it impossible to completely rinse the carbohydrates off the resin. However, the carbohydrates were cleanly eluted from the MB-3 resin, and response factors obtained with MB-3 did not differ significantly from those obtained when ion exchange resin was not used. The MB-3

resin does adsorb the more acidic 1,5-anhydro-6-deoxy-6-thio-D-glucitol, however, so only IR-120 (H^+) resin was used to deionize samples in the search for thio sugars.

The deionized reaction samples were then dried *in vacuo* in 25-mL Erlenmeyer flasks. They were acetylated with anhydrous pyridine (0.66 mL) and distilled acetic anhydride (0.33 mL) overnight (59). The reaction was quenched with water (10 mL), and the solution was extracted with distilled chloroform (2 x 5 mL). The combined organics were washed with hydrochloric acid (1N, 10 mL) and water (2 x 10 mL); reduced *in vacuo* to dryness; transfered to a 4-mL vial with distilled chloroform (*ca.* 2 mL); and reduced *in vacuo* to dryness. The sample was taken up in a few drops of distilled chloroform and analyzed by GLC as described earlier.

Equation (32) was used by the Sigma 10 to calculate the concentration of compound X in each injected sample:

$$M_X = \frac{A_X}{A_{IS}} M_{IS} \frac{W_{IS}}{\rho_{IS}} \frac{\rho_X}{W_X} F_X \qquad (32)$$

where M_X = molarity of compound X, mol L^{-1}

A_X = peak area of compound X

W_X = weight of the reaction sample, g

ρ_X = density of the reaction sample, g L^{-1}

IS = internal standard

Computer programs which calculated average values for the GLC analyses and corrected for the volume expansivity at reaction temperature (see Preparation of Solutions) are presented in Appendix I. The programs then used pseudo-first-order rate expressions and linear regression techniques to evaluate the concentration-time data and obtain pseudo-first-order rate constants for each reaction.

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APPENDIX I

PROGRAM 1

```
$RESET FREE
C
C                LINEAR REGRESSION PROGRAM
C         FOR THE ANALYSIS OF PSEUDO-FIRST ORDER REACTIONS
C
C                        BY D. BLYTHE
C
C     THIS PROGRAM IS DESIGNED TO GENERATE PSEUDO-FIRST ORDER
C     RATE CONSTANTS AND THEIR 95% CONFIDENCE LIMITS DIRECTLY
C     FROM RAW CONCENTRATION MEASUREMENTS.  THE INPUT DATA
C     CONSISTS OF THE SAMPLE TIME (IN MINUTES), THE NUMBER
C     OF CONCENTRATION MEASUREMENTS AT THAT TIME, AND THEN
C     UP TO SIX INDIVIDUAL CONCENTRATION MEASUREMENTS
C     UP TO TWENTY SAMPLE TIMES MAY BE USED.
C
C     THE OUTPUT CONSISTS OF A TABLE SHOWING EACH SAMPLE
C     TIME (IN SECONDS), THE MEAN CONCENTRATION (AT TEMPERATURE),
C     THE CALCULATED (REGRESSION) CONCENTRATION, AND THE
C     DIFFERENCE BETWEEN THE TWO CONCENTRATIONS.
C     THE OUTPUT ALSO INCLUDES THE SLOPE (AND IT'S 95%
C     CONFIDENCE INTERVAL), THE INTERCEPT, AND THE CORRELATION
C     COEFFICIENT FOR THE LEAST-SQUARES REGRESSION LINE.
C
C     THE DATA DECK CONSISTS OF THE FOLLOWING RECORDS:
C     A LEAD RECORD GIVING THE TEMPERATURE OF THE REACTION
C     AND IT'S VOLUME EXPANSIVITY FACTOR (THE RATIO OF VOLUME
C     AT REACTION TEMPERATURE TO VOLUME AT ROOM TEMPERATURE),
C     THEN UP TO 20 DATA RECORDS, AND AN END RECORD OF 0,0,0.
C
C     IF THE OUTPUT IS TO BE DIRECTED TO THE PRINTER,
C     THEN REMOVE THE COMMENT CHARACTER FROM:
CFILE  6(KIND=PRINTER,MYUSE=OUT,MAXRECSIZE=22)
C     AND COMPILE WITH FORTRAN.
C
      INTEGER NO,X,Y,I,N
      REAL TMIN,CONC(6),TSEC(20),AVG,CHI(20),POINT(20),TEMP,TFACT
      REAL SUMX,SUMX2,SUMY,SUMY2,SUMXY,M,B,DENOM,CC
      REAL SSY,SSX,SSXY,THETA,ERROR,T(20),CALC(20),DIFF(20)
      READ(5,/)TEMP,TFACT
9000  FORMAT(2F10.4)
      WRITE(6,9001)TEMP
9001  FORMAT(1H /,'   THE TEMPERATURE OF THE REACTION WAS ',F8.2,/)
      Y=1
      X=1
C     THIS LOOP FINDS THE MEAN OBSERVED CONCENTRATIONS
C     NO IS THE NUMBER OF RAW CONCENTRATION MEASUREMENTS
 1    READ (5,/) TMIN,NO,(CONC(I),I=1,NO)
9002  FORMAT(F10.1,I4,6F10.9)
```

```
C     THIS TESTS FOR THE LAST DATA CARD
      IF(NO)9,9,2
2     TSEC(X)=TMIN*60.
      X=X+1
      AVG=0.
      DO 3 I=1,NO
3     AVG=CONC(I)+AVG
C     CHI IS THE MEAN OBSERVED CONCENTRATION
      CHI(Y)=(AVG/NO)/TFACT
      POINT(Y)=ALOG(CHI(Y))
      Y=Y+1
      GO TO 1
C     N IS THE NUMBER OF SAMPLING TIMES (DATA CARDS)
9     N=Y-1
      WRITE(6,9003)N
9003  FORMAT(1H /,'   THE NUMBER OF DATA POINTS IS ',I5,/)
C     THIS SECTION FINDS THE REGRESSION PARAMETERS
      SUMX=0.
      SUMX2=0.
      SUMY=0.
      SUMY2=0.
      SUMXY=0.
      DO 10 I=1,N
      SUMX=TSEC(I)+SUMX
      SUMX2=TSEC(I)*TSEC(I)+SUMX2
      SUMY=POINT(I)+SUMY
      SUMY2=POINT(I)*POINT(I)+SUMY2
10    SUMXY=TSEC(I)*POINT(I)+SUMXY
C     CC IS THE CORRELATION COEFFICIENT
      DENOM=((SUMX2-(SUMX*SUMX)/N)*(SUMY2-(SUMY*SUMY)/N))**.5
      CC=(SUMXY-(SUMX*SUMY)/N)/DENOM
C     B IS THE INTERCEPT
      B=(SUMX2*SUMY-SUMX*SUMXY)/(N*SUMX2-SUMX*SUMX)
C     M IS THE SLOPE
      M=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX*SUMX)
C     THIS SECTION FINDS THE CONFIDENCE INTERVAL ON THE SLOPE
      SSY=SUMY2-(SUMY*SUMY/N)
      SSX=SUMX2-(SUMX*SUMX/N)
      SSXY=SUMXY-(SUMX*SUMY/N)
      THETA=((SSY-M*SSXY)/N)**.5
C     THIS IS A TABLE OF STUDENT'S T VALUES AT THE 0.95 LEVEL
      T(1)=12.706
      T(2)=4.303
      T(3)=3.182
      T(4)=2.776
      T(5)=2.571
      T(6)=2.447
      T(7)=2.365
      T(8)=2.306
      T(9)=2.262
      T(10)=2.228
      T(11)=2.201
```

```
      T(12)=2.179
      T(13)=2.160
      T(14)=2.145
      T(15)=2.131
      T(16)=2.120
      T(17)=2.110
      T(18)=2.101
      T(19)=2.093
      T(20)=2.086
      ERROR=T(N-2)*THETA*((N/((N-2)*SSX))**.5)
C     THIS CALCULATES THE REGRESSION CONCENTRATIONS
      DO 30 I=1,N
      CALC(I)=EXP(M*TSEC(I)+B)
30    DIFF(I)=CHI(I)-CALC(I)
C     THIS SECTION WRITES THE OUTPUT DATA
      WRITE(6,9004)
9004  FORMAT('   SECONDS    CONCENTRATION    CALC. CONC.    DIFFERENCE')
      WRITE(6,9005)(TSEC(I),CHI(I),CALC(I),DIFF(I),I=1,N)
9005  FORMAT(F10.1,3F15.6)
      WRITE(6,9006)M
9006  FORMAT(1H /,'   THE SLOPE OF THE REGRESSION LINE IS',E12.4,/)
      WRITE(6,9007)ERROR
9007  FORMAT('   THE CONFIDENCE INTERVAL ON THE SLOPE IS',E12.4,/)
      WRITE(6,9008)B
9008  FORMAT('   THE INTERCEPT OF THE LINE IS',E12.4,/)
      WRITE(6,9009)CC
9009  FORMAT('   THE CORRELATION COEFFICIENT IS  ',F6.4,/)
      STOP
      END
```

PROGRAM 2

```
$RESET FREE
C
C                LINEAR REGRESSION PROGRAM
C       FOR ANALYSIS OF THE FORMATION OF REACTION PRODUCTS
C
C                        BY D. BLYTHE
C
C     THIS PROGRAM IS DESIGNED TO GENERATE PSEUDO-FIRST ORDER
C     RATE CONSTANTS AND THEIR 95% CONFIDENCE LIMITS DIRECTLY
C     FROM RAW CONCENTRATION MEASUREMENTS.  THE INPUT DATA
C     CONSISTS OF THE SAMPLE TIME (IN MINUTES), THE NUMBER
C     OF CONCENTRATION MEASUREMENTS AT THAT TIME, AND THEN
C     UP TO SIX INDIVIDUAL CONCENTRATION MEASUREMENTS.
C     A MAXIMUM OF TWENTY SAMPLE TIMES MAY BE USED.
C
C     THE OUTPUT CONSISTS OF A TABLE SHOWING EACH SAMPLE
C     TIME (IN SECONDS), THE MEAN CONCENTRATION (AT TEMPERATURE),
C     THE CALCULATED (REGRESSION) CONCENTRATION, AND THE
C     DIFFERENCE BETWEEN THE TWO CONCENTRATIONS.
C     THE OUTPUT ALSO INCLUDES THE SLOPE (AND IT'S 95%
C     CONFIDENCE INTERVAL), THE INTERCEPT, AND THE CORRELATION
C     COEFFICIENT FOR THE LEAST-SQUARES REGRESSION LINE.
C
C
C     THE DATA DECK CONSISTS OF THE FOLLOWING RECORDS:
C     A RECORD GIVING THE TEMPERATURE AND VOLUME EXPANSIVITY
C     FACTOR FOR THE REACTION, THE INITIAL CONCENTRATION OF
C     REACTANT (AT REACTION TEMPERATURE), AND THE REACTANT'S RATE
C     OF DISAPPEARANCE (IN MOLES/LITER); THEN UP TO 20 DATA CARDS;
C     AND AN END RECORD OF 0,0,0.
C
C     NOTE - THE FIRST DATA CARD MUST BE THE TIME ZERO
C     CARD, EVEN IF THE CONCENTRATION OF THE PRODUCT IS ZERO.
C
C     IF THE OUTPUT IS TO BE DIRECTED TO THE PRINTER,
C     THEN REMOVE THE COMMENT CHARACTER FROM:
CFILE  6(KIND=PRINTER,MYUSE=OUT,MAXRECSIZE=22)
C     AND COMPILE WITH FORTRAN.
C
      INTEGER NO,X,Y,I,N
      REAL TMIN,CONC(6),TSEC(20),AVG,CHI(20),POINT(20),TEMP,TFACT
      REAL SUMX,SUMX2,SUMY,SUMY2,SUMXY,M,B,DENOM,CC,R,KR,XVAL(20)
      REAL SSY,SSX,SSXY,THETA,ERROR,T(20),CALC(20),DIFF(20)
      READ(5,/)TEMP,TFACT,R,KR
9000  FORMAT(4F10.9)
      WRITE(6,9001)TEMP
9001  FORMAT(1H /,'   THE TEMPERATURE OF THE REACTION WAS ',F8.2,/)
      WRITE(6,9002)R
9002  FORMAT('   THE INITIAL REACTANT CONCENTRATION WAS ',F8.4,/)
      WRITE(6,9003)KR
9003  FORMAT('   THE RATE OF DISAPPEARANCE OF REACTANT WAS ',E12.4,/)
```

```
      Y=1
      X=1
C     THIS LOOP FINDS THE MEAN OBSERVED CONCENTRATIONS
C     NO IS THE NUMBER OF RAW CONCENTRATION MEASUREMENTS
 1    READ (5,/) TMIN,NO,(CONC(I),I=1,NO)
9004  FORMAT(F10.1,I4,6F10.9)
C     THIS TESTS FOR THE LAST DATA CARD
      IF(NO)9,9,2
2     TSEC(X)=TMIN*60.
      XVAL(X)=(R/KR)*(1.-EXP(-KR*TSEC(X)))
      X=X+1
      AVG=0.
      DO 3 I=1,NO
3     AVG=CONC(I)+AVG
C     CHI IS THE MEAN OBSERVED CONCENTRATION
      CHI(Y)=(AVG/NO)/TFACT
      POINT(Y)=CHI(Y)-CHI(1)
      Y=Y+1
      GO TO 1
C     N IS THE NUMBER OF SAMPLING TIMES (DATA CARDS)
9     N=Y-1
      WRITE(6,9005)N
9005  FORMAT(1H /,'   THE NUMBER OF DATA POINTS IS ',I5,/)
C     THIS SECTION FINDS THE REGRESSION PARAMETERS
      SUMX=0.
      SUMX2=0.
      SUMY=0.
      SUMY2=0.
      SUMXY=0.
      DO 10 I=1,N
      SUMX=XVAL(I)+SUMX
      SUMX2=XVAL(I)*XVAL(I)+SUMX2
      SUMY=POINT(I)+SUMY
      SUMY2=POINT(I)*POINT(I)+SUMY2
10    SUMXY=XVAL(I)*POINT(I)+SUMXY
C     CC IS THE CORRELATION COEFFICIENT
      DENOM=((SUMX2-(SUMX*SUMX)/N)*(SUMY2-(SUMY*SUMY)/N))**.5
      CC=(SUMXY-(SUMX*SUMY)/N)/DENOM
C     B IS THE INTERCEPT
      B=(SUMX2*SUMY-SUMX*SUMXY)/(N*SUMX2-SUMX*SUMX)
C     M IS THE SLOPE
      M=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX*SUMX)
C     THIS SECTION FINDS THE CONFIDENCE INTERVAL ON THE SLOPE
      SSY=SUMY2-(SUMY*SUMY/N)
      SSX=SUMX2-(SUMX*SUMX/N)
      SSXY=SUMXY-(SUMX*SUMY/N)
      THETA=((SSY-M*SSXY)/N)**.5
C     THIS IS A TABLE OF STUDENT'S T VALUES AT THE 0.95 LEVEL
      T(1)=12.706
      T(2)=4.303
      T(3)=3.182
      T(4)=2.776
      T(5)=2.571
```

```
      T(6)=2.447
      T(7)=2.365
      T(8)=2.306
      T(9)=2.262
      T(10)=2.228
      T(11)=2.201
      T(12)=2.179
      T(13)=2.160
      T(14)=2.145
      T(15)=2.131
      T(16)=2.120
      T(17)=2.110
      T(18)=2.101
      T(19)=2.093
      T(20)=2.086
      ERROR=T(N-2)*THETA*((N/((N-2)*SSX))**.5)
C     THIS CALCULATES THE REGRESSION CONCENTRATIONS
      DO 30 I=1,N
      CALC(I)=M*XVAL(I)+B+CHI(1)
30    DIFF(I)=CHI(I)-CALC(I)
C     THIS SECTION WRITES THE OUTPUT DATA
      WRITE(6,9006)
9006  FORMAT('   SECONDS    CONCENTRATION    CALC. CONC.    DIFFERENCE')
      WRITE(6,9007)(TSEC(I),CHI(I),CALC(I),DIFF(I),I=1,N)
9007  FORMAT(F10.1,3F15.6)
      WRITE(6,9008)M
9008  FORMAT(1H /,'   THE SLOPE OF THE REGRESSION LINE IS',E12.4,/)
      WRITE(6,9009)ERROR
9009  FORMAT('   THE CONFIDENCE INTERVAL ON THE SLOPE IS',E12.4,/)
      WRITE(6,9010)B
9010  FORMAT('   THE INTERCEPT OF THE LINE IS',E12.4,/)
      WRITE(6,9011)CC
 9011 FORMAT('   THE CORRELATION COEFFICIENT IS  ',F6.4,/)
      STOP
      END
```

