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Alkali Treatment of Glycolaldehyde, Glucose and Cellobiose in the Presence of Anthraquinone

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Treatment of glycolaldehyde with anthraquinone and sodium hydroxide in 75 % ethanol gives glycolic acid in high yield. With glucose, the same treatment leads to the formation of aldonic acids and promotes the formation of glyceric, glycolic and 3-deoxypentonic acids while 2-hydroxypropanoic, 3-deoxytetronic and 3-deoxyhexonic acids are less abundant.

The reducing glucose residue in cellobiose is oxidized to a hexosulose group which is converted to a mannonic acid group. Minor amounts of gluconic but no pentonic or tetronic acid groups are formed. Anthraquinone promotes the formation of 3-deoxypentonic acids but suppresses the formation of most of the acidic fragmentation products obtained from 4-deoxy-2,3-hexodiulose in the absence of oxidant.

Anthraquinone (AQ) present during alkaline cooking of wood leads to a stabilization of the carbohydrates which is related to the oxidation of reducing sugar end groups to aldonic acid groups.[1–3] Aldobionic acids were, on the other hand, not obtained when an aqueous solution of cellobiose was heated with sodium hydroxide in the presence of AQ.[2] This report on the effect of AQ on the alkaline degradation of cellobiose describes experiments carried out in aqueous ethanol. For comparison, parallel experiments were made with glycolaldehyde and glucose which are formed as intermediates during alkaline treatments of cellobiose.

REACTIONS OF GLYCOLALDEHYDE

In alkaline media, aldol condensation of glycolaldehyde results in a wide variety of sugars. The relative sugar composition and the yield depend on the reaction time and the concentration and alkalinity of the reaction mixture. An unpublished study of the reactions in aqueous sodium hydrogen carbonate solution shows that large amounts of tetroses and hexoses were present after 1 h at 82 °C and that trioses, pentoses and octoses were also formed. The results given in Table 1 show that 3-deoxytetronic acid was the predominant hydroxy acid formed during heating in sodium hydroxide in the absence of AQ. The formation of 3-deoxytetronic acid is explained by β-elimination of OH-3 in the tetroses followed by a benzilic acid rearrangement.

Analogous reactions of pentoses and hexoses explain the formation of 3-deoxypentonic and 3-deoxyhexonic acids. 2-Hydroxypropanoic acid was the second most abundant acid. Trioses are important precursors of this acid.[4] A larger proportion of 2-hydroxypropanoic acid was produced at the higher alkali concentration. Similarly, glycolic acid is formed from hexoses and other sugars even in the absence of oxidants.

The product composition changed substantially when AQ was present. Glycolic acid was the predominant hydroxy acid. This shows that the oxidation of glycolaldehyde was more rapid than the aldol condensation. This was also reflected in lower yields of 3-deoxyaldonic acids. The formation of 3-deoxytetronic acid was also suppressed due to a competing oxidation of the tetroses which yielded erythronic and threonic acids as final products. Analogously, the formation of 2-hydroxypropanoic acid was suppressed while glyceric acid, which can be formed by oxidation of trioses, was

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Table 1. Yields of monocarboxylic acids after alkali treatment of 1 g of glycolaldehyde in 75 % ethanol with and without addition of AQ.

Acid	0.09 M sodium hydroxide		0.5 M sodium hydroxide	
	Blank mg	AQ mg	Blank mg	AQ mg
2-Hydroxypropanoic	83	68	159	58
3-Deoxytetronic	449	96	435	101
3-Deoxy-*erythro*-pentonic	5	2	11	4
3-Deoxy-*threo*-pentonic	30	15	14	9
3-Deoxyhexonic	37	7	85	21
Glycolic	46	350	8	320
Glyceric	4	28	7	50
Erythronic	7	47	4	79
Threonic	9	53	2	59
Total (nonvolatile acids)	670	666	725	701
Acetic			24	20
Formic			44	61

much more abundant than in the blank. Only trace amounts of pentonic and hexonic acids were formed. In the presence of the quinone 2-hydroxypropanoic acid was still one of the major products although the reaction path *via* aldoses should be less important. The yield of formic acid increased when AQ was present while acetic acid was less abundant.

REACTIONS OF GLUCOSE

A very small amount of glyceric acid was produced from glucose in the blank without AQ while this acid was among the most abundant acids when AQ was present. Oxidation of glyceraldehyde following a reverse aldol reaction explains the formation of glyceric acid. The decreased proportion of 2-hydroxypropanoic acid which is one of the main stable products from glyceraldehyde in the absence of oxidants, supports this reaction scheme.

