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ALKALI AND OXYGEN–ALKALI TREATMENT OF D-*arabino*-HEXOSULOSE AND *O*-β-D-GLUCOPYRANOSYL-(1→4)-D-*arabino*-HEXOSULOSE

LARS-ÅKE LINDSTRÖM AND OLOF SAMUELSON

Department of Engineering Chemistry, Chalmers University of Technology, Fack, S-402 20 Gothenburg (Sweden)

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ABSTRACT

Benzilic acid rearrangement of D-*arabino*-hexosulose (**1**) and *O*-β-D-glucopyranosyl-(1→4)-D-*arabino*-hexosulose (**2**) favours formation of mannonic acid and mannonic acid moieties, respectively. The results show that formation of aldonic acid end-groups *via* terminal aldosulose moieties is of little importance during oxygen–hydrogencarbonate treatment of (1→4)-linked polysaccharides. The major reaction of **1** in the absence of oxygen involves loss of C-1 as formic acid. The enediol intermediate gives rise to pentoses and pentuloses (degraded completely at high alkalinity), and 3-deoxypentonic acids. The yield of 3-deoxypentonic acids is decreased in the presence of oxygen, whereas that of arabinonic, erythronic, and glycolic acids is increased. The main reaction of **2** giving rise to aliphatic hydroxy acids is β-elimination of the glucose moiety, yielding a tricarbonyl intermediate (**3**) which, in sodium hydrogencarbonate, is decomposed mainly to 3,4-dihydroxybutanoic and glycolic acids. In sodium hydroxide, 3-deoxypentonic acids are among the major reaction products. In addition, a complex mixture of u.v.-absorbing solutes is formed, some of which are held irreversibly by anion exchangers.

INTRODUCTION

Processes in which wood and wood pulps are subjected to oxidation in alkaline media have become increasingly important. While there is strong evidence that aldosulose end-groups are important intermediates during oxygen treatment of (1→4)-linked polysaccharides in strongly alkaline media[1], it is still an open question whether this reaction path is of importance at low concentrations of hydroxide ion. Experiments with D-*arabino*-hexosulose (**1**) and *O*-β-D-glucopyranosyl-(1→4)-D-*arabino*-hexosulose (**2**) were made to elucidate this question, and to study the reaction products obtained from these compounds in alkaline media.

RESULTS AND DISCUSSION

Formation of aldonic acids. — In agreement with results reported by other investigators[2–4], benzilic acid rearrangement of **1** in sodium hydroxide led to a much

TABLE I

DEGRADATION PRODUCTS FROM D-*arabino*-HEXOSULOSE[a] (1)

Product	*0.05M $NaHCO_3$ 30 min*		*0.05M NaOH 30 min*		*0.05M $NaHCO_3$ 15 min, 0.4 MPa[b]*		*0.05M NaOH 15 min, 0.4 MPa[b]*	
	Yield (mg)	*(mmol/mol of reacted 1)*	*Yield (mg)*	*(mmol/mol of reacted 1)*	*Yield (mg)*	*(mmol/mol of reacted 1)*	*Yield (mg)*	*(mmol/mol of reacted 1)*
Arabinose (including ribose)	6.4	77	0		1.4	17	0	
erythro-Pentulose	8.3	101	0		1.4	17	0	
Trioses (including ulose)	4.0	81	0		0.5	10	0	
Gluconic acid	1.8	17	1.8	17	0.8	7.4	1.9	18
Mannonic acid	3.8	35	6.3	58	2.4	22	5.0	46
Arabinonic acid[c]	3.5	38	1.3	14	18.0	197	10.2	112
Ribonic acid[c]	0.6	6.6	<0.1		0.9	9.8	3.1	34
Erythronic acid	2.0	27	<0.1		13.3	178	7.9	106
Glyceric acid	<0.1		<0.1		0.8	14	0.3	5.1
3,6-Anhydrohexonic acid I	2.5	26	0.9	9.2	0.4	4.1	0.5	5.1
3,6-Anhydrohexonic acid II	0.8	8.2	<0.1		<0.1		0.4	4.1
3-Deoxy-*threo*-pentonic acid[c]	7.0	85	14.8	179	2.0	24	5.1	62
3-Deoxy-*erythro*-pentonic acid[c]	1.3	16	3.2	39	0.4	4.8	1.2	15
3,4-Dihydroxybutanoic acid	0.8	12	<0.1		1.0	15	1.4	21
2-Hydroxypropanoic acid	<0.1		2.9	59	<0.1		1.7	34
Glycolic acid[d]	1.1	26	3.7	88	9.5	227	6.5	155
Formic acid[d]	13.4	529	14.5	573	12.7	501	14.6	576
Dicarboxylic acids	0		0		1.6		2.0	
Identified compounds (total)	57.3	1085	49.4	1036	67.1	1248	61.8	1193
Unidentified compounds								
Eluted with water	18.8		5.0		9.0		1.7	
Eluted with 5M HOAc	14.0		29.4		21.0		24.0	