PROGRAM 3

```
$RESET FREE
C
C                  LINEAR REGRESSION PROGRAM
C          FOR THE ANALYSIS OF REACTIVE INTERMEDIATES
C
C                          BY D. BLYTHE
C
C     THIS PROGRAM IS DESIGNED TO GENERATE A PSEUDO-FIRST ORDER
C     RATE CONSTANT FOR THE FORMATION OF LEVOGLUCOSAN DURING
C     HIGH TEMPERATURE ALKALINE DEGRADATIONS.  THE INPUT DATA
C     CONSISTS OF THE SAMPLE TIME (IN MINUTES), THE NUMBER OF
C     CONCENTRATION MEASUREMENTS AT THAT TIME, AND THEN UP TO
C     SIX INDIVIDUAL CONCENTRATION MEASUREMENTS.  A MAXIMUM OF
C     TWENTY SAMPLE TIMES MAY BE USED.
C
C     THE OUTPUT CONSISTS OF A TABLE SHOWING THE SAMPLE
C     TIME (IN SECONDS), THE MEAN CONCENTRATION (AT TEMPERATURE),
C     THE CALCULATED (REGRESSION) CONCENTRATION, AND THE
C     DIFFERENCE BETWEEN THE TWO CONCENTRATIONS.  THE
C     OUTPUT ALSO INCLUDES THE SLOPE (AND IT'S 95% CONFIDENCE
C     INTERVAL), THE INTERCEPT, AND THE CORRELATION COEFFICIENT
C     FOR THE LEAST SQUARES REGRESSION LINE.
C
C     THE DATA DECK CONSISTS OF THE FOLLOWING RECORDS:
C     A LEAD RECORD GIVING THE REACTION TEMPERATURE, THE
C     VOLUME EXPANSIVITY FACTOR, AND THE RATE OF DEGRADATION
C     OF LEVO AND OF THE REACTANT UNDER THE REACTION
C     CONDITIONS (IN SEC -1); THEN UP TO 20 DATA CARDS; AND
C     AN END RECORD OF 0,0,0.
C
C  *** IMPORTANT - THE FIRST DATA CARD MUST BE THE TIME ZERO CARD
C     SHOWING REACTANT CONCENTRATION MEASUREMENTS, AND THE SECOND
C     CARD MUST BE TIME ZERO LEVO MEASUREMENTS.  THE REST
C     OF THE LEVO MEASUREMENTS THEN FOLLOW IN ANY ORDER.
C
C     IF THE OUTPUT IS TO BE DIRECTED TO THE PRINTER,
C     THEN REMOVE THE COMMENT CHARACTER FROM:
CFILE  6(KIND=PRINTER,MYUSE=OUT,MAXRECSIZE=22)
C     AND COMPILE WITH FORTRAN.
C
      INTEGER NO,A,I,N
      REAL TMIN,CONC(6),TSEC(20),AVG,CHI(20),X(20),Y(20),KD,KR
      REAL SUMX,SUMX2,SUMY,SUMY2,SUMXY,M,B,DENOM,CC,TEMP,TFACT
      REAL SSY,SSX,SSXY,THETA,ERROR,T(20),CALC(20),DIFF(20),CLC(20)
      READ(5,/)TEMP,TFACT,KD,KR
9000  FORMAT(4F10.9)
      WRITE(6,9001)TEMP
9001  FORMAT(1H /,'   THE TEMPERATURE OF THE REACTION WAS ',F8.2,/)
      WRITE(6,9002)KD
9002  FORMAT('   THE RATE OF DISAPPEARANCE OF LEVO WAS ',E10.4,/)
      WRITE(6,9003)KR
```

```
 9003 FORMAT('   THE RATE OF DISAPPEARANCE OF REACTANT WAS ',E10.4,/)
C     THIS LOOP FINDS THE MEAN OBSERVED CONCENTRATIONS
C     NO IS THE NUMBER OF RAW CONCENTRATION MEASUREMENTS
      A=1
 1    READ (5,/) TMIN,NO,(CONC(I),I=1,NO)
 9004 FORMAT(F10.1,I4,6F10.9)
C     THIS TESTS FOR THE LAST DATA CARD
      IF(NO)9,9,2
2     TSEC(A)=TMIN*60.
      AVG=0.
      DO 3 I=1,NO
 3    AVG=CONC(I)+AVG
C     CHI IS THE MEAN OBSERVED CONCENTRATION
      CHI(A)=(AVG/NO)/TFACT
      A=A+1
      GO TO 1
C     N IS THE NUMBER OF SAMPLING TIMES (DISCOUNTING T ZERO)
9     A=A-1
      N=A-1
      WRITE(6,9005)N
 9005 FORMAT(1H /,'   THE NUMBER OF DATA POINTS IS ',I5,/)
      DO 10 I=2,A
      X(I)=(CHI(1)/(KD-KR))*(EXP(-KR*TSEC(I))-EXP(-KD*TSEC(I)))
 10   Y(I)=CHI(I)-CHI(2)*EXP(-KD*TSEC(I))
C     THIS SECTION FINDS THE REGRESSION PARAMETERS
      SUMX=0.
      SUMX2=0.
      SUMY=0.
      SUMY2=0.
      SUMXY=0.
      DO 20 I=2,A
      SUMX=X(I)+SUMX
      SUMX2=X(I)*X(I)+SUMX2
      SUMY=Y(I)+SUMY
      SUMY2=Y(I)*Y(I)+SUMY2
20    SUMXY=X(I)*Y(I)+SUMXY
C     CC IS THE CORRELATION COEFFICIENT
      DENOM=((SUMX2-(SUMX*SUMX)/N)*(SUMY2-(SUMY*SUMY)/N))**.5
      CC=(SUMXY-(SUMX*SUMY)/N)/DENOM
C     B IS THE INTERCEPT
      B=(SUMX2*SUMY-SUMX*SUMXY)/(N*SUMX2-SUMX*SUMX)
C     M IS THE SLOPE
      M=(N*SUMXY-SUMX*SUMY)/(N*SUMX2-SUMX*SUMX)
C     THIS SECTION FINDS THE CONFIDENCE INTERVAL ON THE SLOPE
      SSY=SUMY2-(SUMY*SUMY/N)
      SSX=SUMX2-(SUMX*SUMX/N)
      SSXY=SUMXY-(SUMX*SUMY/N)
      THETA=((SSY-M*SSXY)/N)**.5
C     THIS IS A TABLE OF STUDENT'S T VALUES AT THE 0.95 LEVEL
      T(1)=12.706
      T(2)=4.303
      T(3)=3.182
      T(4)=2.776
```

```
      T(5)=2.571
      T(6)=2.447
      T(7)=2.365
      T(8)=2.306
      T(9)=2.262
      T(10)=2.228
      T(11)=2.201
      T(12)=2.179
      T(13)=2.160
      T(14)=2.145
      T(15)=2.131
      T(16)=2.120
      T(17)=2.110
      T(18)=2.101
      T(19)=2.093
      T(20)=2.086
      ERROR=T(N-2)*THETA*((N/((N-2)*SSX))**.5)
C     THIS CALCULATES THE REGRESSION CONCENTRATIONS
      DO 30 I=2,A
      CLC(I)=M*X(I)+B
      CALC(I)=CLC(I)+CHI(2)*EXP(-KD*TSEC(I))
 30   DIFF(I)=CHI(I)-CALC(I)
C     THIS SECTION WRITES THE OUTPUT DATA
      WRITE(6,9006)
 9006 FORMAT('   SECONDS    CONCENTRATION    CALC. CONC.    DIFFERENCE')
      WRITE(6,9007)(TSEC(I),CHI(I),CALC(I),DIFF(I),I=2,A)
 9007 FORMAT(F10.1,3F15.6)
      WRITE(6,9008)M
 9008 FORMAT(1H /,'   THE SLOPE OF THE REGRESSION LINE IS',E12.4,/)
      WRITE(6,9009)ERROR
 9009 FORMAT('   THE CONFIDENCE INTERVAL ON THE SLOPE IS',E12.4,/)
      WRITE(6,9010)B
 9010 FORMAT('   THE INTERCEPT OF THE LINE IS',E12.4,/)
      WRITE(6,9011)CC
 9011 FORMAT('   THE CORRELATION COEFFICIENT IS  ',F6.4,/)
      STOP
      END
```

PROGRAM 4

```
$RESET FREE
C                LINEAR REGRESSION PROGRAM
C            FOR ANALYSIS OF THE LAW OF UNIVERSAL
C                      REACTION RATES
C
C                        BY D. BLYTHE
C
C     THIS PROGRAM USES THE UNIVERSAL RATE EQUATION TO FIND THE
C     ACTIVATION ENERGY OF A REACTION.  THE INPUT CONSISTS OF
C     RATE CONSTANT, TEMPERATURE (C) PAIRS, FOLLOWED BY
C     A RECORD OF 0,0. THE END RECORD THEN SPECIFIES THE
C     TEMPERATURE FOR THE ENTROPY,ENTHALPY, AND FREE ENERGY.
C     CALCULATIONS.
C
C     THE OUTPUT CONSISTS OF A TABLE SHOWING EACH TEMPERATURE,
C     THE OBSERVED RATE, THE CALCULATED (REGRESSION) RATE, AND
C     THE DIFFERENCE BETWEEN THE RATES.  THE SLOPE, INTERCEPT,
C     AND CORRELATION COEFFICIENT OF THE REGRESSION LINE ARE GIVEN.
C     THE ENTHALPY, ENTROPY, AND FREE ENERGY OF ACTIVATION, AND
C     THE ARRHENIUS ENERGY OF ACTIVATION ARE CALCULATED, WITH
C     THEIR CONFIDENCE INTERVALS.
C
C     IF THE OUTPUT IS TO BE DIRECTED TO THE PRINTER,
C     THEN REMOVE THE COMMENT CHARACTER FROM:
CFILE  6(KIND=PRINTER,MYUSE=OUT,MAXRECSIZE=22)
C     AND COMPILE WITH FORTRAN.
C
      INTEGER I,N
      REAL SUMX,SUMX2,SUMY,SUMY2,SUMXY,SSX,SSY,SSXY,T(20),H,A,S,F
      REAL M,B,DENOM,CC,Z,TEMP,K1,X(20),Y(20),SSR,SE,ERROR,TEM
      REAL CALC(20),DIFF(20),R(20),C(20)
C     THIS SECTION READS AND MANIPULATES THE INPUT DATA
      N=1
 1    READ (5,/) K1,TEMP
 9002 FORMAT(2F10.5)
C     THIS TESTS FOR THE LAST DATA CARD
      IF(TEMP)9,9,2
 2    X(N)=1/(TEMP+273.)
      Y(N)=ALOG(K1*X(N))
      C(N)=TEMP
      R(N)=K1
      N=N+1
      GO TO 1
 9    N=N-1
      WRITE(6,9003)N
 9003 FORMAT(1H /,'   THE NUMBER OF DATA POINTS IS ',I5,/)
C     THIS SECTION FINDS THE REGRESSION PARAMETERS
      SUMX=0.
      SUMX2=0.
      SUMY=0.
      SUMY2=0.
```

```
      SUMXY=0.
      DO 20 I=1,N
      SUMX=X(I)+SUMX
      SUMX2=X(I)*X(I)+SUMX2
      SUMY=Y(I)+SUMY
      SUMY2=Y(I)*Y(I)+SUMY2
 20   SUMXY=X(I)*Y(I)+SUMXY
      SSY=SUMY2-(SUMY*SUMY/N)
      SSX=SUMX2-(SUMX*SUMX/N)
      SSXY=SUMXY-(SUMX*SUMY/N)
C     M IS THE SLOPE
      M=SSXY/SSX
C     B IS THE INTERCEPT
      B=SUMY/N-M*SUMX/N
C     CC IS THE CORRELATION COEFFICIENT
      CC=SSXY/((SSX*SSY)**.5)
C     THIS SECTION FINDS THE CONFIDENCE INTERVAL
      SSR=SSY-M*SSXY
      SE=(SSR/(N-2))**.5
C     THIS IS A TABLE OF STUDENT'S T VALUES AT THE .095 LEVEL
      T(1)=12.706
      T(2)=4.303
      T(3)=3.182
      T(4)=2.776
      T(5)=2.571
      T(6)=2.447
      T(7)=2.365
      T(8)=2.306
      T(9)=2.262
      T(10)=2.228
      T(11)=2.201
      T(12)=2.179
      T(13)=2.160
      T(14)=2.145
      T(15)=2.131
      T(16)=2.120
      T(17)=2.110
      T(18)=2.101
      T(19)=2.093
      T(20)=2.086
C     THIS CALCULATES THE REGRESSION RATES
      DO 30 I=1,N
      CALC(I)=EXP(M*X(I)+B)
      CALC(I)=CALC(I)/X(I)
 30   DIFF(I)=R(I)-CALC(I)
C     THIS SECTION WRITES THE OUTPUT DATA
      WRITE(6,9004)
 9004 FORMAT('    TEMP         RATE          CALC. RATE       DIFFERENCE ')
      WRITE(6,9005)(C(I),R(I),CALC(I),DIFF(I),I=1,N)
 9005 FORMAT(F9.1,E14.4,E15.4,E16.4)
      WRITE(6,9006)M
 9006 FORMAT(1H /,'   THE SLOPE OF THE REGRESSION LINE IS',E12.4,/)
      WRITE(6,9007)B
```

```
9007 FORMAT('   THE INTERCEPT OF THE LINE IS',E12.4,/)
     WRITE(6,9008)CC
9008 FORMAT('   THE CORRELATION COEFFICIENT IS  ',F6.4,/)
     READ(5,/)TEMP
     TEM=TEMP+273
     H=-M*1.9872
     Z=H+(1.9872*TEM)
     A=EXP(B)
     S=1.9872*B-47.215
     F=H-TEM*S
     WRITE(6,9009)TEMP
9009 FORMAT('   AT ',F5.1,' DEGREES C :',/)
     WRITE(6,9010)H
9010 FORMAT('     THE ENTHALPY OF ACTIVATION IS',E12.5,/)
     WRITE(6,9011)Z
9011 FORMAT('     THE ACTIVATION ENERGY IS',E12.5,/)
     WRITE(6,9012)F
9012 FORMAT('     THE FREE ENERGY OF ACTIVATION IS',E12.5,/)
     ERROR=(T(N-2)*SE/(SSX**.5))*1.9872
     WRITE(6,9013)ERROR
9013 FORMAT('     THE CONFIDENCE INTERVAL ON THESE VALUES IS',E12.5,/)
     WRITE(6,9014)S
9014 FORMAT('     THE ENTROPY OF ACTIVATION IS',E12.4,/)
     ERROR=T(N-2)*SE/N**.5
     ERROR=1.9872*ERROR
     WRITE(6,9015)ERROR
9015 FORMAT('     THE CONFIDENCE INTERVAL ON THE ENTROPY IS',E12.4,/)
     STOP
     END
```

PROGRAM 5

```
$RESET FREE
C
C           RATE CONSTANT TEMPERATURE ADJUSTMENT
C
C                     BY D. BLYTHE
C
C      THIS PROGRAM USES THE ARRHENIUS EQUATION TO ADJUST
C      A RATE CONSTANT FROM ONE TEMPERATURE TO ANOTHER.
C      THE INPUT CONSISTS OF RECORDS SPECIFYING THE OBSERVED
C      RATE OF REACTION AND TEMPERATURE (C), THE ACTIVATION
C      ENERGY OF THE REACTION (CAL), AND THE DESIRED TEMPERATURE.
C      THE END CARD IS 0,0,0,0.
C
C      THE OUTPUT SHOWS THE INPUT DATA AND THE CALCULATED
C      REACTION RATE AT THE DESIRED TEMPERATURE
C
C      IF THE OUTPUT IS TO BE DIRECTED TO THE PRINTER,
C      THEN REMOVE THE COMMENT CHARACTER FROM:
CFILE   6(KIND=PRINTER,MYUSE=OUT,MAXRECSIZE=22)
C      AND COMPILE WITH FORTRAN
C
       REAL TSET,K1,T1,KSET,ACTE
       WRITE(6,8887)
 8887  FORMAT(1H /,'   INPUT T     INPUT K     ACTIV. E.     TSET
      1         KSET')
 1     READ(5,/)K1,T1,ACTE,TSET
 9999  FORMAT(2F10.5)
       IF(K1)4,4,3
 3     KSET=EXP(ALOG(K1)-(ACTE/1.9872)*(1/(TSET+273.)-1/(T1+273.)))
       WRITE(6,8888)T1,K1,ACTE,TSET,KSET
 8888  FORMAT(F10.2,E15.5,F14.0,F15.2,E15.5)
       GO TO 1
 4     STOP
       END
```

APPENDIX II

ATTEMPTED PREPARATION OF 1,5-ANHYDRO-4-DEOXY-4-THIO-D-GALACTITOL

The synthetic approach to 1,5-anhydro-4-deoxy-4-thio-D-galactitol used in this study is shown in Fig. 20. The scheme is analogous to that used by Gero and Guthrie (66) and Cook and Overend (67) to synthesize methyl 4-deoxy-4-thio-α-D-glucopyranoside and methyl 4-deoxy-4-thio-α-D-galactopyranoside, respectively. Unfortunately, the synthesis failed, as the sulfonyl group could not be displaced from (XXXIII) or (XXXIV) to give the thiocyanate (XXXV). The same stumbling block was encountered by Owen and Ragg (68) when they attempted to synthesize methyl 4-deoxy-4-thio-β-D-glucopyranoside. Why this should happen is not clear.

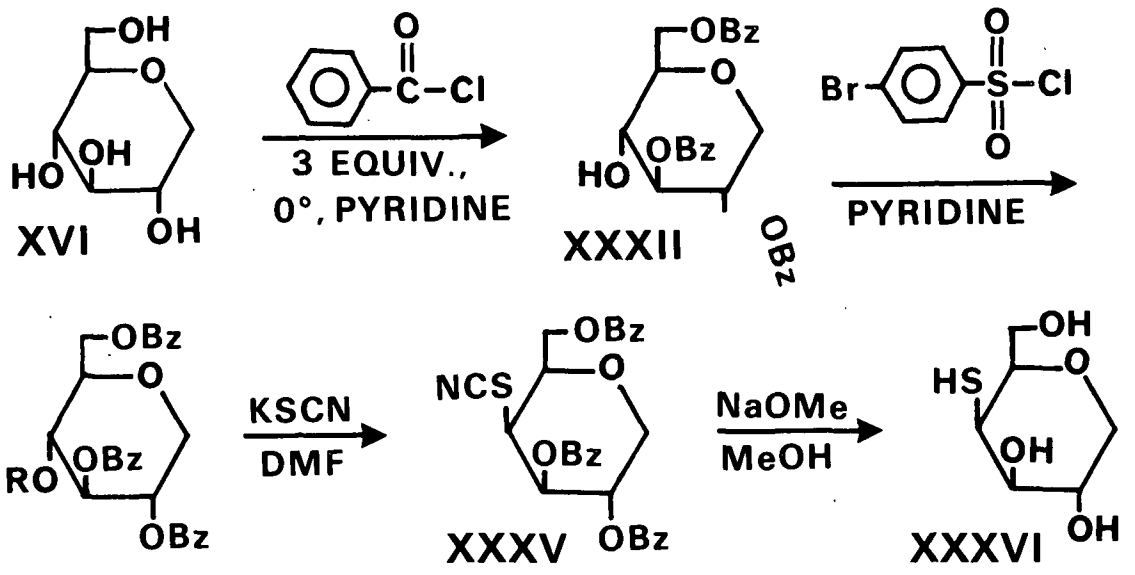

Figure 20. Proposed synthetic route to 1,5-anhydro-4-deoxy-4-thio-D-galactitol.