Other striking effects of AQ are the decreased proportions of 3-deoxyhexonic acids, formed by β-elimination of OH-3 and subsequent benzilic acid rearrangement of 3-deoxy-*erythro*-hexosulose, and of 3-deoxytetronic acid which can be formed from erythrose by an analogous reaction. Erythrose can be formed, together with glycolaldehyde, by a reverse aldol reaction. The absence of 2-deoxy-*erythro*-pentonic and 3-hydroxypropanoic acids shows that in contrast to oxygen treatment in the presence of sodium hydroxide [5] no cleavage of dicarbonyl intermediates between the carbonyl groups occurred during alkali treatment with the addition of AQ. The lowered yield of 3-deoxyaldonic acids is explained by an oxidation of glucose and erythrose to aldonic acids. The large proportion of mannonic acid compared to its C-2 epimer indicates that D-*arabino*-hexosulose is a precursor to the hexonic acids.[6] Oxidation with AQ yields glycolic acid as the most abundant hydroxy acid from glycolaldehyde (Table 1) and contributes to the increased proportion of glycolic acid in the experiments with glucose. The tetronic and pentonic acids were much more abundant after the treatment with the addition of AQ at the lower hydroxide concentration than at the higher one. This indicates that an important reaction path is *via* pentoses and tetroses.

Among the less abundant products was 3,4-dideoxypentonic acid. As expected [7] the largest proportion was obtained at the lowest sodium hydroxide concentration. This acid seems to have escaped observation in previous investigations on alkali treatment of glucose. Both in the experiments with glucose and in those with cellobiose AQ suppressed the formation of this acid by approximately 50 %. An oxidation of intermediates explains the decrease in yield.

The diastereomeric 3-deoxypentonic acids belonged to the most abundant hydroxy acids formed by sodium hydroxide treatment of D-*arabino*-hexosulose with exclusion of oxygen.

Table 2. Monocarboxylic acids after treatment of glucose and cellobiose with 0.09 M and 0.5 M sodium hydroxide in 75 % ethanol with and without addition of AQ. The weights refer to products obtained from 1 g of cellobiose and 0.5 g glucose respectively.

Monocarboxylic acids	0.09 M sodium hydroxide				0.5 M sodium hydroxide			
	No quinone addition		Anthraquinone (AQ)		No quinone addition		Anthraquinone (AQ)	
	Glucose mg	Cellobiose mg	Glucose mg	Cellobiose mg	Glucose mg	Cellobiose mg	Glucose mg	Cellobiose mg
4-*O*-(β-D-Glucopyranosyl)-D-mannonic				90				62
4-*O*-(β-D-Glucopyranosyl)-D-gluconic				5				3
3-Deoxy-2-*C*-hydroxymethyl-*threo*-pentonic		116		68		219		139
3-Deoxy-2-*C*-hydroxymethyl-*erythro*-pentonic		46		23		75		36
1,4-Anhydro-3-deoxypentitol-2-carboxylic		13		7		7		5
3-Deoxy-*threo*-pentonic	7	21	40	195	9	9	17	104
3-Deoxy-*erythro*-pentonic	1	6	9	53	2	3	9	37
3,4-Dideoxypentonic	6	63	3	31	2	33	2	12
3,4-Dideoxyhexonic				9				13
2-Deoxytetronic (3,4-dihydroxybutanoic)		12	6	14		4		8
Glycolic	37	43	75	106	27	19	60	60
2-Hydroxypropanoic	185	93	75	52	202	210	94	76
3-Deoxy-*arabino*-hexonic		94		55				
3-Deoxy-*arabino*-hexonic + 3-deoxy-*ribo*-hexonic acids	102		41		100	149	67	86
3-Deoxy-*ribo*-hexonic		21		12				
3-Deoxytetronic (2,4-dihydroxybutanoic)	58	52	29	33	51	70	20	18
Glyceric	5	5	52	25	10	4	69	56
Threonic			7	9			5	4
Erythronic			17	12			11	10
Arabinonic			21	4			5	5
Ribonic			11	3			2	2
Gluconic			5	16			3	2
Mannonic			32	40			41	37
Total (nonvolatile acids)	401	585	423	862	403	802	405	775
Acetic					11	18	13	17
Formic					35	51	45	75

The presence of these acids after alkali treatment with the addition of AQ supports the conclusion that this dicarbonyl intermediate is produced.[8] The formation of minor amounts of 3-deoxypentonic acids in the absence of any oxidant may occur *via* pentoses.[9]

The yield of acetic acid was hardly affected in the presence of AQ while that of formic acid was enhanced.