[a]Degradation of 1 (100 mg; purity, 98%) at 90°. [b]Partial pressure of oxygen. [c]Relative amounts of the diastereomers determined by ion-exchange chromatography. [d]Determined by ion-exchange chromatography.

TABLE II

DEGRADATION PRODUCTS FROM *O*-β-D-GLUCOPYRANOSYL-(1→4)-D-*arabino*-HEXOSULOSE[a] (2)

Product	*0.05M $NaHCO_3$ 10 min 135°*		*0.05M $NaHCO_3$ 30 min 90°*		*0.05M NaOH 30 min 90°*		*0.05M $NaHCO_3$ 15 min, 0.4 MPa[b] 90°*		*0.05M NaOH 15 min, 0.4 MPa[b] 90°*	
	Yield (mg)	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*
Glucose (including mannose)	5.6	119	24.7	537	0		37.2	792	0	
Fructose	4.4	94	1.2	26	0		0.8	17	0	
Pentoses (including uloses)	0.4	10	0		0		0		0	
3-Deoxypentulose	0.8	23	2.0	58	0		2.6	74	0	
Tetroses (including ulose)	0.3	10	0		0		0		0	
Trioses (including ulose)	0.4	17	0		0		0		0	
4-*O*-β-D-Glucopyranosyl-D-gluconic acid	1.6	17	0.4	4.4	1.1	12	0.6	6.4	1.2	13
4-*O*-β-D-Glucopyranosyl-D-mannonic acid	2.9	31	0.9	9.8	5.8	62	0.7	7.5	3.4	36
4-*O*-β-D-Glucopyranosyl-D-arabinonic acid	0.5	5.8	1.0	12	2.4	28	2.4	28	5.7	67
4-*O*-β-D-Glucopyranosyl-D-erythronic acid	0.4	5.1	0.4	5.2	0.5	6.4	0.3	3.8	3.1	40
Mannonic acid	0		0		0		0		0.3	5.9
Arabinonic acid	0		0		0		0		2.5	58
Ribonic acid	0		0		0		0		0.7	16
Erythronic acid	0		0		0		0		1.5	42
Threonic acid	0		0		0		0		0.4	11
Glyceric acid	0		0		<0.1		0		3.4	123
3-Deoxy-*arabino*-hexonic acid	2.7	57	0		2.8	60	0		0	
3-Deoxy-*ribo*-hexonic acid	0.3	6.4	0		0.6	13	0		0	
2-Deoxy-*erythro*-pentonic acid	0		0		0		0		2.0	51
3-Deoxy-*threo*-pentonic acid	1.6	41	0.7	18	4.6	118	0.9	23	4.8	123
3-Deoxy-*erythro*-pentonic acid	0.7	18	0.6	15	2.2	56	0.5	13	1.9	49
3,4-Dideoxypentonic acid	0.2	5.7	0		0.9	26	0		0	
3,4-Dihydroxybutanoic acid	9.3	297	8.3	270	3.3	105	9.1	290	7.9	252
2,4-Dihydroxybutanoic acid	1.1	35	0		1.7	54	0		0.5	16

TABLE II (continued)

DEGRADATION PRODUCTS FROM *O*-β-D-GLUCOPYRANOSYL-(1→4)-D-*arabino*-HEXOSULOSE[a] (2)