1,5-ANHYDRO-2,3,6-TRI-O-BENZOYL-D-GLUCITOL

1,5-Anhydro-D-glucitol (10 g) was dissolved in anhydrous pyridine (100 mL), and the solution was stirred at 0°C for thirty minutes with the exclusion of moisture.

Benzoyl chloride (21.2 mL, 3.0 equiv.) was added dropwise to the solution over two hours and then the slurry was allowed to warm slowly to room temperature. The reaction was monitored by TLC (chloroform:ethyl acetate, 4:1 vol.). The reaction mixture was dissolved in chloroform (100 mL) and poured into a stirred mixture of ice (200 mL) and hydrochloric acid (6N, 150 mL). The organic layer was separated; washed with hydrochloric acid (3N, 3 x 100 mL), dilute hydrochloric acid (1N, 2 x 50 mL), saturated sodium bicarbonate (2 x 50 mL), and water (100 mL); dried over calcium chloride; and reduced in vacuo to a solid. A small portion of the product mixture (4 g) was purified by column chromatography (Merck Kieselgel 60, 70-230 mesh; 2.5 x 90 cm; eluent $CHCl_3$). This gave 1.5 g of pure compound: m.p. 180.5-181.5°C, $[\alpha]_D$ +105.6° (c 1.5, $CHCl_3$). Literature: m.p. 181-183°C, $[\alpha]_D$ +72.7° (c 2.3, $CHCl_3$) (69). Recrystallization of the rest of the solid from methanol required seeding, and gave a total of 12.5 g (43%). A small amount of 1,5-anhydro-2,3,4,6-tetra-O-benzoyl-D-glucitol was also recovered from the column chromatography. ^{13}C-NMR spectra of both these compounds are presented in Appendix III (Fig. 34 and 28).

Anal. Calc. for $C_{27}H_{24}O_8$: C, 68.07; H, 5.04. Found: C, 67.91; H, 5.11.

1,5-ANHYDRO-2,3,6-TRI-O-BENZOYL-4-O-METHANESULFONYL-D-GLUCITOL

1,5-Anhydro-2,3,6-tri-O-benzoyl-D-glucitol (3.5 g) was dissolved in anhydrous pyridine (15 mL), and methanesulfonyl chloride (1.75 mL, 3.0 equiv.) was added. Moisture was excluded as the solution was stirred for twenty-four hours. Water (35 mL) was added to the reaction mixture. The tan precipitate which formed was recovered by filtration and dissolved in chloroform (60 mL). The chloroform solution was washed with saturated sodium bicarbonate (3 x 50 mL) and water (30 mL); dried

over sodium sulfate; and reduced *in vacuo* to a syrup. The syrup was dissolved in hot 95% ethanol, and the product formed as a gel on cooling. The gel was filtered, decolorized with carbon, and recrystallized from 95% ethanol to give 3 g (74%): m.p. 163-164°C, $[\alpha]_D$ +102.2° (*c* 1.5, $CHCl_3$). Literature: m.p. 167-168°C, $[\alpha]_D$ + 104° (*c* 1.0, $CHCl_3$) (69). The ^{13}C-NMR spectrum is included in Appendix III (Fig. 35).

Anal. Calc. for $C_{28}H_{26}O_{10}S$: C, 60.65; H, 4.69; S, 5.78. Found: C, 60.62; H, 4.72, S, 5.55.

1,5-ANHYDRO-2,3,6-TRI-*O*-BENZOYL-4-*O*-p-BROMOBENZENESULFONYL-D-GLUCITOL

1,5-Anhydro-2,3,6-tri-*O*-benzoyl-D-glucitol (5 g) was dissolved in anhydrous pyridine (25 mL) and p-bromobenzenesulfonyl chloride (5 g, 1.9 equiv.) was added. Moisture was excluded as the reaction was stirred for three days. The reaction solution was poured into water (500 mL), and extracted with methylene chloride (3 x 50 mL). The organic phase was washed with water (6 x 200 mL); decolorized with carbon; dried over sodium sulfate; and reduced *in vacuo* to a thick syrup. Crystallization from absolute ethanol gave 6.4 g (88%): m.p. 154.5-155.5°C, $[\alpha]_D$ +45.0° (*c* 1.5, $CHCl_3$). The ^{13}C-NMR spectrum is given in Appendix II (Fig. 36).

Anal. Calc. for $C_{33}H_{27}O_{10}SBr$: C, 56.98; H, 3.88; S, 4.60; Br, 11.51. Found: C, 57.03; H, 3.77; S, 4.88; Br, 11.30.

ATTEMPTED PREPARATION OF 1,5-ANHYDRO-2,3,6-TRI-*O*-BENZOYL-4-DEOXY-4-*S*-THIOCYANO-D-GALACTITOL

1,5-Anhydro-2,3,6-tri-*O*-benzoyl-4-*O*-p-bromobenzenesulfonyl-D-glucitol (0.40 g) was dissolved in anhydrous DMF (25 mL), and dry potassium thiocyanate (0.5 g, 9 equiv.) was added. The solution was stirred at 90°C (12 hours), at 120°C (24 hours), and finally at reflux (153°C, 12 hours). The reaction, followed by TLC (chloroform: ethyl acetate, 5:1, vol.), showed no progress. The solution was cooled, dissolved in chloroform (50 mL), washed with water (7 x 100 mL), decolorized with carbon, and reduced *in vacuo* to a syrup. No evidence of the desired product was found. Similar reactions of the 4-mesyl and 4-brosyl sulfonates for extended times resulted only in progressive decomposition of the starting material.

APPENDIX III

MASS SPECTRA

Mass spectra of various compounds were obtained from their acetate derivatives. The EI mass spectra did not show a moleclar ion. They were characterized by the loss of acetyl groups as neutral molecules of acetic acid (M - 60) or ketene (M - 42). The glucosides underwent fragmentation on both sides of the glycosidic linkage to give glycone and aglycone cations. Both of these also lost acetyl groups. The aglycone cation was the base peak in the EI spectra of the disaccharides.

The CI mass spectra also showed the loss of acetyl groups as neutral molecules (M - 60, or M - 42) from cations. However, loss of the acetate anion from the neutral molecule (M - 59) was also favored, and it was the base peak for the 1,5-anhydrides. The glucosides again showed fragmentation on both sides of the glycosidic oxygen, and the glycone cation was the base peak for these compounds. Methane used in the CI mode resulted in characteristic peaks of M + 1 (gain of H^+), M + 29 (gain of $C_2H_5^+$), and M + 41 (gain of $C_3H_5^+$). The molecular ion was not generally observed.

NCI mass spectra showed a fairly strong M - 1 (loss of H^+) peak. Acetyl groups were lost from the neutral molecule as CH_3CO^+ ions (M - 43), or from anions as neutral molecules (for example M - 43 - 42). Characteristic peaks resulted from anion attack on the neutral molecule to give peaks at M + 59 (gain of acetate anion), M + 35 (gain of chloride anion), and M + 37 (gain of chloride-37 isotope anion). Apparently the chloride ion is generated from the chloroform solvent used to inject the samples into the GLC-MS.

TABLE XIV

EI MASS SPECTRUM OF 1,5-ANHYDROCELLOBIITOL HEPTAACETATE

M/E	Intensity	Assignment
332	2.3	C-13 isotope
331	12.0	Glycone
319	7.5	
274	13.5	C-13 isotope
273	100.0	Aglycone
259	12.0	
243	8.7	
242	9.6	
231	8.7	Aglycone - 42
212	5.6	
200	11.6	
199	5.0	
187	5.5	Glycone - 42 - 42 - 60
171	15.4	Aglycone - 42 - 60
170	8.1	
169	39.0	Glycone - 60 - 60 - 42
157	16.6	

TABLE XV

CI MASS SPECTRUM OF 1,5-ANHYDROCELLOBIITOL HEPTAACETATE

M/E	Intensity	Assignment
661	2.1	M + 41
650	1.6	C-13 isotope
649	5.5	M + 29
562	1.3	C-13 isotope
561	5.1	M - 59
333	3.4	C-13 isotope
332	17.3	C-13 isotope
331	100.0	Glycone
329	1.6	
289	1.3	Glycone - 42
273	1.3	Aglycone
271	5.4	Glycone - 60
229	1.0	
169	1.9	

TABLE XVI

NCI MASS SPECTRUM OF 1,5-ANHYDROCELLOBIITOL HEPTAACETATE

M/E	Intensity	Assignment
681	8.9	C-13 isotope
680	30.3	C-13 isotope
679	100.0	M + 59
657	5.1	Cl-37 isotope
655	12.0	M + 35
620	12.2	C-13 isotope
619	40.7	M - 1
577	6.8	M - 43
535	8.0	M - 43 - 42
456	6.4	
407	13.7	
398	5.9	
349	20.8	
228	8.5	
198	5.7	

TABLE XVII

EI MASS SPECTRUM OF 1,5-ANHYDRO-2-DEOXY-3,6-DI-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-ARABINO-HEXITOL

M/E	Intensity	Assignment
332	2.3	C-13 isotope
331	13.3	Glycone
271	3.2	
261	6.4	
243	8.9	
242	8.8	
233	4.2	
216	10.4	C-13 isotope
215	100.0	Aglycone
201	6.4	
200	10.6	
169	47.4	Glycone - 60 - 60 - 42
157	14.4	

TABLE XVIII

CI MASS SPECTRUM OF 1,5-ANHYDRO-2-DEOXY-3,6-DI-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-ARABINO-HEXITOL

M/E	Intensity	Assignment
604	1.0	C-13 isotope
603	3.1	M + 41
592	1.9	C-13 isotope
591	5.9	M + 29
504	1.2	C-13 isotope
503	5.3	M - 59
502	1.0	M - 60
333	3.0	C-13 isotope
332	17.1	C-13 isotope
331	100.0	Glycone
329	1.6	
271	6.1	Glycone - 60
229	0.6	
215	0.7	Aglycone
169	2.2	

TABLE XIX

EI MASS SPECTRUM OF 1,5-ANHYDRO-DIDEOXY-MONO-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-HEXITOL

M/E	Intensity	Assignment
332	4.1	C-13 isotope
331	25.3	Glycone
315	5.0	
271	5.6	
211	3.5	Glycone - 60 - 60
170	5.5	C-13 isotope
169	70.7	Glycone - 60 - 60 - 42
158	9.2	C-13 isotope
157	100.0	Aglycone

TABLE XX

CI MASS SPECTRUM OF 1,5-ANHYDRO-DIDEOXY-MONO-O-ACETYL-4-O-(2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL)-D-HEXITOL

M/E	Intensity	Assignment
545	1.4	M + 41
533	3.3	M + 29
445	3.6	M - 59
333	3.4	C-13 isotope
332	16.7	C-13 isotope
331	100.0	Glycone
271	10.7	Glycone less AcOH
229	1.6	
169	5.8	
157	3.3	Aglycone

TABLE XXI

EI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4,6-TETRA-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
213	2.1	C-13 isotope
212	18.1	M - 60 - 60
199	1.6	
187	2.5	
171	6.4	
170	44.0	M - 60 - 60 - 42
157	10.2	
43	100.0	CH_3CO

TABLE XXII

CI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4,6-TETRA-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
373	1.6	M + 41
361	2.6	M + 29
333	23.5	M + 1
291	5.6	M + 1 - 42
274	13.2	C-13 isotope
273	100.0	M - 59
212	2.2	
171	4.0	M - 59 - 60

TABLE XXIII

NCI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4,6-TETRA-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
392	6.0	C-13 isotope
391	44.5	M + 59
369	10.9	Cl - 37 isotope
368	5.6	C-13 isotope
367	32.6	M + 35
332	14.9	C-13 isotope
331	100.0	M - 1
289	6.5	M - 43
185	8.4	
119	9.9	
110	7.2	

TABLE XXIV

EI MASS SPECTRUM OF 1,5-ANHYDRO-DEOXY-TRI-O-ACETYL-D-HEXITOL

M/E	Intensity	Assignment
215	1.2	
172	2.2	
155	6.9	
154	23.7	M - 60 - 60
142	3.2	
141	40.7	
130	2.2	
129	26.9	
126	5.2	
116	3.1	
115	3.1	
113	20.0	
112	100.0	M - 60 - 60 - 42
102	4.7	
99	35.0	

TABLE XXV

CI MASS SPECTRUM OF 1,5-ANHYDRO-DEOXY-TRI-O-ACETYL-D-HEXITOL

M/E	Intensity	Assignment
315	1.0	M + 41
303	1.2	M + 29
276	1.8	
275	13.2	M + 1
233	3.0	M + 1 - 42
217	1.6	
216	11.0	C-13 isotope
215	100.0	M - 59
173	1.1	M - 59 - 42
155	6.3	M - 59 - 60
113	11.9	

TABLE XXVI

NCI MASS SPECTRUM OF 1,5-ANHYDRO-DEOXY-TRI-O-ACETYL-D-HEXITOL

M/E	Intensity	Assignment
333	2.7	M + 59
315	1.4	
275	3.2	
274	13.3	C-13 isotope
273	100.0	M - 1
234	1.7	
231	2.5	M - 43

TABLE XXVII

EI MASS SPECTRUM OF 1,5-ANHYDRO-DIDEOXY-DI-O-ACETYL-D-HEXITOL

M/E	Intensity	Assignment
157	1.5	C-13 isotope
156	14.8	M - 60
144	2.6	
143	32.1	
115	7.1	C-13 isotope
114	89.7	M - 60 - 42
113	10.9	
101	7.5	
97	4.8	
96	15.7	M - 60 - 60
83	7.5	
72	5.4	
71	100.0	

TABLE XXVIII

CI MASS SPECTRUM OF 1,5-ANHYDRO-DIDEOXY-DI-O-ACETYL-D-HEXITOL

M/E	Intensity	Assignment
217	5.9	M + 1
158	7.4	C-13 isotope
157	100.0	M - 59
97	35.6	M - 59 - 60

TABLE XXIX

EI MASS SPECTRUM OF 2-ACETOXYETHYL 2,3,4,6-TETRA-O-ACETYL-1-THIO-β-D-GLUCOPYRANOSIDE

M/E	Intensity	Assignment
331	10.7	Glycone
271	5.9	Glycone - 60
270	5.7	
257	5.9	
228	5.1	
215	9.9	
211	6.9	Glycone - 60 - 60
170	9.2	C-13 isotope
169	100.0	Glycone - 60 - 60 - 42

TABLE XXX

CI MASS SPECTRUM OF 2-ACETOXYETHYL 2,3,4,6-TETRA-O-ACETYL-1-THIO-β-D-GLUCOPYRANOSIDE

M/E	Intensity	Assignment
451	0.2	M + 1
392	1.7	C-13 isotope
391	8.3	M - 59
333	3.0	C-13 isotope
332	15.1	C-13 isotope
331	100.0	Glycone
289	1.8	
273	1.1	
272	4.0	C-13 isotope
271	27.5	Glycone - 60
229	1.8	
211	2.8	
170	2.9	
169	30.8	

TABLE XXXI

NCI MASS SPECTRUM OF 2-ACETOXYETHYL 2,3,4,6-TETRA-O-ACETYL-1-THIO-β-D-GLUCOPYRANOSIDE

M/E	Intensity	Assignment
511	9.3	C-13 and S-34 isotopes
510	23.7	C-13 isotope
509	100.0	M + 59
487	3.8	C-1 - 37 isotope
485	10.3	M + 35
450	2.9	C-13 isotope
449	14.0	M - 1
407	4.7	M - 43
228	15.6	
185	8.1	

TABLE XXXII

EI MASS SPECTRUM OF DI-1,5-ANHYDRO-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL 6,6'-DISULFIDE

M/E	Intensity	Assignment
610	2.9	M
278	1.2	
274	1.1	
273	7.7	
231	1.9	
213	4.6	
202	1.1	
199	1.4	
185	3.5	Monomer - 60 - 60
43	100.0	CH_3CO

TABLE XXXIII

CI MASS SPECTRUM OF DI-1,5-ANHYDRO-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL 6,6'-DISULFIDE

M/E	Intensity	Assignment
651	4.0	M + 41
640	2.2	C-13 isotope
639	7.2	M + 29
613	4.7	S-34 isotope and ?
612	7.3	C-13 isotope
611	27.7	M + 1
610	7.1	M
553	10.6	S-34 isotope and ?
552	19.6	C-13 isotope
551	70.1	M - 59
550	8.8	M - 60
449	7.8	
307	8.4	
249	2.4	S-34 isotope
248	5.8	C-13 isotope
247	43.9	Monomer - 60
213	5.3	
187	33.2	M - 59 - 60
61	100.0	H_3COOCH_2

TABLE XXXIV

NCI MASS SPECTRUM OF DI-1,5-ANHYDRO-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL 6,6'-DISULFIDE

M/E	Intensity	Assignment
669	2.5	M + 59
610	7.6	M ?
609	2.5	M - 1
490	9.3	
337	5.8	
336	11.1	
306	11.6	S-34 isotope and ?
305	8.1	C-13 isotope and monomer
304	100.0	Monomer - 1
263	9.0	Monomer - 42
262	10.4	Monomer - 43
244	6.7	

TABLE XXXV

EI MASS SPECTRUM OF 1,5-ANHYDRO-6-DEOXY-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
306	0.1	M
246	0.7	M - 60
204	1.0	M - 60 - 42
199	1.4	
186	7.1	M - 60 - 60
171	1.2	
157	8.5	
144	7.2	M - 60 - 60 - 42
43	100.0	CH_3CO

TABLE XXXVI

CI MASS SPECTRUM OF 1,5-ANHYDRO-6-DEOXY-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
347	1.1	M + 41
335	1.4	M + 29
309	1.5	S-34 isotope
308	2.9	C-13 isotope
307	20.8	M + 1
289	5.5	
275	8.6	
265	6.9	M + 1 - 42
249	6.1	S-34 isotope
248	12.9	C-13 isotope
247	100.0	M - 59
205	5.7	
189	3.3	
188	7.4	C-13 isotope
187	70.5	M - 59 - 60

TABLE XXXVII

NCI MASS SPECTRUM OF 1,5-ANHYDRO-6-DEOXY-6-THIO-2,3,4-TRI-O-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment[a]
610	1.6	Dimer
365	2.1	M + 59
341	2.1	M + 35
308	1.0	S-34 isotope
307	5.6	C-13 and S-34 isotopes
306	31.6	M ?
305	28.9	M - 1, or monomer
304	22.9	Monomer - 1
265	8.4	S-34 isotope and ?
264	15.3	C-13 isotope and M - 42
263	100.0	M - 43
221	4.6	M - 43 - 42

[a]This spectrum shows evidence of the formation of the 6,6'-dimer in the spectrometer, and the fragmentation of that compound (see Table XXXIV).