REACTIONS OF THE REDUCING GLUCOSE RESIDUE IN CELLOBIOSE

No detectable amounts of sugars were present after boiling with sodium hydroxide in 75 % ethanol. Table 2 shows that a large number of hydroxy acids, an appreciable proportion of formic acid and a small amount of acetic acid were formed. At low sodium hydroxide concentration the yield of acids was much higher in the experiment with AQ than in the blank without oxidant. The results indicate that cyclization and polymerization were suppressed by oxidation. Similar results have been observed in the presence of oxygen during alkaline treatments.[10]

The high yield of identified carboxylic acids after the treatment of cellobiose in 0.5 M sodium hydroxide is consistent with previous observations made for aqueous solutions. At this concentration AQ had no significant influence on the total yield of monocarboxylic acids, while the product composition was markedly affected.

At the lowest sodium hydroxide concentration almost 10 % of the cellobiose was oxidized to aldobionic acids while at the highest concentration the conversion to aldobionic acids was approximately 6 %. Among these acids 4-*O*-*β*-D-glucopyranosyl-D-mannonic acid predominated. Only a small amount of the C-2 epimer was present. These observations permit the conclusion that the aldobionic acids were formed *via* 4-*O*-*β*-D-glucopyranosyl-D-*arabino*-hexosulose.[6,8] No detectable amounts (less than 0.05 % of the cellobiose) of 3-*O*-*β*-D-glucopyranosyl-D-arabinonic and 2-*O*-*β*-D-glucopyranosyltetronic acids were present. Evidently, oxidative cleavage of the hexosulose moiety which occurs in the presence of oxygen is of no importance under the conditions applied here.

The predominant reaction leading to a cleavage of the glycosidic bond in alkaline medium is an isomerization of the reducing glucose moiety followed by a *β*-elimination of glucose and the formation of 4-deoxy-2,3-hexodiulose. Benzilic acid rearrangement gives the well-known 3-deoxy-2-*C*-(hydroxymethyl)-pentonic acids. At both alkali levels the amounts of these decreased by about 50 % in the presence of AQ. The largest proportion of these acids was obtained at the highest alkali concentration. The formation of 1,4-anhydro-3-deoxy-pentitol-2-carboxylic acid was also suppressed by AQ.

Another important reaction of 4-deoxy-2,3-hexodiulose results in a loss of C-1 as formic acid and the formation of 3-deoxypentulose.[7] One of the main reactions of this sugar in alkaline medium is a *β*-elimination of OH-4 followed by rearrangements yielding 3,4-dideoxypentonic acid. In addition large amounts of cyclic and polymerized products are formed. The higher yield of 3,4-dideoxypentonic acid and the lower total yield of nonvolatile monocarboxylic acids at the lower sodium hydroxide concentration are consistent with previously reported experiments with 4-deoxy-2,3-hexodiulose.[10] At both alkali levels, the yield of 3,4-dideoxypentonic acid was markedly suppressed in the presence of AQ indicating that precursors are oxidized by AQ.

The observation that only aldobionic acids with hexonic acid groups were formed indicates that the hexosulose group was destroyed rapidly. In addition to benzilic acid rearrangement giving rise to the hexonic acid groups a rapid *β*-elimination of glucose must occur. This leads to a tricarbonyl intermediate which in sodium hydroxide gives the diastereomeric 3-deoxypentonic acids as main products. In agreement with the results obtained after alkaline degradation of 4-*O*-*β*-D-glucopyranosyl-D-*arabino*-hexosulose [8] and after oxidation of 3-deoxy-*erythro*-pentose and 4-deoxy-2,3-hexodiulose with oxygen in alkaline medium the *threo* form was more abundant than the *erythro* form. A smaller but significant effect of AQ on the formation of 3-deoxypentonic acids was observed in aqueous sodium hydroxide although, as discussed above, no aldobionic acids were formed.[2]

In contrast to the acids discussed above,

3,4-dideoxyhexonic acid formed from cellobiose in the experiments with addition of AQ is a typical reduction product. This acid was previously obtained after treatment of cellobiose [2] and hydrocellulose [11] in aqueous sodium hydroxide with the addition of AQ. In agreement with previous observations, it was not formed in the absence of AQ. The fact that no traces of the compound were produced from glucose is in agreement with the reaction scheme suggested previously.[11]

A larger amount of formic acid was produced from cellobiose than from glucose. This was expected since formic acid was the most abundant acid produced during treatment of 4-deoxy-2,3-hexodiulose [10] with sodium hydroxide. AQ promoted the formation of formic acid.