Product	*0.05M NaHCO3 10 min 135°*		*0.05M NaHCO3 30 min 90°*		*0.05M NaOH 30 min 90°*		*0.05M NaHCO3 15 min, 0.4 MPa[b] 90°*		*0.05M NaOH 15 min, 0.4 MPa[b] 90°*	
	Yield (mg)	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*	*Yield (mg)*	*(mmol/mol of reacted 2)*
2-Hydroxypropanoic acid	0.9	38	<0.1		4.2	179	2.3	98	3.2	136
Glycolic acid	5.7	287	6.1	312	4.7	237	5.9	298	6.0	303
Formic acid	4.4	367	1.3	110	7.2	600	2.1	175	11.7	975
Tartronic acid	0		0		0		<0.1		0.3	9
C-(2,3-Dihydroxypropyl)tartronic	0		0		0		0.2	4	2.9	56
Identified compounds (total)	44.2	1484	47.6	1378	42	1556	65.6	1830	63.4	2382
Unidentified compounds eluted with water	12.5		36.1		1.6		20.4		1.9	

[a]Degradation of 100 mg of **2**. [b]Partial pressure of oxygen.

larger amount of mannonic acid than gluconic acid (Table I). Similarly, the formation of mannonic acid moieties from **2** (Table II) is favoured compared to gluconic acid moieties. For both dicarbonyl compounds, the same is true during treatment with hydrogencarbonate solution. In both media, mannonic acid was also favoured when oxygen was present.

During O_2–NaOH treatment of cellulose[5,6] and cellobiose[1,7], mannonic acid moieties are formed in larger numbers than gluconic acid groups. Similarly, lyxonic acid end-groups are more abundant than xylonic acid groups after O_2–NaOH treatment of xylan[8]. The results in Tables I and II support the previous conclusion that, during O_2–NaOH treatment of (1→4)-linked polysaccharides, aldosulose end-groups are precursors of the aldonic acid end-groups.

In contrast, the formation of gluconic acid moieties is favoured, compared to mannonic acid, during O_2–$NaHCO_3$ treatment of cellobiose[9]. Similarly, xylan oxidation in this medium leads to xylonic acid end-groups, and only a few lyxonic acid groups are formed[10]. The results obtained with **1** and **2** permit the conclusion that the formation of aldonic acid end-groups *via* terminal aldosulose moieties is of little importance in $NaHCO_3$.

Previous investigators have reported only the relative amounts of identified hydroxy acids. Table I shows that, under the conditions employed in the present work, 3.2–8.1 % of **1** was converted into hexonic acids, while **2** yielded only 1.3–6.9 % of glucosylhexonic acids. The benzilic acid rearrangement was favoured at high temperature and alkalinity, and suppressed by the presence of oxygen.

In agreement with Malinen and Sjöström[3], the degradation of **1** to arabinonic and erythronic acids in NaOH was favoured by the presence of oxygen. It is noteworthy that these acids were much more abundant after the $NaHCO_3$ treatments. The corresponding aldobionic acids were formed from **2**. The formation of arabinonic acid moieties was favoured by oxygen in both media. The highest yield was obtained at the lowest temperature. The presence of oxygen led to an increased yield of erythronic acid moieties in the experiments in NaOH, but not in $NaHCO_3$.

Formation of other monocarboxylic acids and sugars. — As expected[2], appreciable amounts of pentoses and formic acid were present after treatment of **1** with $NaHCO_3$