TABLE XXXVIII

EI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4-TRI-O-ACETYL-6-DEOXY-6-S-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
288	0.6	M - 60
259	1.6	
258	2.1	
228	3.0	M - 60 - 60
199	3.4	
198	2.3	
186	5.1	M - 60 - 60 - 42
185	3.3	
157	9.0	
43	100.0	CH_3CO

TABLE XXXIX

CI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4-TRI-O-ACETYL-6-DEOXY-6-S-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
389	1.7	M + 41
377	7.0	M + 29
351	2.3	S-34 isotope
350	5.4	C-13 isotope
349	32.5	M + 1
307	6.1	M + 1 - 42
291	6.7	S-34 isotope
290	13.9	C-13 isotope
289	100.0	M - 59
247	5.2	
187	25.3	M - 59 - 60

TABLE XL

NCI MASS SPECTRUM OF 1,5-ANHYDRO-2,3,4-TRI-O-ACETYL-6-DEOXY-6-S-ACETYL-D-GLUCITOL

M/E	Intensity	Assignment
407	6.6	M + 59
383	4.1	M + 35
349	5.3	C-13 and S-34 isotopes
348	14.0	C-13 isotope
347	72.9	M - 1
307	7.8	C-13 and S-34 isotopes
306	22.8	C-13 isotope and M - 42
305	100.0	M - 43
304	30.9	
264	7.0	C-13 isotope
263	65.6	M - 43 - 42
247	5.1	
245	7.8	
231	5.5	
230	6.1	
203	9.3	
202	6.2	
201	9.0	
187	11.9	

^{13}C-NMR SPECTRA

^{13}C-NMR spectra were obtained for various compounds in the course of this study. Fortunately, the carbon resonances for two of the key compounds, 1,5-anhydrocellobiitol and 1,5-anhydro-D-glucitol, have been assigned (54,57). The other sugars were assigned by comparison with these two, and without substantial supporting evidence. Therefore these assignments must be regarded as tentative. In general, off-resonance spectra were of little assistance since the peaks in question were expected to show the same off-resonance splitting patterns. However, these patterns are included on several spectra, with the notations (s), (d), (t), or (q) indicating singlet, doublet, triplet, or quartet off-resonance splitting.

Derivatives of 1,5-anhydro-D-glucitol make up the largest portion of this data. Table XLI is provided for easy comparison of the chemical shifts (relative to external TMS) of the C-1 to C-6 resonances in these compounds.

TABLE XLI

^{13}C-NMR ASSIGNMENTS FOR THE C-1 TO C-6 RESONANCES OF 1,5-ANHYDRO-D-GLUCITOL AND SEVERAL OF ITS DERIVATIVES[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6
1,5-Anhydro-D-glucitol	70.0	70.5	78.7	70.9	81.4	62.1
-2,3,4,6-tetra-O-acetate	67.9	69.6	74.8	70.1	77.6	63.3
-2,3,6-tri-O-benzoate	68.2	70.5[b]	78.2	70.8[b]	80.3	64.9
-2,3,4,6-tetra-O-benzoate	67.2	69.7	73.9	70.1	76.9	63.0
-4-O-methanesulfonyl-2,3,6-tri-O-benzoate	68.2	71.6	74.5	75.5	78.0	63.5
-4-O-p-bromobenzenesulfonyl-2,3,6-tri-O-benzoate	68.2	71.2	74.3	77.0	78.0	63.5
-6-O-methanesulfonyl-2,3,4-tri-O-benzoate	68.2[b]	70.0	74.7	71.0	77.7	68.7[b]
-6-S-thiocyano-2,3,4-tri-O-benzoate	68.3	70.9	74.4	73.7	78.2	37.0
-2,3,4-tri-O-acetyl 6,6'-disulfide	67.9	70.3	74.7	72.7	78.2	42.9
-2,3,4-tri-O-acetyl 6-thiol	67.8	70.3	74.9	72.2	79.8	27.3
-2,3,6-tri-O-acetyl-6-S-acetate	67.9	70.2	74.7	71.7	78.5	31.3
-6-thio-D-glucitol	70.1	70.6	78.5	72.9	81.3	26.5

[a]Chemical shifts in ppm relative to external TMS.
[b]Assignment is questionable, see spectrum.

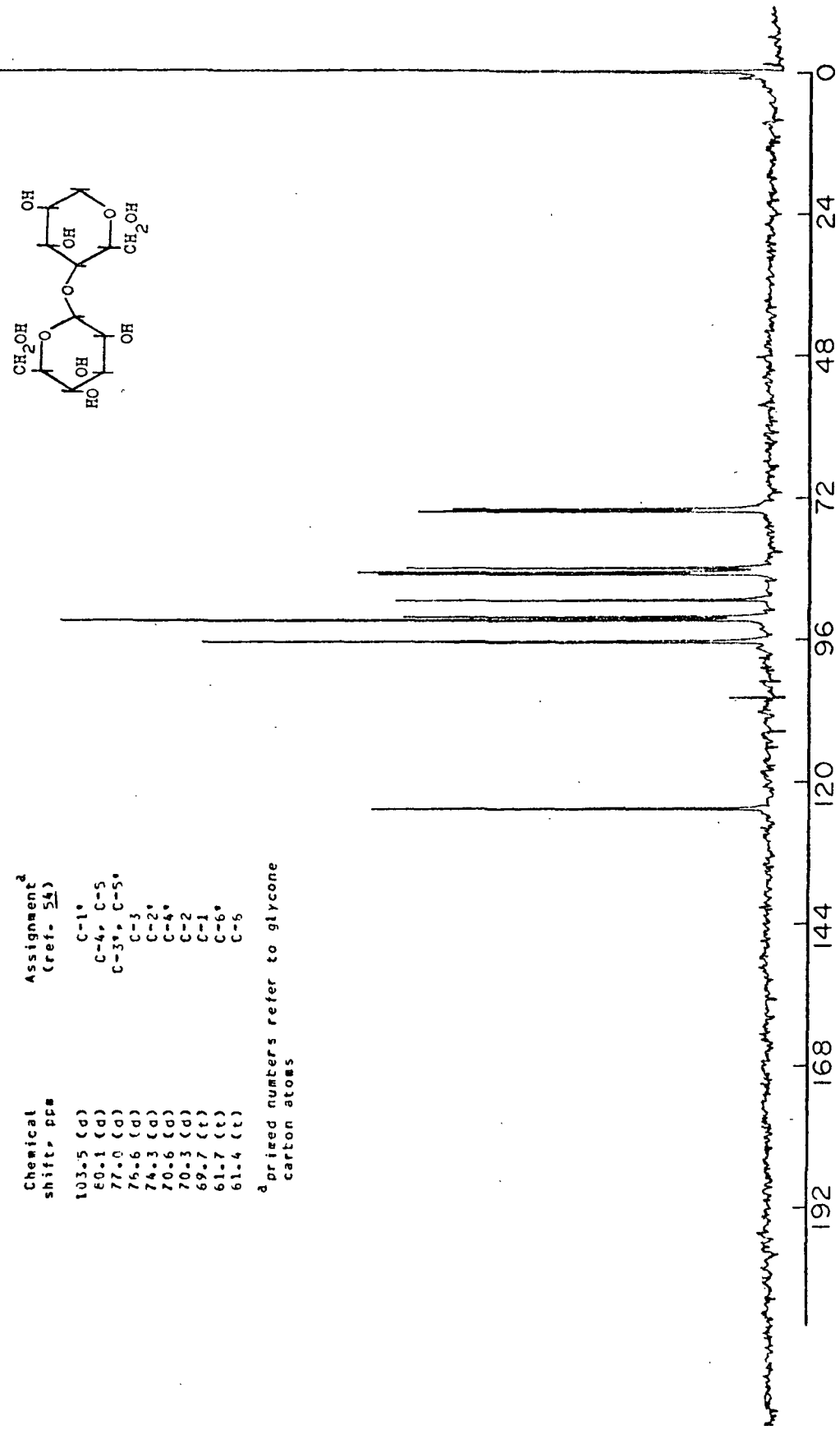

Figure 21. ^{13}C-NMR spectrum of 1,5-anhydrocellobiitol in D_2O.

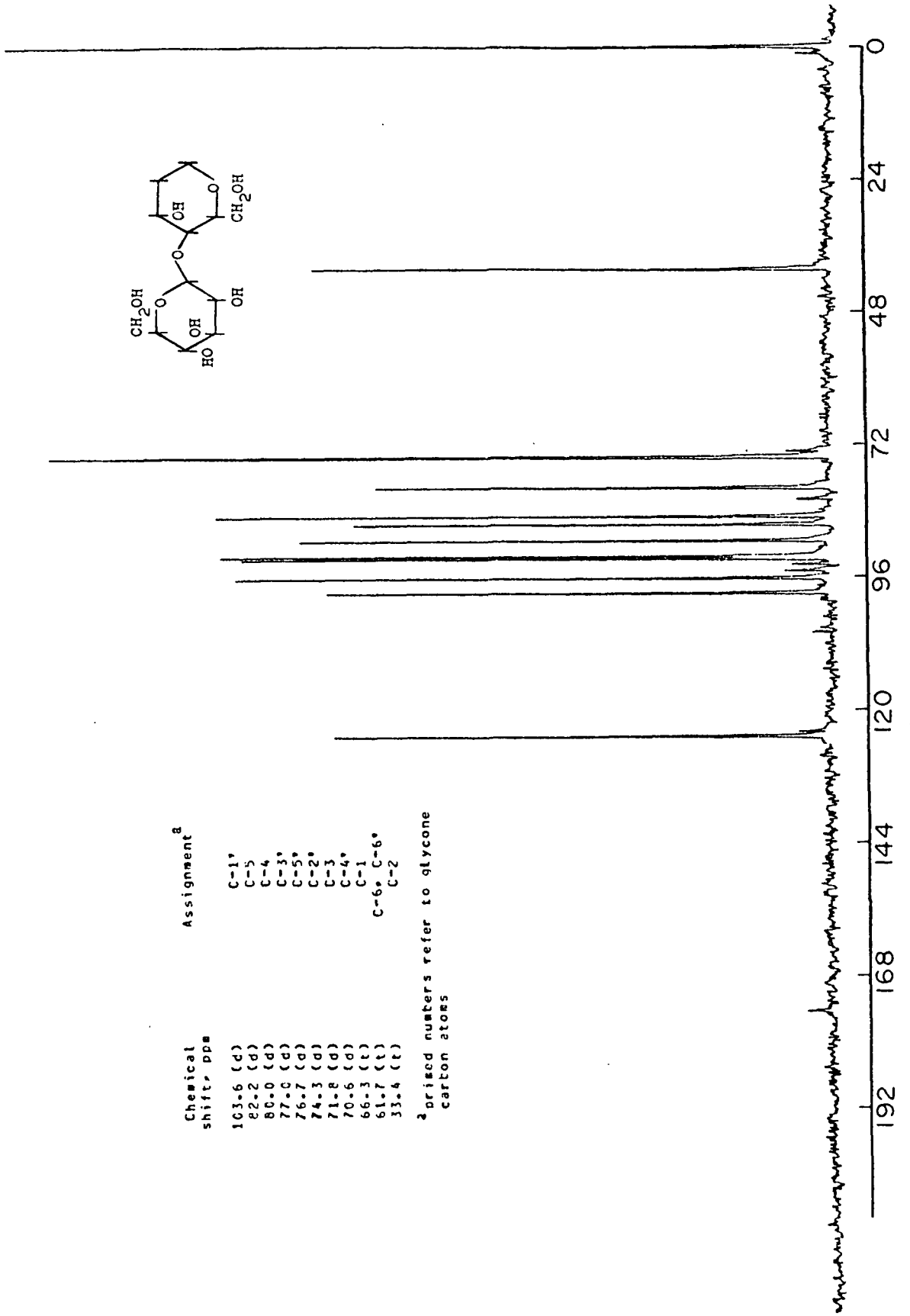

Figure 22. ^{13}C-NMR spectrum of 1,5-anhydro-2-deoxy-4-O-(β-D-glucopyranosyl)-D-arabino-hexitol in D_2O.

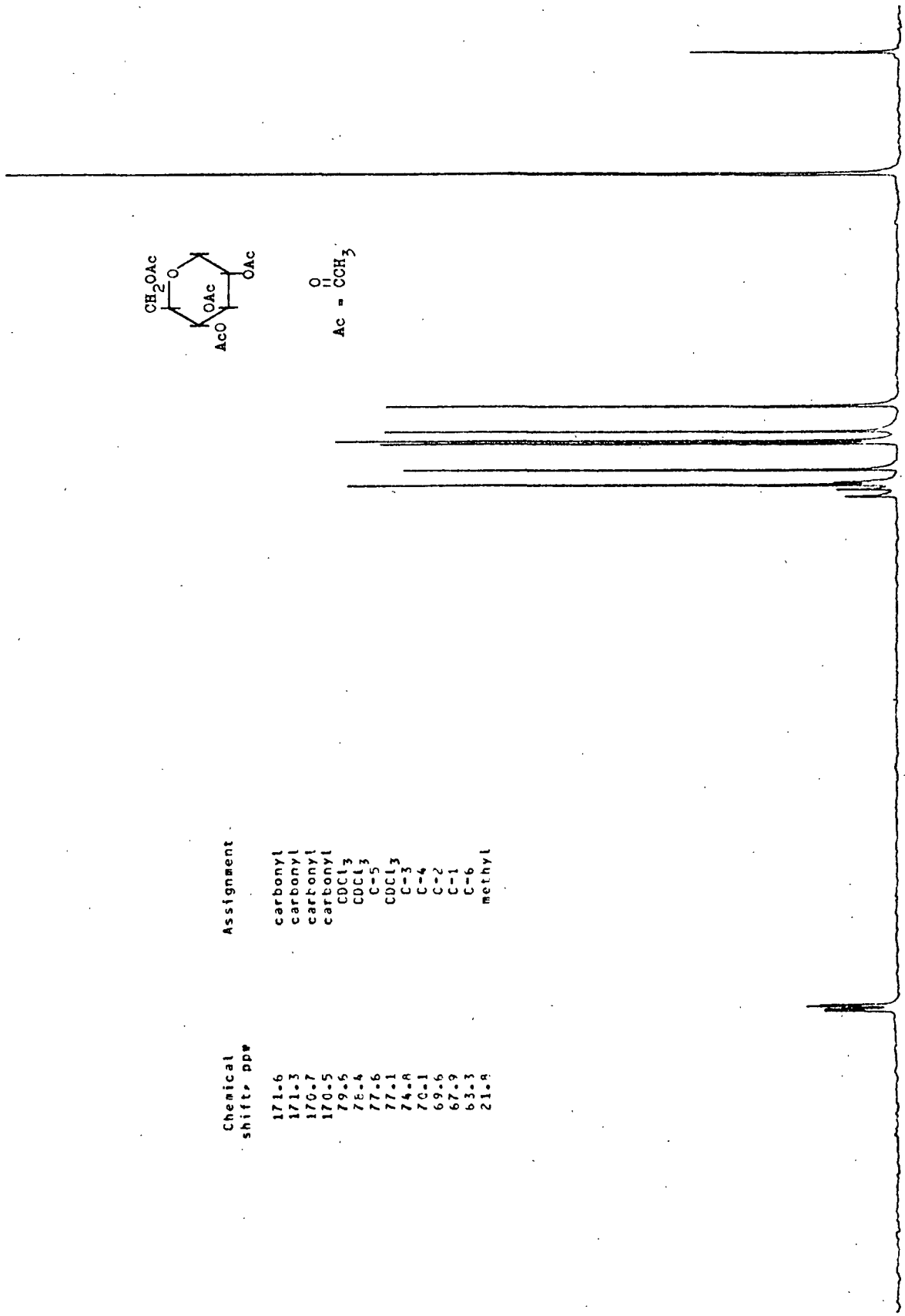

Figure 23. ^{13}C-NMR spectrum of 1,5-anhydro-2,3,4,6-tetra-O-acetyl-D-glucitol in $CDCl_3$.