REACTIONS OF GLUCOSE FORMED FROM CELLOBIOSE

The results given in Table 2 indicate that the products from glucose liberated by degradation of cellobiose are the same as those obtained in the experiments with glucose, while the proportions are changed to some extent. This occurs in the experiments both with and without the addition of AQ. One effect of AQ on the products belonging to this group is that the formation of 3-deoxyhexonic, 2-deoxytetronic and 2-hydroxypropanoic acids from cellobiose was markedly suppressed in the experiments with the addition of AQ. This is explained by the competing reactions referred to above.

The initial concentration of sodium hydroxide was the same in the experiments with both sugars. Due to the fast reactions of the reducing moiety in cellobiose, a large proportion of the hydroxide ions was consumed rapidly in the experiments at the lowest hydroxide ion concentration. This explains the much lower yield of 2-hydroxypropanoic acid from cellobiose than from glucose.

The above results show that an appreciable proportion of the additive was consumed rapidly in the experiments with cellobiose. Moreover, the amount of AQ added per g of cellobiose was the same as that per 0.5 g of glucose. This may explain why larger amounts of glyceric acid and some aldonic acids were formed from 0.5 g of glucose than from 1.0 g of cellobiose.

CONCLUDING REMARKS

In the investigation referred to in the introduction, aldobionic acids were not found after treatment of cellobiose at 97 °C with an aqueous solution of sodium hydroxide in the presence of an excess of suspended AQ. Enhanced yields of glycolic, 3-deoxypentonic and glyceric acids were obtained in comparison with a blank without any additive, but on the whole the effect of the additive was small.[2] The results indicate that the rate of dissolution of AQ was low compared to that of the alkaline degradation of the disaccharide and the consecutive reactions leading mainly to monocarboxylic acids. The higher solubility of AQ in aqueous ethanol and the increased rate of dissolution explain the dramatic effect of AQ on the product composition observed in the present study, including the formation of an appreciable proportion of aldobionic acids.

The finding that a small addition of AQ is capable of converting a large proportion of the reducing sugar end groups to aldonic acid end groups when wood meal is treated with aqueous sodium hydroxide at 80–100 °C supports the conclusion [2,3] that anthrahydroquinone formed mainly in carbohydrate reactions is oxidized by the lignin. In this way an oxidized form of the additive is regenerated. Evidently, carbohydrate and lignin reactions with different forms of the additive are both of great importance during the heating up period in alkaline digestion of wood.

EXPERIMENTAL

Glycolaldehyde (0.14 g), glucose (0.18 g) or cellobiose (0.36 g) dissolved in 3.8 ml hot, boiled water was injected into boiling solutions containing 17.4 g water, 64.4 g ethanol, 0.60 g AQ and 0.35 g sodium hydroxide. The boiling was done under reflux cooling with a stream of nitrogen introduced into the upper part of the cooler and discharged at the top. The reaction mixture became brownish green. The dissolution of AQ was incomplete at the end of the reaction period. After 3 h the flask was cooled with ice-water and neutralized by stirring with a cation exchange resin (Dowex

50W-X8, H^+) in the presence of air. The resin and precipitated AQ were filtered off and the ethanol was removed by evaporation and addition of water. The solution was stirred at pH 10.3 for 1 h at room temperature to split any ester linkages formed during the treatment with the cation exchanger. After filtration to remove precipitated AQ, acetic acid was added to obtain pH 9. The solution was then evaporated to dryness.

Blanks were carried out under identical conditions without addition of AQ. Experiments were also made in which the addition of sodium hydroxide was increased to 2.00 g. Except for the duration of the treatment which was shortened to 1 h the conditions were the same. In these experiments the reaction mixture became blood-red.

Anion exchange chromatography in acetate media [1] combined with gas chromatography of the trimethylsilyl derivatives on two stationary phases [12] was employed for determination of the nonvolatile acids. Formic acid was determined by anion exchange chromatography and acetic acid by gas chromatography.[5]

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