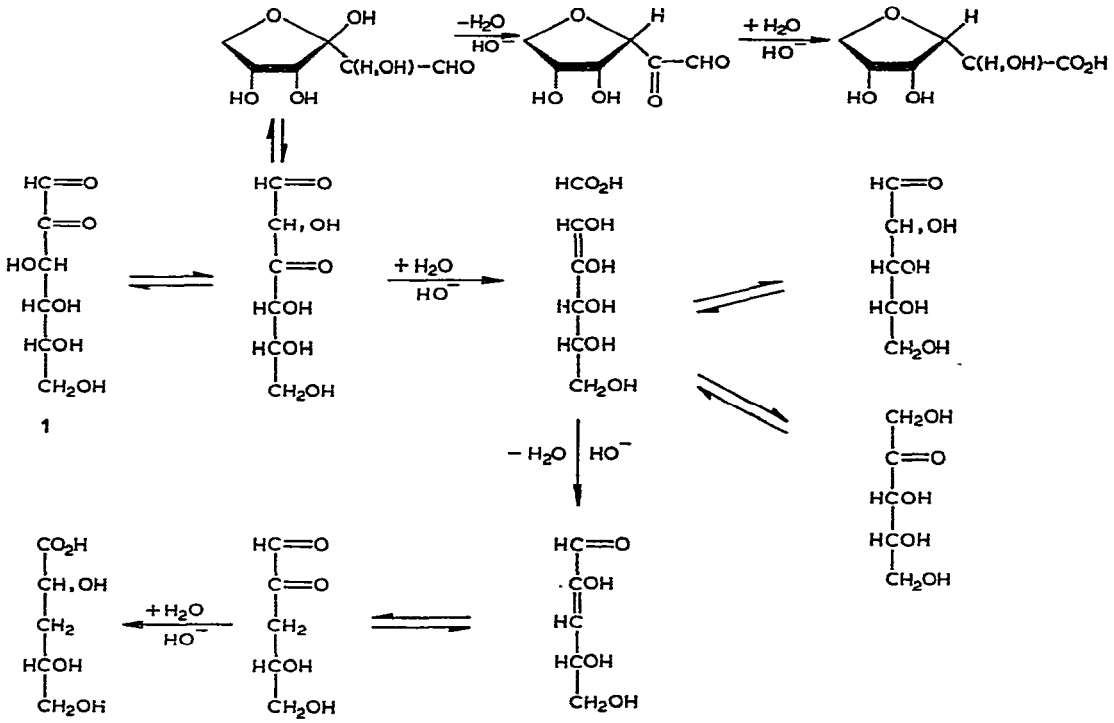
TABLE III

DEGRADATION PRODUCTS FROM ARABINOSE[a]

Product	*Yield (mg)*
Arabinose (including ribose and *erythro*-pentulose)	95.3
Trioses	0.95
3-Deoxy-*threc*-pentonic acid	0.64
3-Deoxy-*erythro*-pentonic acid	0.17
2-Hydroxypropanoic acid	0.06
Glycolic acid	0.19

[a] From treatment of 100 mg of arabinose in 0.05M $NaHCO_3$ at 90° for 30 min in the absence of oxygen.

in the absence of oxygen (Table I). Arabinose and *erythro*-pentulose belonged to the major products, while ribose was less abundant. Other prominent products were trioses (glyceraldehyde and dihydroxyacetone) and 3-deoxypentonic acids. Table III shows that arabinose is degraded very slowly under the conditions used in the experiments with **1**. The major hydroxy acids formed were the expected 3-deoxypentonic acids[3]. In addition, appreciable proportions of trioses were present. The proportions of these products were, however, much less than those formed from **1**. Hence, arabinose cannot be the primary precursor of the 3-deoxypentonic acids. The results suggest that these acids are produced *via* the 1,2-enediol of arabinose obtained after an isomerization of **1** and the loss of C-1 as formic acid, as indicated in Scheme 1 (ionic forms omitted for simplicity). The competition between *β*-hydroxy elimination of HO-3, followed by benzilic acid rearrangement, and the isomerization to pentoses explains the product composition.



Scheme 1

No sugars were present after the severe treatment in NaOH. The increased yield of 3-deoxypentonic acids and the high yield of formic acid indicate that the primary reactions are the same in this medium. The increased yield of glycolic and 2-hydroxypropanoic acids, formed during alkaline degradation of pentoses[4], is consistent with this reaction scheme.

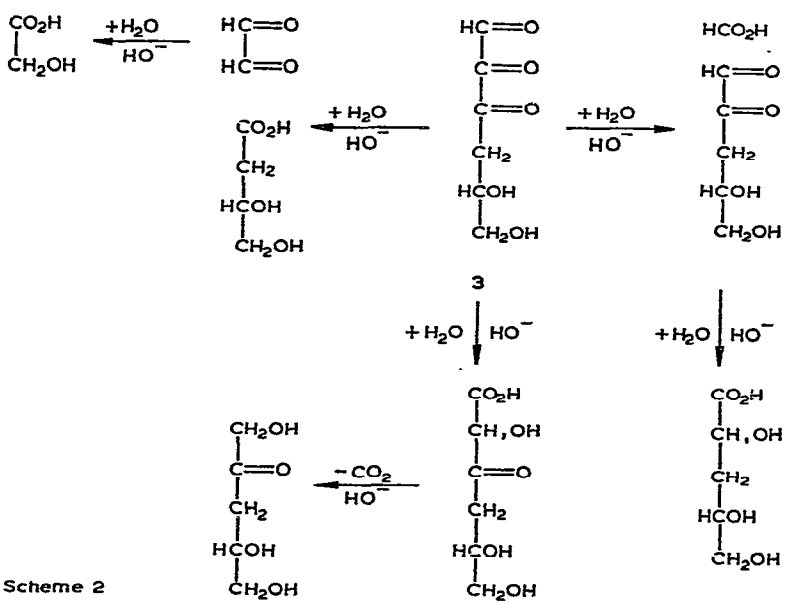
The alkaline treatments of **1** in the absence of oxygen gave appreciable amounts