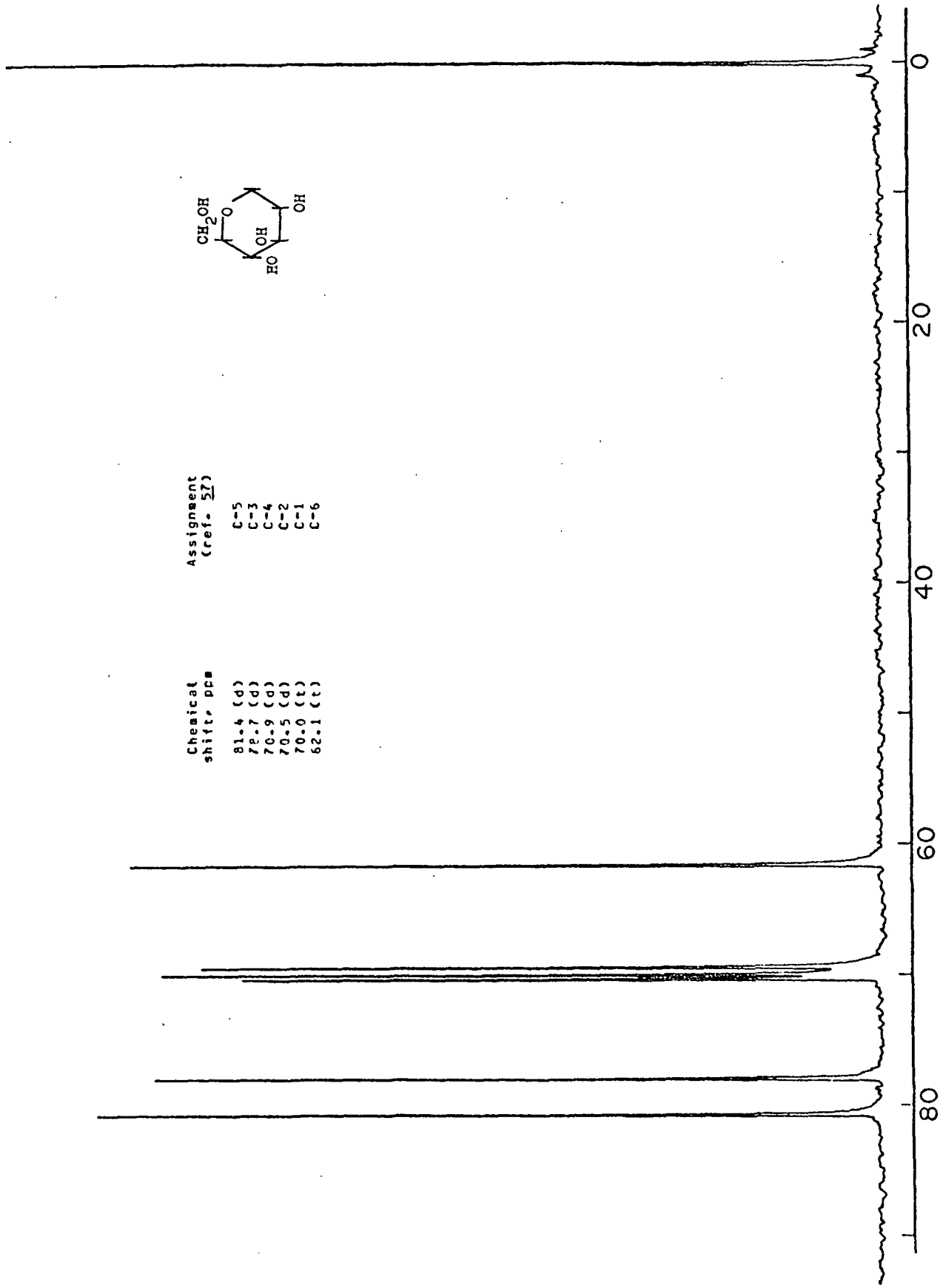

Figure 24. ^{13}C-NMR spectrum of 1,5-anhydro-D-glucitol in D_2O.

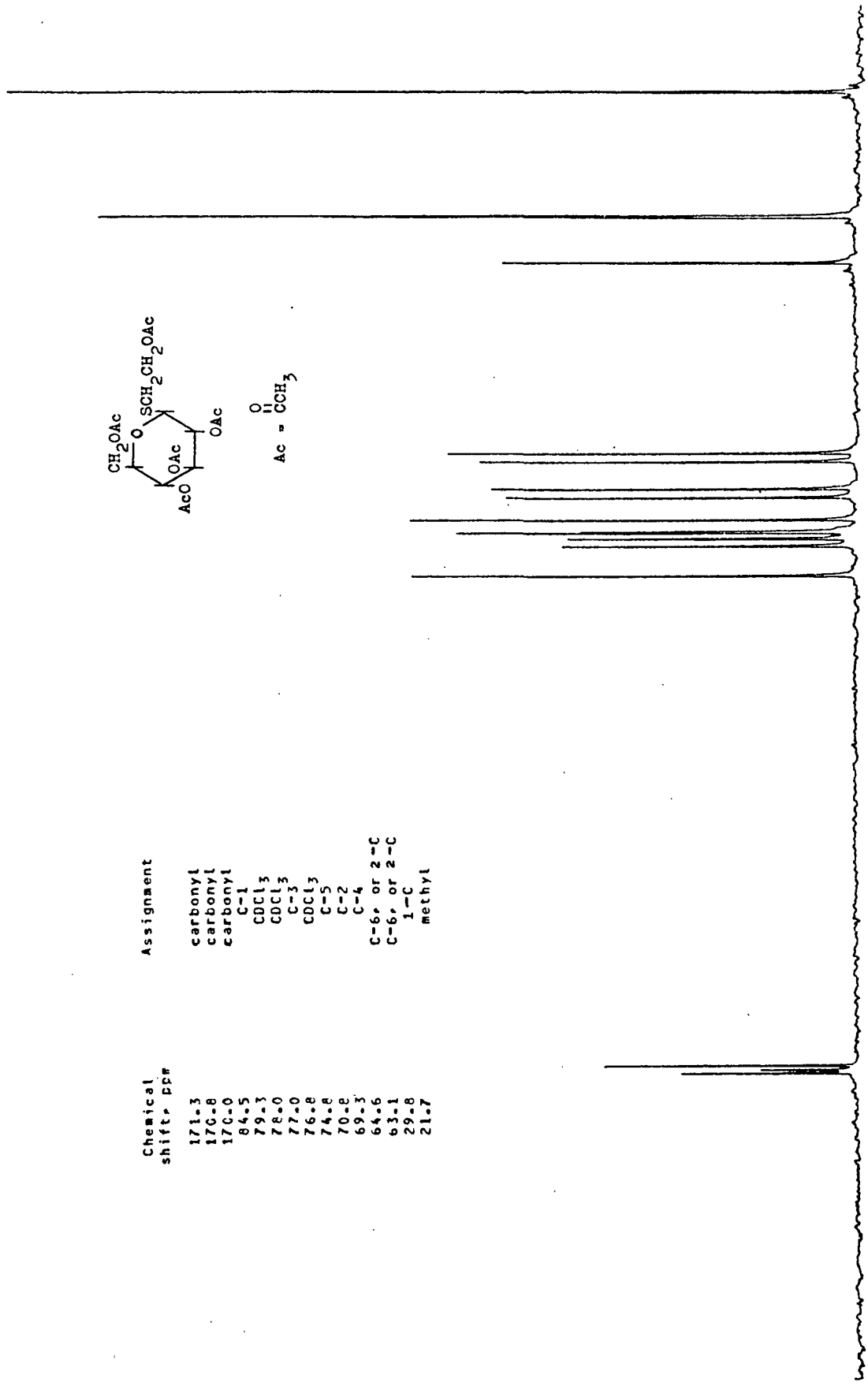

Figure 25. ^{13}C-NMR spectrum of 2-acetoxyethyl 1-thio-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside in $CDCl_3$.

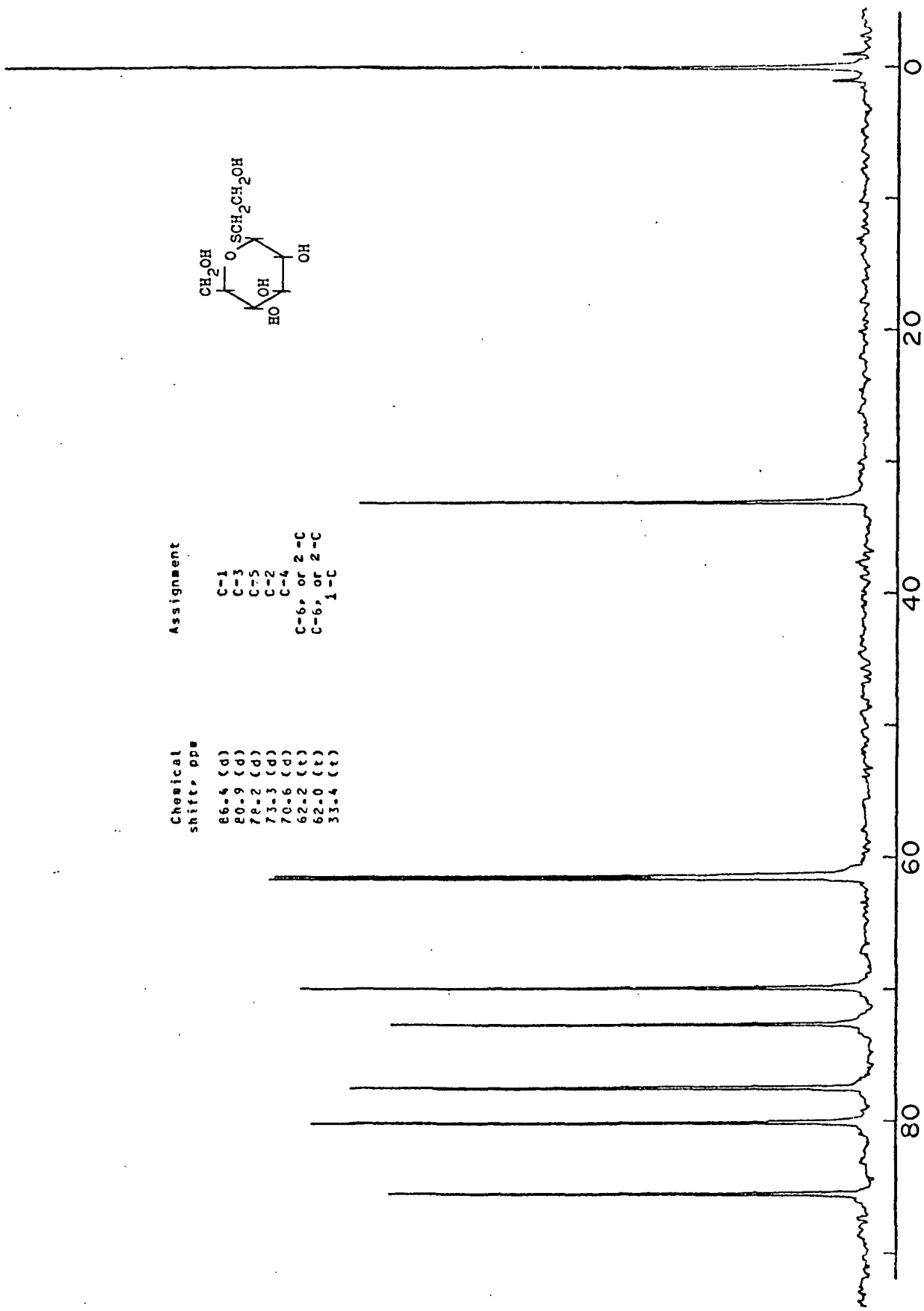

Figure 26. ^{13}C-NMR spectrum of 2-hydroxyethyl 1-thio-β-D-glucopyranoside in D_2O.

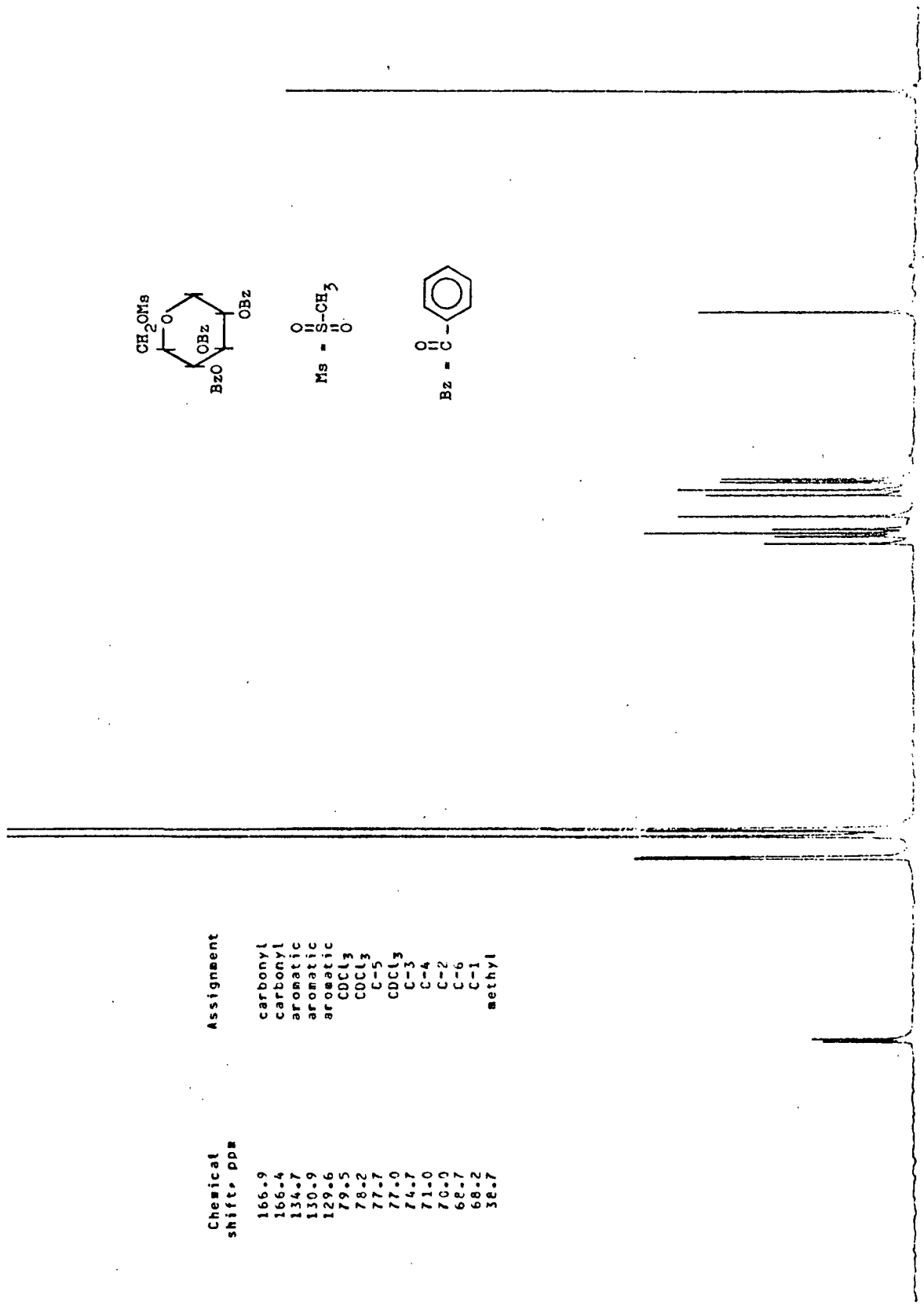

Figure 27. ^{13}C-NMR spectrum of 1,5-anhydro-6-O-methanesulfonyl-2,3,4-tri-O-benzoyl-D-glucitol in $CDCl_3$.

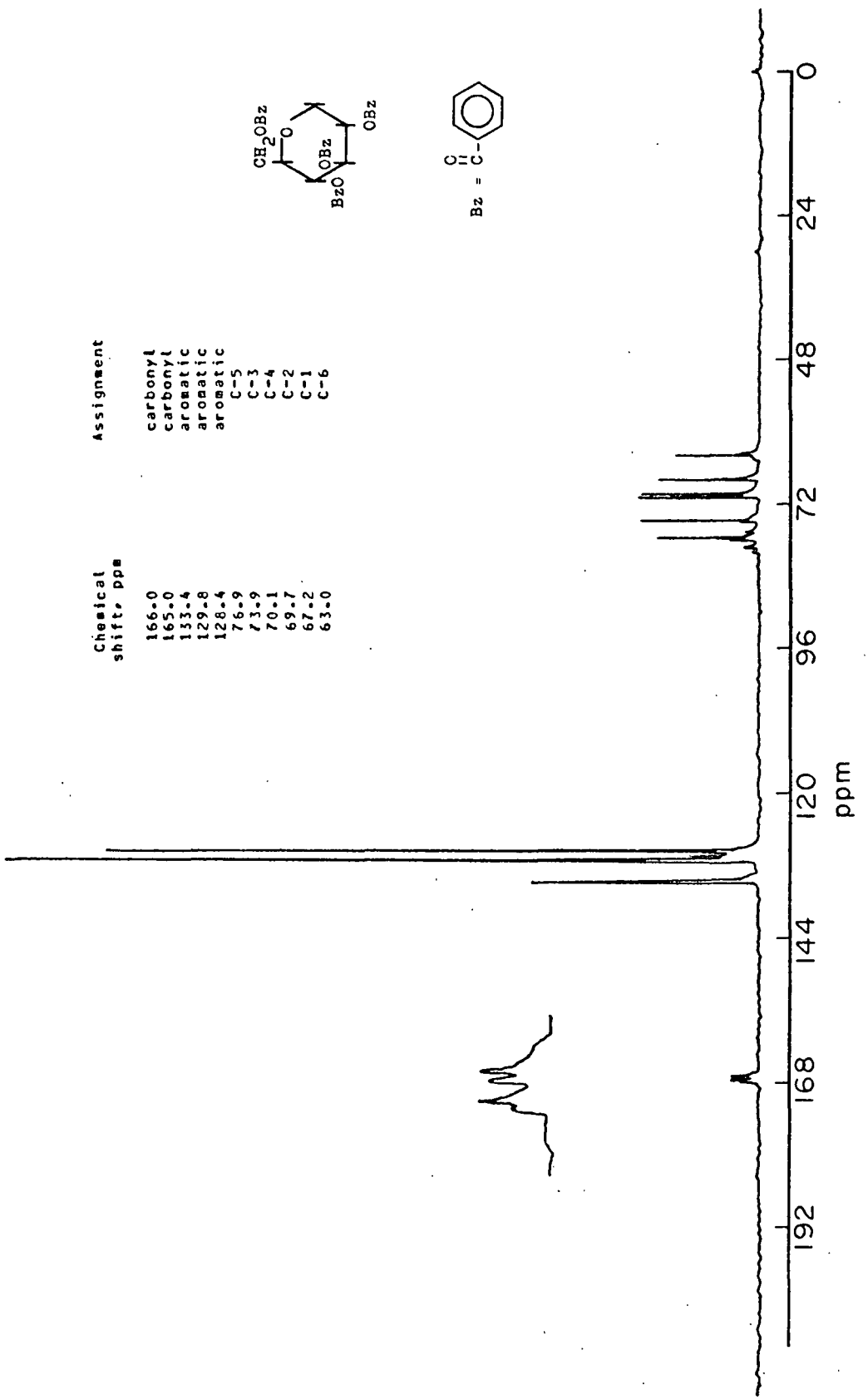

Figure 28. ^{13}C-NMR spectrum of 1,5-anhydro-2,3,4,6-tetra-O-benzoyl-D-glucitol in $CDCl_3$.

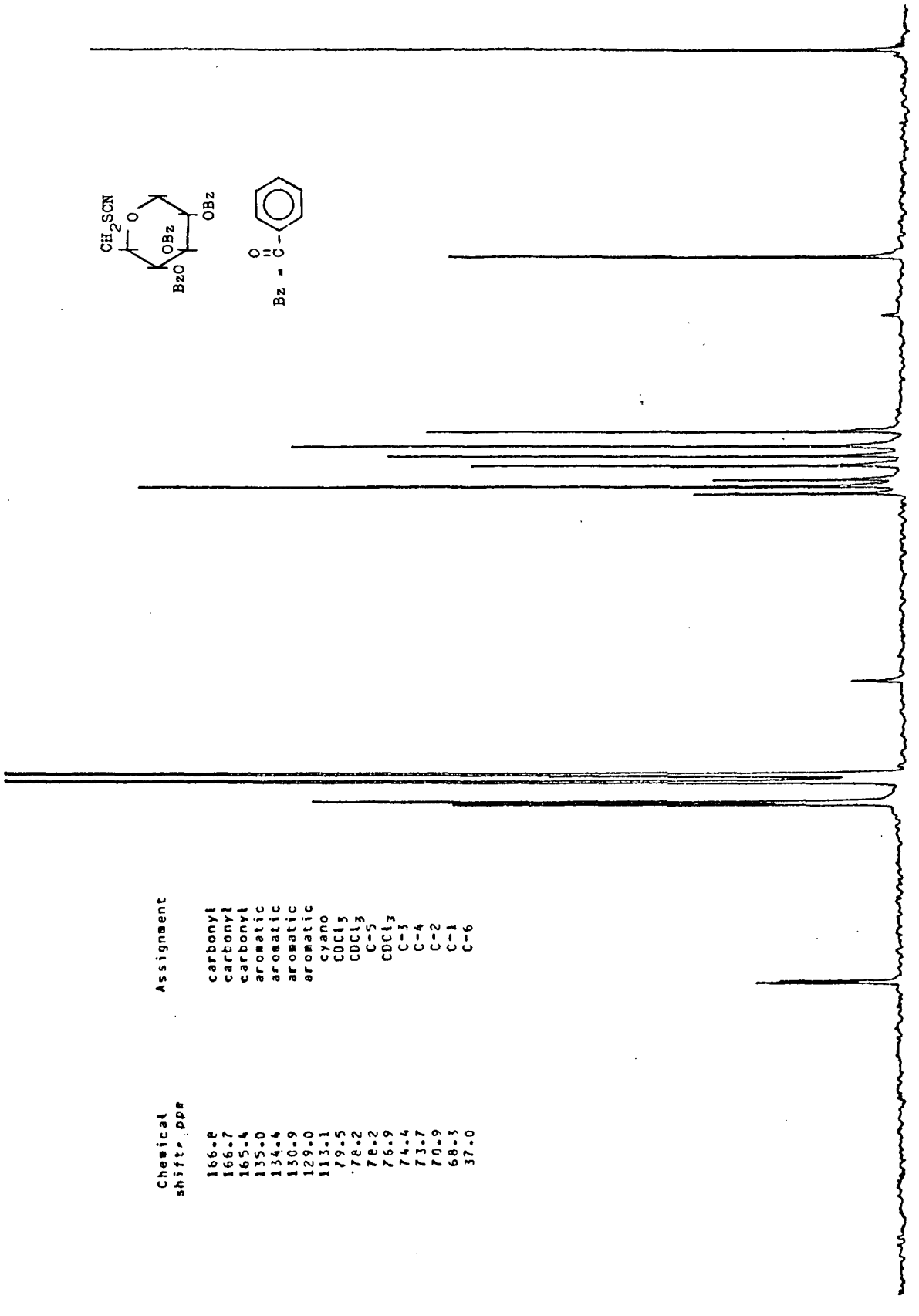

Figure 29. ^{13}C-NMR spectrum of 1,5-anhydro-6-S-thiocyano-2,3,4-tri-O-benzoyl-D-glucitol in $CDCl_3$.

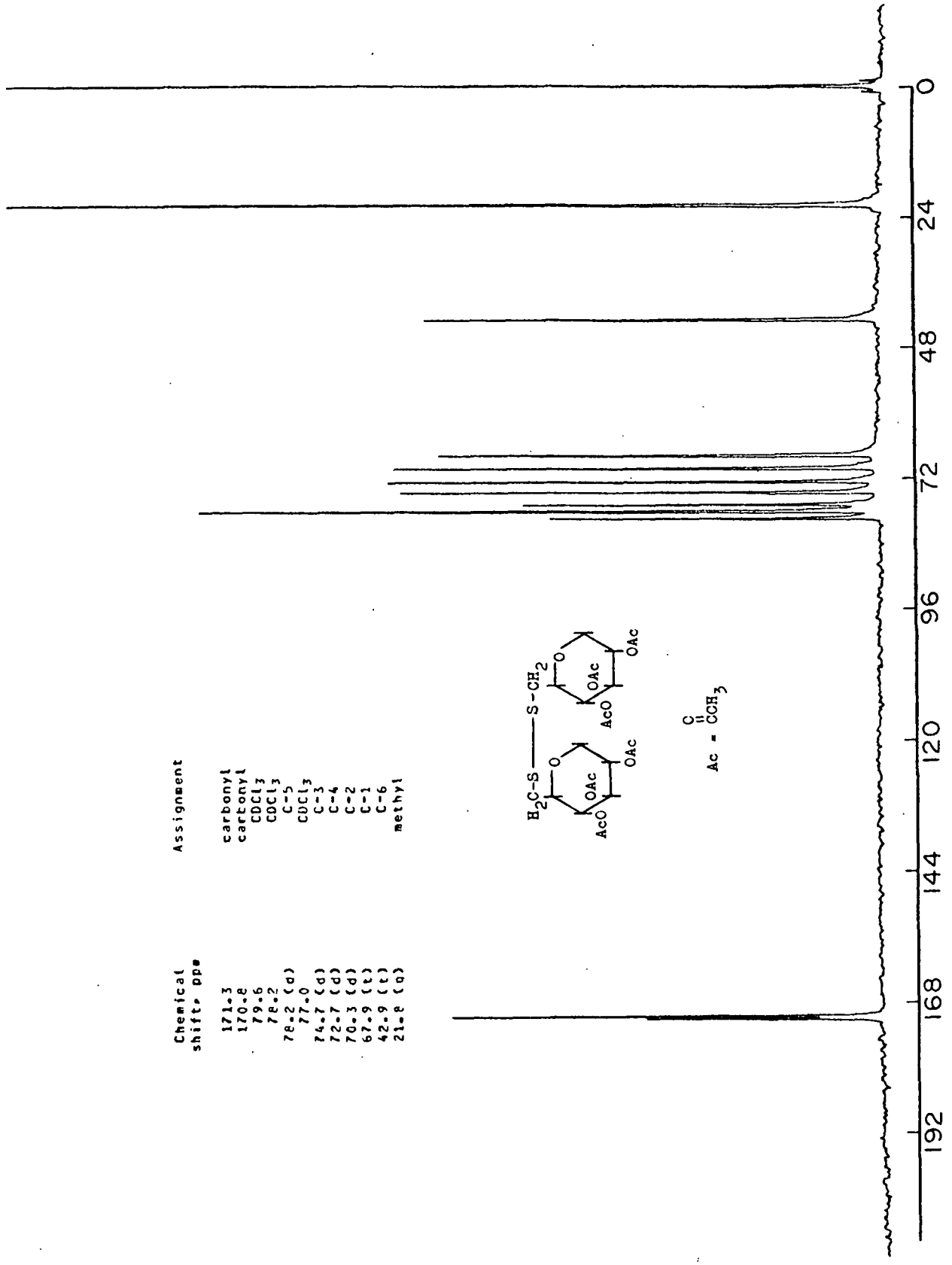

Figure 30. ^{13}C-NMR spectrum of di-1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol 6,6'-disulfide in $CDCl_3$.

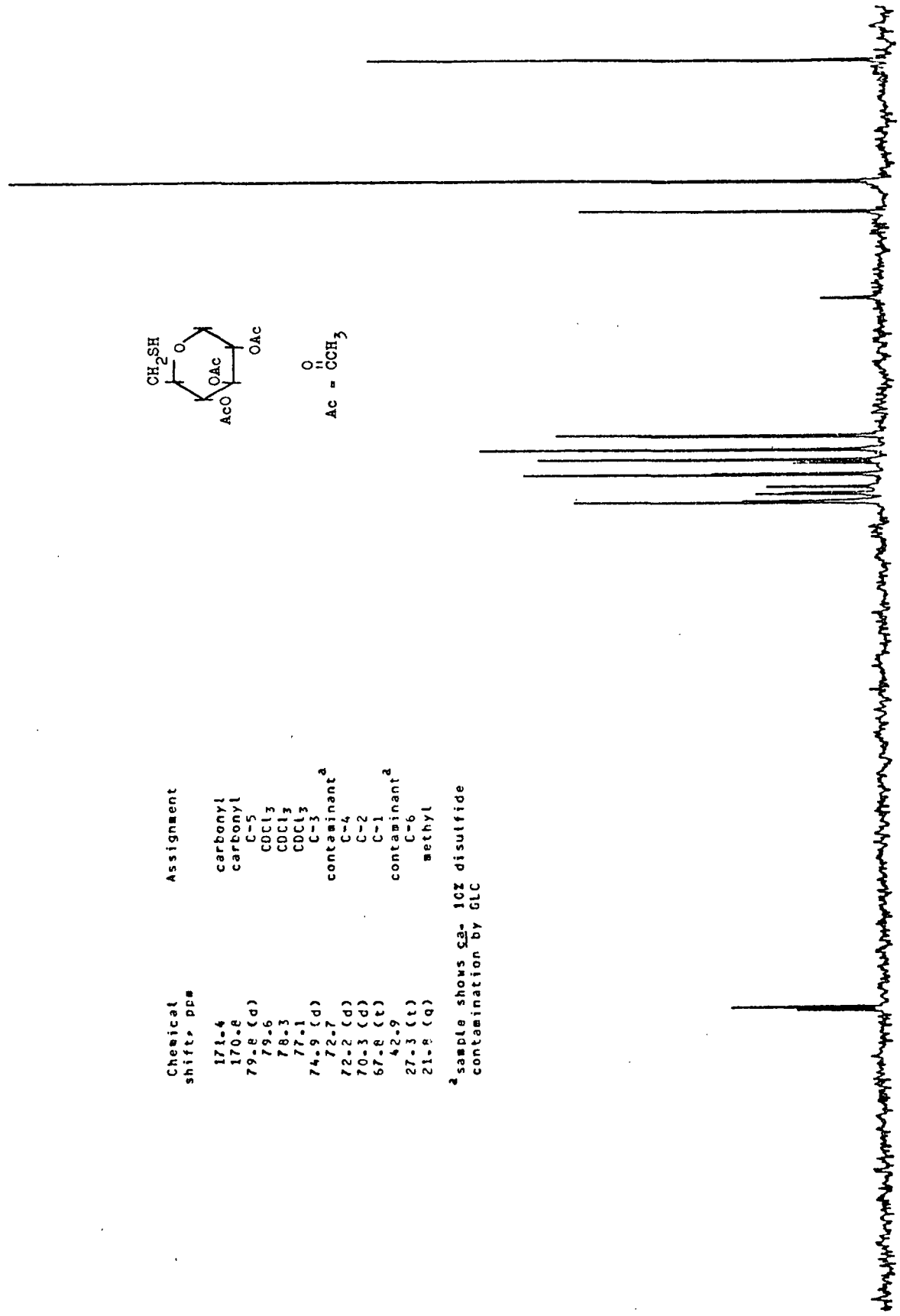

Figure 31. ^{13}C-NMR spectrum of 1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-thio-D-glucitol in $CDCl_3$.

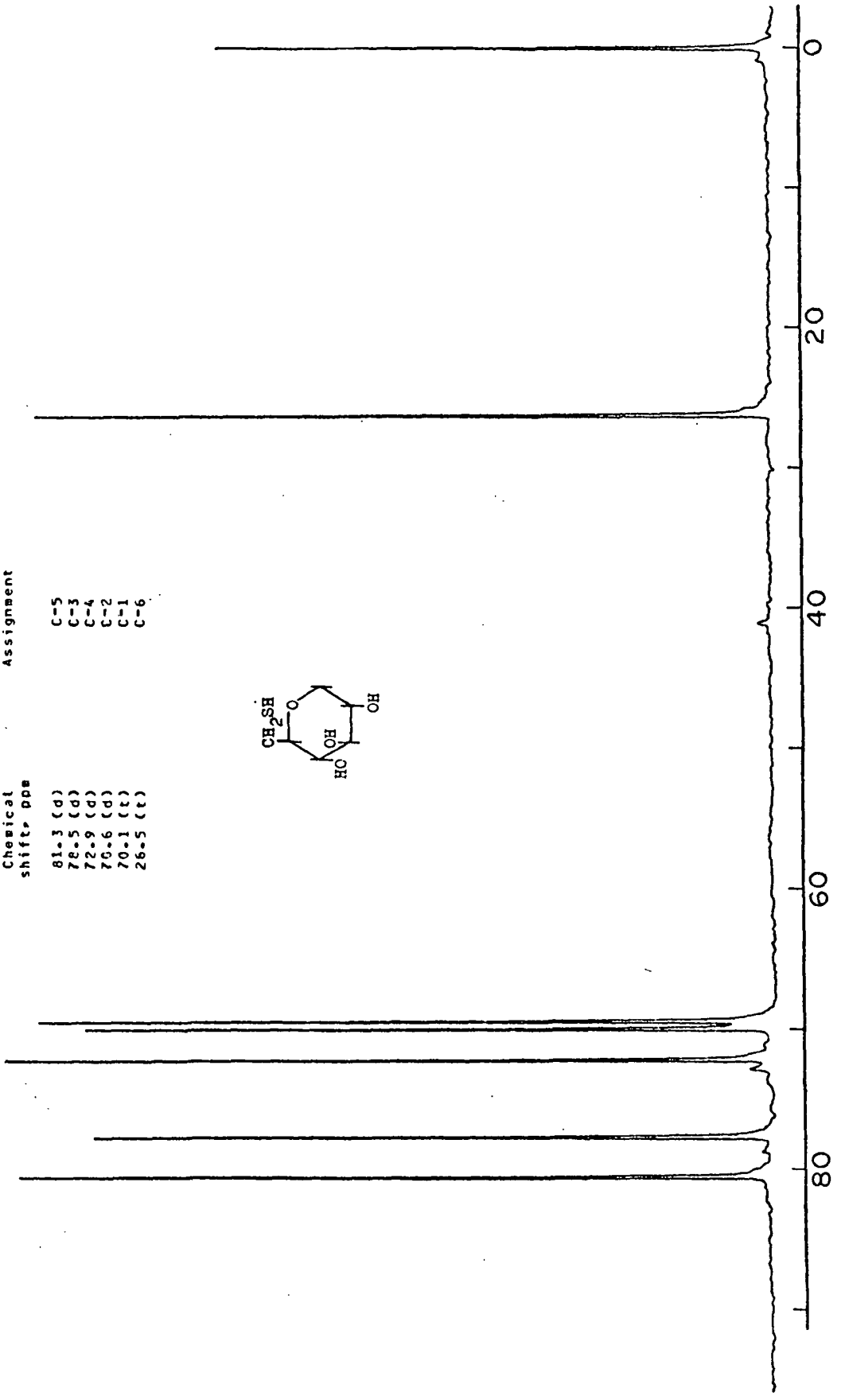

Figure 32. ^{13}C-NMR spectrum of 1,5-anhydro-6-deoxy-6-thio-D-glucitol in D_2O.

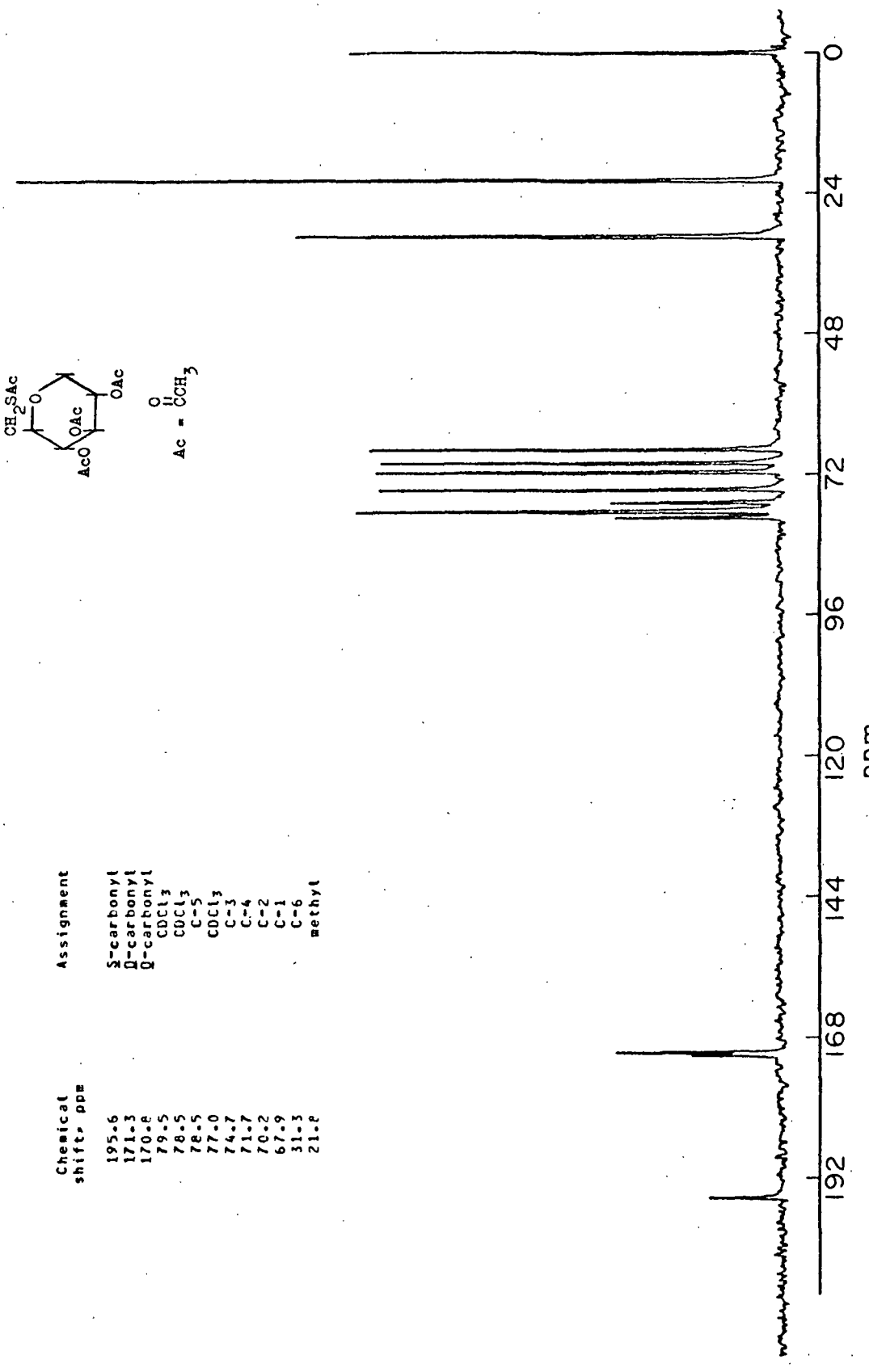

Figure 33. ^{13}C-NMR spectrum of 1,5-anhydro-2,3,4-tri-O-acetyl-6-deoxy-6-S-acetyl-D-glucitol in $CDCl_3$.