of two isomeric 3,6-anhydrohexonic (mannonic and gluconic) acids. The yields were lower in the experiments under oxygen pressure. These acids have escaped observation in previous investigations of **1**. A plausible reaction-path for the formation of the 3,6-anhydrohexonic acids is dehydration of the hemiacetal form of the 3-hexosulose isomer of **1** followed by benzilic acid rearrangement, as indicated in Scheme 1. Analogously, 4-deoxy-2,3-hexodiulose[11], cellobiose[12], and hydrocellulose[13] give rise to "anhydroisosaccharinic" (1,4-anhydro-3-deoxypentitol-2-carboxylic) acid, in both hydrogencarbonate and sodium hydroxide media.

The amounts of sugars were much lower after O_2–$NaHCO_3$ treatment than in the absence of oxygen. Similarly, the formation of 3-deoxypentonic acids was suppressed drastically in both media by the presence of oxygen. This is explained by oxidative cleavages, giving rise to arabinonic plus formic, and erythronic plus glycolic, acids.

Table II shows that the effect of oxygen on the acid composition was much less for **2** than for **1**, if the products derived from the liberated glucose are disregarded. Evidently, the reactions of the dicarbonyl moiety in **2** were so rapid that oxygen had only a slight effect on them.

The structure of **2** suggests that its 2,3-enediol will give rise to a rapid β-elimination, producing glucose and an unstable intermediate, **3**, containing three adjacent carbonyl groups (see Scheme 2). The presence of very large proportions of glucose (including minor amounts of fructose and mannose) after the experiments in $NaHCO_3$ indicates that this is a very important reaction in all media. Hydroxide ions cause cleavage of the tricarbonyl compound to 3,4-dihydroxybutanoic acid and glyoxal, which then rearranges to glycolic acid (*cf.* Ref. 14). Treatment of the trimeric dihydrate of glyoxal in $NaHCO_3$ and NaOH media at 90° for 30 min yielded more



Scheme 2

than 90% of glycolic acid. The formation of very large and, in hydrogencarbonate medium, approximately equimolar amounts of 3,4-dihydroxybutanoic and glycolic acids supports this reaction scheme.

Attack of a hydroxide ion on C-1 in **3** would yield formic acid and 3-deoxypentosulose, which by benzilic acid rearrangement is converted into the *threo* and *erythro* forms of 3-deoxypentonic acid. Both diastereomers were more abundant after NaOH treatment than after $NaHCO_3$ treatment, while the highest yield of 3,4-dihydroxybutanoic acid was obtained during the $NaHCO_3$ treatment. It has been suggested[3] that **3**, formed after β-hydroxy elimination of HO-4 in **1**, should also be mainly responsible for the formation of 3-deoxypentonic acids from **1**. The observation that 3,4-dihydroxybutanoic acid belonged to the minor reaction products from **1** (Table I), whereas it was one of the major products from **2**, indicates that, for **1**, the reaction path *via* **3** is of minor importance. It is likely that the reaction path *via* the 1,2-enediol of arabinose is more important. Both reactions proceed *via* 3-deoxypentosulose, and it may therefore seem puzzling that the proposed benzilic acid rearrangement of this intermediate, under comparable conditions, gave a much higher preference for the *threo* form in the experiments with **1** as compared to those with **2**.

In agreement with the results obtained with 3-deoxy-D-*erythro*-hexosulose[15], g.l.c. of trimethylsilylated D-*arabino*-hexosulose yielded several peaks. Evidently, dicarbonyl compounds can adopt several forms. It is likely that their relative proportions are of vital importance for the degradation routes.

Benzilic acid rearrangement of **3**, with hydroxide-ion attack on C-1, would yield two diastereomeric β-keto acids. Acids of this type are known to be easily decarboxylated. This property explains the presence of 3-deoxypentulose after the $NaHCO_3$ treatment. Treatment of 3-deoxy-*erythro*-pentose (which isomerizes to 3-deoxypentulose) with NaOH yields 3,4-dideoxypentonic acid. The presence of an appreciable amount of this acid after the treatment with NaOH in the absence of oxygen indicates that 3-deoxypentulose was also formed in this medium. Elimination of HO-4, followed by benzilic acid rearrangement, yields the dideoxypentonic acid. These reactions become less important in the presence of oxygen[11,12]. Accordingly, no detectable amount of 3,4-dideoxypentonic acid was formed in the experiments under oxygen pressure.