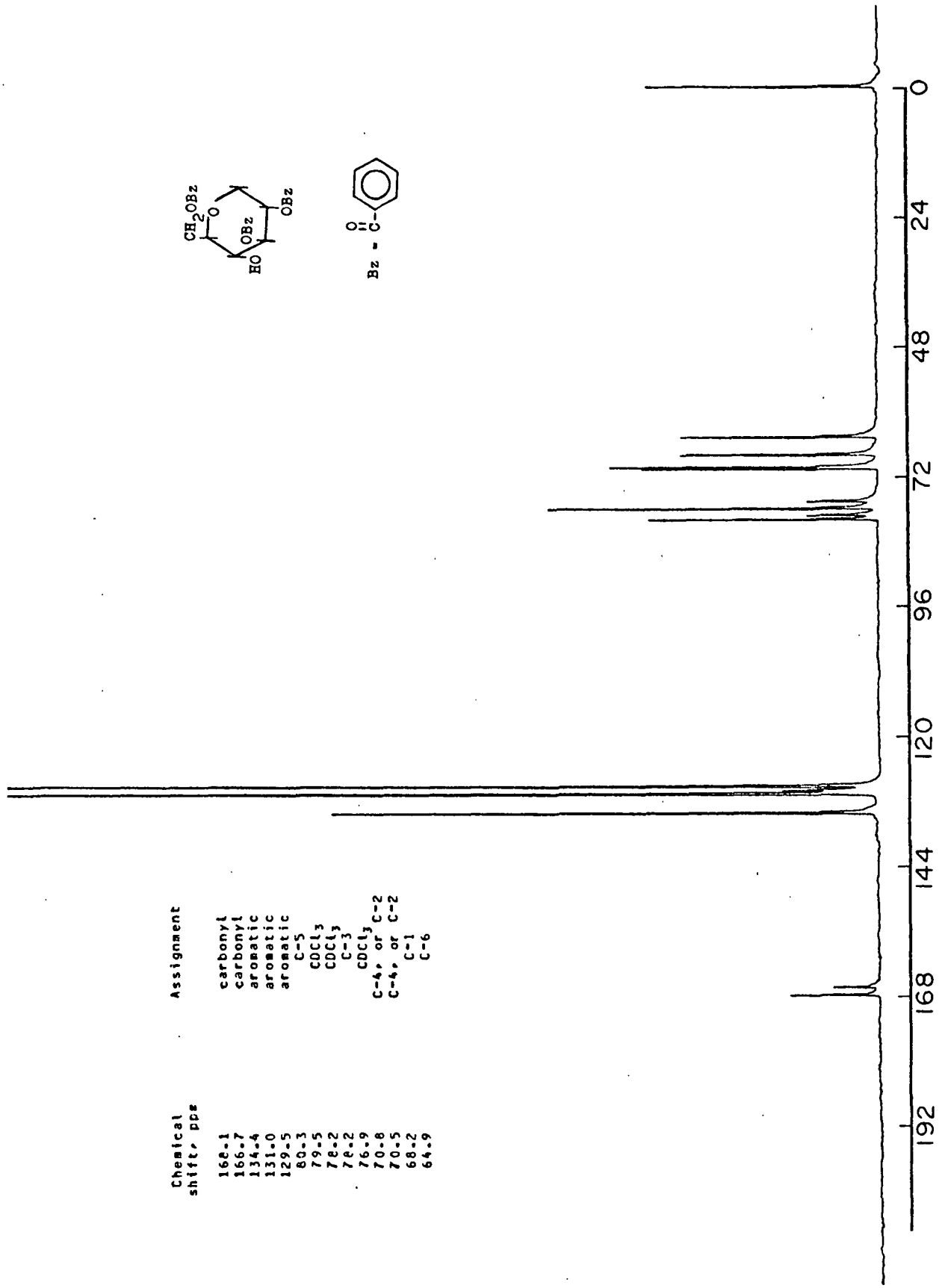

Figure 34. ^{13}C-NMR spectrum of 1,5-anhydro-2,3,6-tri-O-benzoyl-D-glucitol in $CDCl_3$.

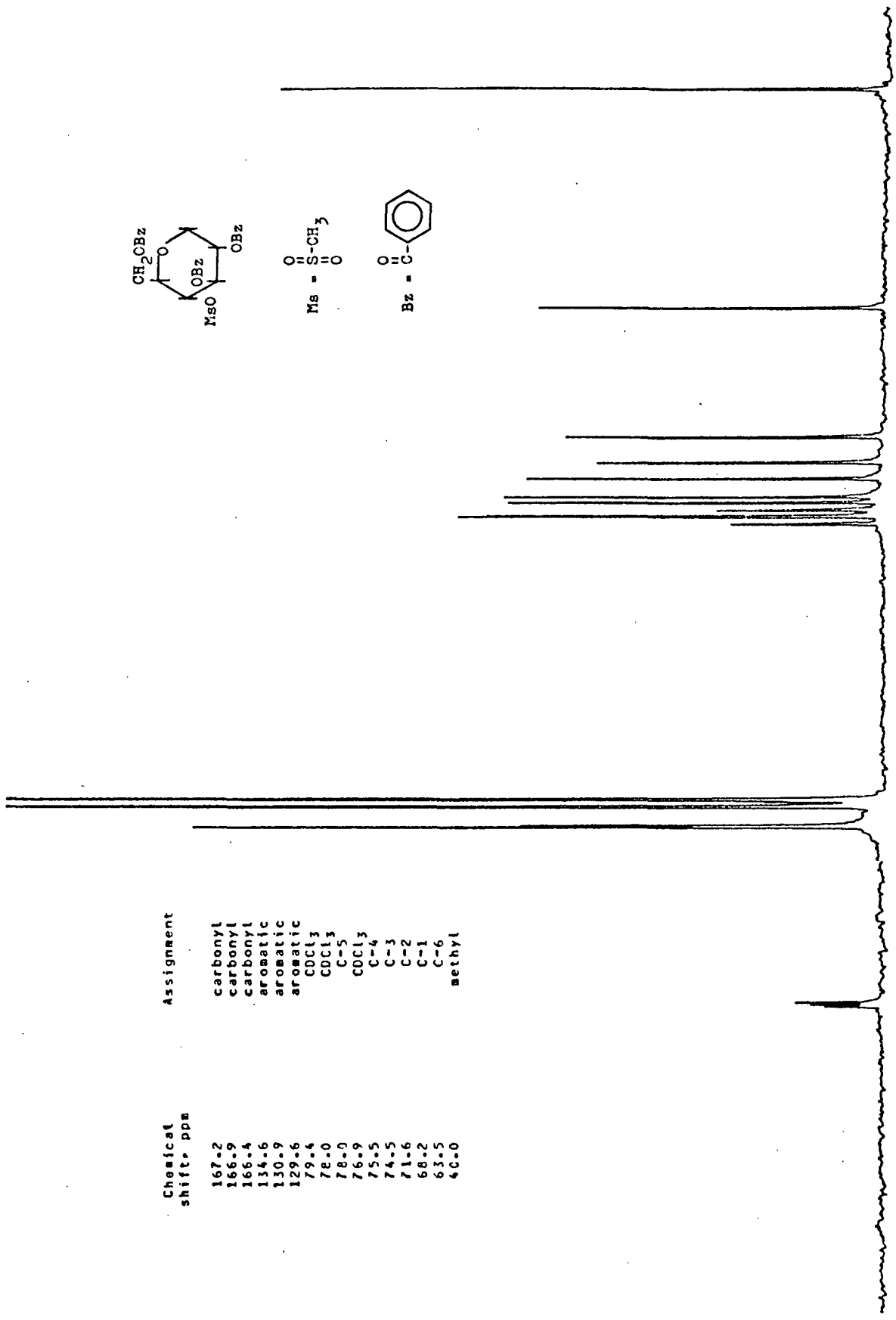

Figure 35. ^{13}C-NMR spectrum of 1,5-anhydro-4-O-methanesulfonyl-2,3,6-tri-O-benzoyl-D-glucitol in $CDCl_3$.

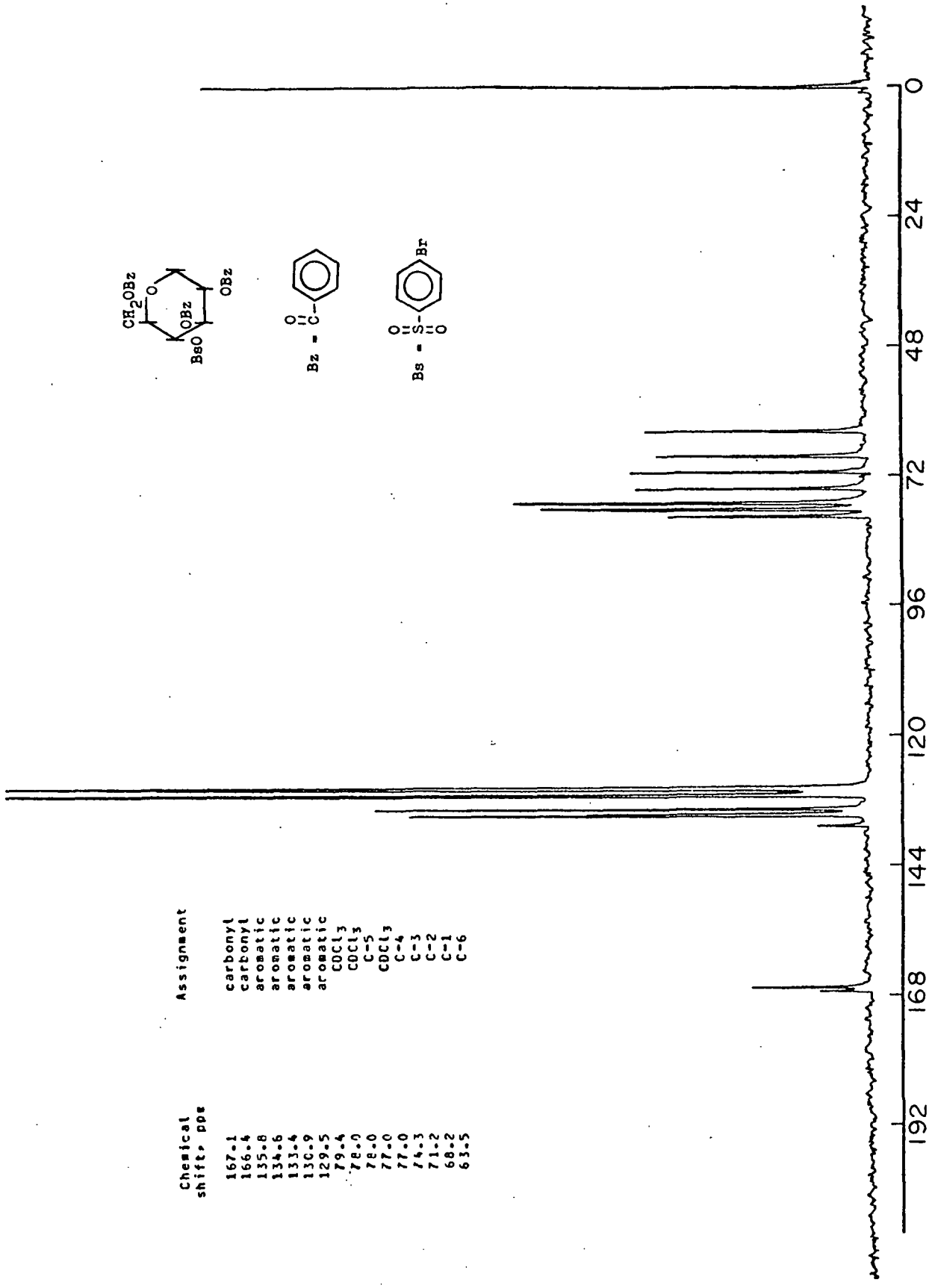

Figure 36. ^{13}C-NMR spectrum of 1,5-anhydro-4-O-p-bromobenzenesulfonyl-2,3,6-tri-O-benzoyl-D-glucitol in $CDCl_3$.

APPENDIX IV

EXPERIMENTAL DATA*

TABLE XLII

EFFECT OF REACTOR HEADSPACE ON DETERMINATION OF VOLATILE PRODUCTS; METHANOL AND METHYL MERCAPTAN IN 1.0M SODIUM HYDROXIDE AND 0.2M SODIUM SULFIDE AT 180.5°C

Volume Removed from Reactor, mL	Methanol, M	Methyl Mercaptan, M
3.0	0.00551	0.00978
10.0	0.00535	0.00965
20.0	0.00537	0.00980
30.0	0.00534	0.00985
40.0	0.00538	0.01008
50.0	0.00523	--
51.0	0.00531	0.00969

TABLE XLIII

STABILITY OF 1,5-ANHYDRO-6-DEOXY-6-THIO-D-GLUCITOL IN 1.003M SODIUM HYDROXIDE AND 0.201M SODIUM SULFIDE AT 170.5°C

Time, minutes	6-Thio-D-glucitol, M
0.6	0.00011
20.7	0.00010
8160.0	0.00008
10086.3	0.00008

*All concentrations are reported at reaction temperature. The thermal expansivity of water was taken into account as described in the text.

TABLE XLIV

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.01M) IN 1.040M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 170.5°C

Time, minutes	1,6-Anhydro-glucose, M
1.0	0.00840
38.3	0.00700
54.5	0.00676
69.9	0.00621
85.4	0.00578
102.2	0.00538
115.6	0.00505
131.1	0.00476
163.3	0.00409
195.8	0.00344

$k_r = 7.53 \pm 0.28 \times 10^{-5}$, sec^{-1}

TABLE XLV

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.02M) IN 0.997M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 170.8°C

Time, minutes	1,6-Anhydro-glucose, M
90.4	0.01000
120.2	0.00881
136.3	0.00824
151.7	0.00763
180.3	0.00678
209.8	0.00598
210.2	0.00608
271.0	0.00448
305.9	0.00388
306.9	0.00370

$k_r = 7.50 \pm 0.28 \times 10^{-5}$, sec^{-1}

TABLE XLVI

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.02M) IN 1.000M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 170.5°C

Time, minutes	1,6-Anhydro-glucose, M
0.3	0.01761
15.8	0.01654
46.2	0.01436
60.6	0.01347
90.8	0.01151
122.4	0.01008
180.7	0.00781
212.7	0.00674

$k_r = 7.57 \pm 0.16 \times 10^{-5}$, sec^{-1}

TABLE XLVII

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.01M) IN 1.0M SODIUM HYDROXIDE AND 0.6M SODIUM p-TOLUENESULFONATE AT 170.7°C

Time, minutes	1,6-Anhydro-glucose, M
1.0	0.00788
15.1	0.00738
46.0	0.00647
60.2	0.00629
92.5	0.00560
121.4	0.00505
183.0	0.00409
213.1	0.00360

$k_r = 5.98 \pm 0.24 \times 10^{-5}$, sec^{-1}

TABLE XLVIII

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.01M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 171.0°C

Time, minutes	1,6-Anhydro-glucose, M
1.0	0.00835
17.0	0.00776
48.7	0.00684
60.4	0.00649
90.5	0.00576
120.0	0.00516
180.5	0.00399
211.7	0.00348

$k_r = 6.85 \pm 0.11 \times 10^{-5}$, sec^{-1}

TABLE XLIX

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.01M) IN 1.396M SODIUM HYDROXIDE AT 171.1°C

Time, minutes	1,6-Anhydro-glucose, M
0.1	0.00889
18.7	0.00822
46.1	0.00713
60.3	0.00666
91.7	0.00580
120.4	0.00508
181.7	0.00385
215.4	0.00329

$k_r = 7.68 \pm 0.13 \times 10^{-5}$, sec^{-1}

TABLE L

DEGRADATION OF 1,6-ANHYDRO-β-D-GLUCOPYRANOSE (0.02M) IN 1.387M SODIUM HYDROXIDE AT 170.5°C

Time, minutes	1,6-Anhydro-glucose, M
0.5	0.01843
17.1	0.01720
45.9	0.01504
60.8	0.01422
91.0	0.01240
120.0	0.01082
180.4	0.00821
213.8	0.00711

$k_r = 7.48 \pm 0.10 \times 10^{-5}$, sec^{-1}

TABLE LI

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.000M SODIUM HYDROXIDE AND 0.194M SODIUM SULFIDE AT 161.2°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M	Methyl Mercaptan, M
0.2	0.01932		
0.6	0.01948	0.00010	0.00000
88.7		0.00012	0.00000
3779.1	0.01870		
3779.5	0.01886	0.00076	0.00003
8154.8	0.01798		
8155.2	0.01785	0.00155	0.00004
13804.4	0.01692	0.00240	0.00015
13804.7	0.01679		
21192.9	0.01481		
21193.5	0.01497	0.00419	0.00031
21252.0		0.00427	0.00038

$k_r = 2.06 \pm 0.23 \times 10^{-7}$, sec^{-1}
$k_{MeOH} = 1.89 \pm 0.24 \times 10^{-7}$, sec^{-1}
$k_{MeSH} = 1.58 \pm 0.59 \times 10^{-8}$, sec^{-1}

TABLE LII

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.004M SODIUM HYDROXIDE AND 0.202M SODIUM SULFIDE AT 170.5°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M	Methyl Mercaptan, M
1.0	0.02023	0.00012	0.00000
64.0		0.00011	0.00000
2409.8	0.01959	0.00124	0.00000
5994.6		0.00275	0.00011
9614.3	0.01597	0.00411	0.00024
13198.6	0.01439	0.00543	0.00039
16807.8		0.00651	0.00045
20412.2	0.01186	0.00762	0.00047
20465.0		0.00745	0.00054
25452.7	0.01051	0.00874	0.00063
31220.0		0.00988	0.00075
31285.7		0.01003	0.00078
36993.5	0.00772	0.01108	0.00083
44370.9	0.00638	0.01228	0.00087
44434.0		0.01219	0.00087

$k_r = 4.40 + 0.10 \times 10^{-7}$, sec^{-1}
$k_{MeOH} = 3.81 \pm 0.04 \times 10^{-7}$, sec^{-1}
$k_{MeSH} = 2.95 \pm 0.19 \times 10^{-8}$, sec^{-1}

TABLE LIII

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 170.5°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M
0.7	0.01973	0.00005
3276.9	0.01887	0.00152
7087.7		0.00290
10006.2	0.01598	0.00400
14209.6	0.01469	0.00546
20154.9		0.00725
20223.1		0.00724
24449.1	0.01172	0.00834
28712.8	0.01067	0.00935
33025.4		0.01041
38813.8	0.00864	0.01160
44811.6	0.00757	0.01263
44879.8		0.01259

$k_r = 3.60 \pm 0.08 \times 10^{-7}$, sec^{-1}
$k_{MeOH} = 3.69 \pm 0.02 \times 10^{-7}$, sec^{-1}

TABLE LIV

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.01M) IN 0.991M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 181.9°C

Time, minutes	Methyl α-D-glucoside, M
1.0	0.00972
1381.2	0.00885
2806.1	0.00785
7167.8	0.00566
8625.0	0.00469
10073.6	0.00453
17265.2	0.00228
21534.5	0.00177

$k_r = 1.36 \pm 0.08 \times 10^{-6}$, sec^{-1}

TABLE LV

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.000M SODIUM HYDROXIDE AND 0.201M SODIUM SULFIDE AT 180.1°C

Time, minutes,	Methyl α-D-glucoside, M	Methanol, M	Methyl Mercaptan, M
1.0	0.01926	0.00026	0.00000
48.0		0.00030	0.00000
1431.2	0.01753	0.00189	0.00013
2884.3		0.00342	0.00024
4324.9	0.01453	0.00474	0.00039
5816.4	0.01277	0.00605	0.00046
7266.8		0.00718	0.00052
7439.7		0.00722	0.00058
8685.8	0.01031	0.00811	0.00059
11536.8	0.00893	0.00981	0.00064
14478.8		0.01124	0.00062
14538.4		0.01137	0.00069
17352.2	0.00566	0.01249	0.00071
20213.1	0.00476	0.01376	0.00082
20278.9		0.01365	0.00084
20335.0		0.01376	0.00093

$k_r = 1.16 \pm 0.04 \times 10^{-6}$ sec^{-1}
$k_{MeOH} = 1.07 \pm 0.01 \times 10^{-6}$, sec^{-1}
$k_{MeSH} = 6.35 \pm 0.79 \times 10^{-8}$, sec^{-1}

TABLE LVI

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 180.9°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M
1.2	0.01951	0.00006
53.7		0.00013
1378.7	0.01804	0.00174
2753.3		0.00315
4201.9	0.01522	0.00464
5645.7	0.01406	0.00594
7095.2		0.00722
7190.4		0.00714
8524.9	0.01189	0.00825
11421.3	0.01001	0.01012
14305.6		0.01188
17123.4	0.00717	0.01311
20049.7		0.01394
20122.5	0.00601	0.01430

$k_r = 9.75 \pm 0.04 \times 10^{-7}$, sec^{-1}
$k_{MeOH} = 1.02 \pm 0.01 \times 10^{-6}$, sec^{-1}

TABLE LVII

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 180.6°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M
0.9	0.01957	0.00017
65.6		0.00014
1341.4	0.01808	0.00161
2732.2		0.00309
4183.7	0.01530	0.00456
5613.4	0.01410	0.00587
7057.4		0.00703
7126.2		0.00701
8497.4	0.01168	0.00810
11372.8	0.01012	0.00996
14253.8		0.01171
17140.7	0.00716	0.01307
20016.9		0.01432
20105.8	0.00607	0.01430

$k_r = 9.72 \pm 0.18 \times 10^{-7}$, sec^{-1}
$k_{MeOH} = 1.02 \pm 0.01 \times 10^{-6}$, sec^{-1}

TABLE LVIII

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.399M SODIUM HYDROXIDE AT 180.9°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M
1.1	0.01945	0.00009
70.5		0.00019
1421.8	0.01772	0.00192
2576.6		0.00362
4315.0	0.01454	0.00515
5756.6	0.01323	0.00632
7192.1		0.00769
8632.5	0.01099	0.00874
8695.5		0.00875
11495.5	0.00922	0.01063
14390.3		0.01225
17283.7	0.00612	0.01349
20102.8		0.01452
20163.4		0.01452
20191.7	0.00507	0.01456

$k_r = 1.11 \pm 0.02 \times 10^{-6}$, sec^{-1}
$k_{MeOH} = 1.11 \pm 0.01 \times 10^{-6}$, sec^{-1}

TABLE LIX

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 0.993M SODIUM HYDROXIDE AND 0.201M SODIUM SULFIDE AT 190.5°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M	Methyl Mercaptan, M
0.7	0.01976	0.00022	0.00000
65.4		0.00041	0.00000
721.4	0.01789	0.00225	0.00010
1437.7	0.01582	0.00403	0.00017
2163.8	0.01403	0.00562	0.00031
2883.1		0.00701	0.00041
3614.9	0.01116	0.00819	0.00049
3677.8		0.00827	0.00051
5060.6	0.00880	0.01014	
5165.0		0.01043	0.00056
6496.3	0.00702	0.01200	0.00071
8599.4	0.00500	0.01350	0.00086
8661.7		0.01366	0.00084

$k_r = 2.68 \pm 0.03 \times 10^{-6}$, sec^{-1}
$k_{MeOH} = 2.42 \pm 0.03 \times 10^{-6}$, sec^{-1}
$k_{MeSH} = 1.54 \pm 0.09 \times 10^{-7}$, sec^{-1}

TABLE LX

DEGRADATION OF METHYL α-D-GLUCOPYRANOSIDE (0.02M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 191.4°C

Time, minutes	Methyl α-D-glucoside, M	Methanol, M
0.7	0.01943	0.00005
67.1		0.00027
671.0	0.01776	0.00196
1358.3	0.01602	0.00379
2187.5	0.01425	0.00569
2846.2		0.00706
3529.8	0.01161	0.00830
4888.3	0.00946	0.01067
6380.0	0.00762	0.01254
7862.9	0.00610	0.01404
7923.6		0.01417

$k_r = 2.47 \pm 0.02 \times 10^{-6}$, sec^{-1}
$k_{MeOH} = 2.59 \pm 0.02 \times 10^{-6}$, sec^{-1}

TABLE LXI

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.01M) IN 0.996M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 170.9°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.3	0.00949	0.00012	0.00000	0.00002
0.6	0.00970	0.00013	0.00000	0.00002
361.2	0.00805	0.00141	0.00010	0.00021
725.5	0.00718	0.00251	0.00021	0.00022
1082.0	0.00595	0.00325	0.00029	0.00018
1428.2	0.00523	0.00408	0.00036	0.00015
1802.4	0.00428	0.00464	0.00045	0.00013
2163.4	0.00378	0.00528	0.00050	0.00011
2518.7	0.00316	0.00559	0.00053	0.00009
2884.3	0.00276	0.00616	0.00060	0.00007
3596.4	0.00192	0.00670	0.00062	0.00004
3596.9	0.00196	0.00668	0.00062	0.00005

$k_r = 7.37 \pm 0.17 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.32 \pm 0.11 \times 10^{-6}$, sec^{-1}
$k_{dag} = 6.17 \pm 0.24 \times 10^{-7}$, sec^{-1}
$k_f = 2.34 \pm 0.18 \times 10^{-6}$, sec^{-1}
$k_d = 7.72 \times 10^{-5}$, sec^{-1}

TABLE LXII

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.01M) IN 0.996M SODIUM HYDROXIDE AND 0.200M SODIUM SULFIDE AT 170.5°C

Time, minutes	1,5-Anhydrocellobiitol, M	1,5-Anhydroglucitol, M	1,5:3,6-Dianhydrogalactitol, M	1,6-Anhydroglucose, M
0.4	0.00964	0.00014	0.00000	0.00003
1.1	0.00960	0.00014	0.00000	0.00003
361.0	0.00832	0.00141	0.00011	0.00024
726.9	0.00706	0.00254	0.00020	0.00024
1090.0	0.00601	0.00346	0.00029	0.00021
1449.3	0.00520	0.00426	0.00038	0.00018
1814.7	0.00439	0.00489	0.00048	0.00016
2166.6	0.00373	0.00547	0.00053	0.00013
2529.7	0.00330	0.00596	0.00056	0.00011
2891.9	0.00276	0.00639	0.00061	0.00010
3641.0	0.00202	0.00696	0.00068	0.00007
3641.7	0.00203	0.00703	0.00066	0.00007

$k_r = 7.16 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.48 \pm 0.07 \times 10^{-6}$, sec^{-1}
$k_{dag} = 6.46 \pm 0.26 \times 10^{-7}$, sec^{-1}
$k_f = 2.44 \pm 0.05 \times 10^{-6}$, sec^{-1}
$k_d = 7.47 \times 10^{-5}$, sec^{-1}

TABLE LXIII

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.02M) IN 1.000M SODIUM HYDROXIDE AND 0.201M SODIUM SULFIDE AT 170.5°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose M
0.5	0.01985	0.00020	0.00000	0.00003
0.8	0.01995	0.00022	0.00000	0.00004
355.9	0.01722	0.00271	0.00020	0.00046
716.8	0.01472	0.00488	0.00041	0.00048
1076.7	0.01258	0.00670	0.00059	0.00043
1436.7	0.01084	0.00827	0.00075	0.00036
1800.8	0.00928	0.00960	0.00090	0.00031
2160.2	0.00795	0.01067	0.00100	0.00027
2522.6	0.00679	0.01164	0.00105	0.00022
2883.0	0.00582	0.01249	0.00109	0.00018
3616.1	0.00423	0.01369	0.00122	0.00014
3616.4	0.00418	0.01369	0.00124	0.00014

$k_r = 7.17 \pm 0.05 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.17 \pm 0.06 \times 10^{-6}$, sec^{-1}
$k_{dag} = 5.71 \pm 0.22 \times 10^{-7}$, sec^{-1}
$k_f = 2.34 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_d = 7.47 \times 10^{-5}$, sec^{-1}

TABLE LXIV

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.01M) IN 1.0M SODIUM HYDROXIDE AND 0.6M SODIUM p-TOLUENESULFONATE AT 170.8°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.7	0.00949	0.00007	0.00000	0.00002
1.4	0.00971	0.00008	0.00000	0.00001
366.7	0.00826	0.00121	0.00012	0.00027
729.4	0.00722	0.00230	0.00023	0.00031
1083.8	0.00618	0.00303	0.00031	0.00027
1442.2	0.00532	0.00383	0.00045	0.00025
1800.3	0.00462	0.00438	0.00052	0.00021
2154.4	0.00404	0.00485	0.00060	0.00018
2529.0	0.00352	0.00531	0.00062	0.00014
2866.9	0.00306	0.00579	0.00070	0.00013
3610.1	0.00226	0.00637	0.00076	0.00008
3611.3	0.00229	0.00651	0.00079	0.00009

$k_r = 6.63 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_{ag} = 5.75 \pm 0.10 \times 10^{-6}$, sec^{-1}
$k_{dag} = 7.12 \pm 0.32 \times 10^{-7}$, sec^{-1}
$k_f = 2.56 \pm 0.17 \times 10^{-6}$, sec^{-1}
$k_d = 6.03 \times 10^{-5}$, sec^{-1}

TABLE LXV

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.02M) IN 1.0M SODIUM HYDROXIDE AND 0.6M SODIUM p-TOLUENESULFONATE AT 170.5°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.7	0.01933	0.00015	0.00000	0.00005
1.0	0.01949	0.00019	0.00000	0.00005
355.5	0.01703	0.00245	0.00025	0.00054
716.8	0.01471	0.00443	0.00050	0.00063
1078.7	0.01288	0.00621	0.00072	0.00059
1439.7	0.01116	0.00769	0.00090	0.00052
1798.2	0.00967	0.00894	0.00103	0.00045
2158.5	0.00839	0.00999	0.00116	0.00038
2522.6	0.00730	0.01095	0.00123	0.00032
2894.4	0.00634	0.01185	0.00138	0.00028
3608.1	0.00475	0.01306	0.00144	0.00020
3608.5	0.00477	0.01318	0.00147	0.00021

$k_r = 6.50 \pm 0.04 \times 10^{-6}$, sec^{-1}
$k_{ag} = 5.75 \pm 0.05 \times 10^{-6}$, sec^{-1}
$k_{dag} = 6.59 \pm 0.26 \times 10^{-7}$, sec^{-1}
$k_f = 2.56 \pm 0.17 \times 10^{-6}$, sec^{-1}
$k_d = 6.03 \times 10^{-5}$, sec^{-1}

TABLE LXVI

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.01M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 170.9°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.5	0.00955	0.00017	0.00000	0.00002
1.0	0.00974	0.00018	0.00000	0.00002
359.1	0.00819	0.00143	0.00013	0.00027
719.9	0.00712	0.00250	0.00025	0.00029
1086.3	0.00594	0.00335	0.00039	0.00025
1440.0	0.00528	0.00416	0.00048	0.00022
1797.7	0.00438	0.00471	0.00057	0.00018
2162.9	0.00376	0.00536	0.00063	0.00015
2527.4	0.00314	0.00576	0.00067	0.00012
2885.3	0.00272	0.00619	0.00075	0.00010
3601.3	0.00196	0.00672	0.00080	0.00007
3601.7	0.00197	0.00679	0.00080	0.00007

$k_r = 7.36 \pm 0.11 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.32 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_{dag} = 7.81 \pm 0.21 \times 10^{-7}$, sec^{-1}
$k_f = 2.71 \pm 0.16 \times 10^{-6}$, sec^{-1}
$k_d = 6.79 \times 10^{-5}$, sec^{-1}

TABLE LXVII

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.01M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 170.5°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.4	0.00942	0.00012	0.00000	0.00004
0.9	0.00940	0.00012	0.00000	0.00004
358.5	0.00800	0.00134	0.00013	0.00026
728.8	0.00686	0.00245	0.00026	0.00028
1081.3	0.00587	0.00331	0.00037	0.00026
1439.5	0.00509	0.00410	0.00045	0.00022
1803.0	0.00436	0.00471	0.00053	0.00019
2170.1	0.00370	0.00528	0.00059	0.00016
2526.1	0.00317	0.00575	0.00064	0.00014
2887.2	0.00272	0.00614	0.00068	0.00011
3617.4	0.00200	0.00673	0.00074	0.00008
3618.1	0.00198	0.00679	0.00075	0.00008

$k_r = 7.15 \pm 0.04 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.42 \pm 0.07 \times 10^{-6}$, sec^{-1}
$k_{dag} = 7.26 \pm 0.18 \times 10^{-6}$, sec^{-1}
$k_f = 2.62 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_d = 6.57 \times 10^{-5}$, sec^{-1}

TABLE LXVIII

DEGRADATION OF 1,5-ANHYDROCELLOBIITOL (0.02M) IN 1.2M SODIUM HYDROXIDE AND 0.2M SODIUM p-TOLUENESULFONATE AT 170.5°C

Time, minutes	1,5-Anhydro-cellobiitol, M	1,5-Anhydro-glucitol, M	1,5:3,6-Dianhydro-galactitol, M	1,6-Anhydro-glucose, M
0.3	0.01954	0.00015	0.00000	0.00005
0.6	0.01982	0.00015	0.00000	0.00005
361.4	0.01720	0.00264	0.00027	0.00054
721.7	0.01458	0.00486	0.00053	0.00060
1076.2	0.01249	0.00670	0.00076	0.00054
1441.8	0.01080	0.00827	0.00094	0.00046
1800.3	0.00920	0.00957	0.00107	0.00039
2155.5	0.00798	0.01066	0.00120	0.00033
2515.9	0.00675	0.01171	0.00130	0.00028
2892.6	0.00580	0.01264	0.00142	0.00024
3607.5	0.00425	0.01380	0.00155	0.00017
3607.8	0.00426	0.01383	0.00153	0.00017

$k_r = 7.10 \pm 0.06 \times 10^{-6}$, sec^{-1}
$k_{ag} = 6.31 \pm 0.06 \times 10^{-6}$, sec^{-1}
$k_{dag} = 7.14 \pm 0.16 \times 10^{-7}$, sec^{-1}
$k_f = 2.62 \pm 0.08 \times 10^{-6}$, sec^{-1}
$k_d = 6.57 \times 10^{-5}$, sec^{-1}