The formation and destruction of glucose during treatment of **2** with NaOH is reflected in the large proportions of 3-deoxyhexonic acids and 2-hydroxypropanoic acids observed. Similarly, the presence of glyceric and 2-deoxy-*erythro*-pentonic acids, and the proportions of different aldonic acids, strongly indicate that these acids were produced from glucose, formed as an intermediate during O_2–NaOH treatment of **2** (*cf.* Ref. 16).

Formation of dicarboxylic acids and other products. — In the absence of oxygen, no significant amounts of dicarboxylic acids were obtained from **1**. Trace amounts of several acids were recorded after treatment of **2** with NaOH, whereas no dicarboxylic acids were obtained after treatment with $NaHCO_3$.

Treatment of **1** with O_2–$NaHCO_3$ yielded small and approximately equal

amounts of tartronic, *C*-(hydroxymethyl)tartronic, *C*-(1,2-dihydroxyethyl)tartronic, and *C*-(1,2,3-trihydroxypropyl)tartronic acids, identified by g.l.c.[17]. Tartronic acid was the main dicarboxylic acid formed from **1** on treatment with O_2–NaOH.

C-(2,3-Dihydroxypropyl)tartronic acid, one of the principal dicarboxylic acids formed during O_2–NaOH treatment of cellulose[18] and cellobiose[7], was present in appreciable amounts after O_2–NaOH treatment of **2**, and in minor amounts after O_2–$NaHCO_3$ treatment of **2** (Table II).

A possible reaction path is rearrangement of **3**, yielding a β-keto acid (see Scheme 2), followed by oxidation at C-2. Benzilic acid rearrangement of the dicarbonyl intermediate would yield the product. An alternative reaction path is an oxidation at C-1 in **2**, to give a 2-hexulosonic acid group, followed by a β-elimination of glucose and a benzilic acid rearrangement[19].

A most-striking result, which has not been mentioned before, is that the total yield of hydroxy acids produced from **1** was very low. In the absence of oxygen, the yield was 39% in $NaHCO_3$ and 50% in NaOH. In the presence of oxygen, the corresponding figures were 64% and 62%. The total recovery of hydroxy acids, formic acid, dicarboxylic acids, and sugars was 50–67%. Unidentified compounds, eluted with water (Table I) and obtained as the difference between the weight of the neutral fraction and the sugars determined by chromatographic methods, amounted to 19% for the treatment with $NaHCO_3$ in the absence of oxygen. This fraction was less prominent after the other treatments. Unidentified compounds, eluted with 5M acetic acid and determined as the difference between the weight of the fraction eluted with 5M acetic acid and the amounts of monocarboxylic hydroxy acids determined by chromatographic methods, constituted 14% after the treatment with $NaHCO_3$ in the absence of oxygen, but much more after the other treatments.

No attempt was made to analyze the non-electrolytes, apart from sugars and the unidentified fraction eluted with 5M acetic acid. However, the recorded chromatograms showed that a complex mixture of u.v.-absorbing solutes was present. An example is given in Fig. 1. The monocarboxylic acids listed in Table I were mainly responsible for the response in the refractive-index detector, but, as seen from the

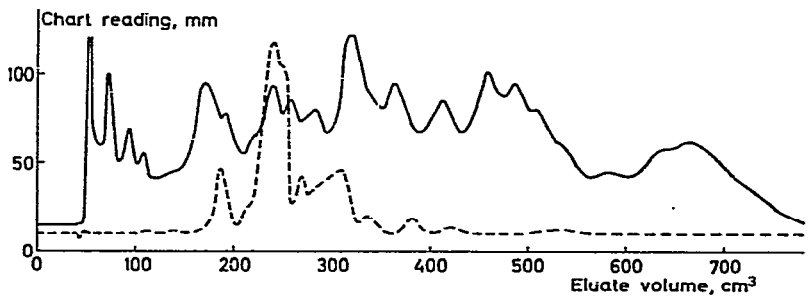


Fig. 1. Treatment of D-*arabino*-hexosulose with $NaHCO_3$: rechromatography (in 0.08M sodium acetate) on an ion exchanger in the acetate form (Dowex 1-X8, 20–27 μm; column, 6 × 870 mm) of the fraction eluted with 5M acetic acid; nominal linear-flow, 2.7 cm/min; ----, refractive-index detector; ——, u.v. detector (254 nm).

chromatogram, a large number of different u.v.-absorbing compounds were recorded within the range studied. It is noteworthy that the major portion of the unidentified compounds was not eluted under the applied conditions and that non-polar compounds, which could not even be eluted with 5M acetic acid, were formed in all experiments. These compounds caused a discoloration of the anion exchanger. Recently, it has been shown[20] that several u.v.-absorbing compounds, *e.g.*, 2-cyclopenten-1-ones, benzenediols, and acetophenones, are formed during alkaline treatment of D-glucose.

The total yield of hydroxy acids and sugars was extremely low after the treatments of **2**. Again, the lowest yields were obtained in the absence of oxygen. The fraction containing non-electrolytes other than sugars constituted 36% after $NaHCO_3$ treatment and 20% after O_2–$NaHCO_3$ treatment. The corresponding figures for the treatments with NaOH were less than 2%. To avoid the risk of acid hydrolysis of aldobionic acids and of potential interfering condensations, the carboxylic acids eluted with 5M acetic acid were determined without previous evaporation to dryness. The low, total yield of compounds listed in Table II and the discoloration of the resins indicate, however, that large proportions of cyclic compounds were formed. Similar results have been obtained in investigations of 4-deoxy-2,3-hexodiulose[11], 3-deoxy-D-*erythro*-pentose and cellobiose[12].

EXPERIMENTAL

Preparation and characterization of **1** *and* **2**. — Compound **1** was prepared[21] by removal of the phenylhydrazine residues from the phenylosazone of D-glucose. The mass spectrum (LKB 9000, EI, 70 eV) of the oxime trimethylsilyl derivative confirmed the identity [*m/e* 640, M^+, (2.7% of base peak at *m/e* 307), 625 (9.8), 551 (0.7), 537 (1.3), 535 (1.2), 461 (3.2), 447 (1.4), 435 (25.7), 406 (9.3), 371 (1.2), 347 (1.2), 334 (3.0), 319 (2.4), 316 (3.5), 307 (100), 277 (9.3), 217 (49.0), 205 (13.8), 147 (41.7), 117 (6.7), 103 (55.4), and 73 (96.1); isotope peaks omitted].

The purity, determined by g.l.c., was 98%.

Compound **2** was prepared analogously from the osazone of cellobiose. Glucose was present as an impurity (11.3%). Since glucose is formed from **2** by β-elimination, this was considered of little importance. Reduction with borodeuteride yielded glucitol (11.3%), *O*-β-D-glucopyranosyl-(1→4)-D-glucitol, and *O*-β-D-glucopyranosyl-(1→4)-D-mannitol. These alditols were isolated by partition chromatography on an anion-exchange resin, in the sulphate form, with 85% aqueous ethanol. Hydrolysis of the glucosylhexitol fraction yielded glucose, glucitol, and mannitol. The hexitols were obtained as a single peak by g.l.c. of their Me_3Si derivatives. The mass spectrum was similar to that of glucitol[22], with shifts of one or two mass units towards higher mass of relevant peaks. Peaks of approximately equal intensity were recorded at *m/e* 103 and 104, 205 and 207, 217 and 219, 307 and 309, and 319 and 321. As expected, *m/e* 422 and 423 were the highest mass peaks recorded.

Procedure. — In the experiments at 90°, the procedure was the same as that

used in a recent study of 4-deoxy-2,3-hexodiulose[11]. In the experiments at 135°, nitrogen was passed through the reaction solution, and **2** was injected by means of a sample inlet valve. Under the conditions reported in the Tables, **1** (60 mg) was consumed completely. In the experiments with **2** (160 mg), 2% remained after treatment with $NaHCO_3$ at 90°, whereas the sample was consumed completely in the other experiments. Glyoxal (100 mg of trimeric dihydrate) was degraded in the absence of oxygen at 90° in 90 ml of 0.05M $NaHCO_3$ and NaOH solutions for 30 min.

Formic acid was determined in an aliquot of the reaction solution[23]. The other products were analyzed, following group separation on an anion-exchange resin in the acetate form, by g.l.c. of the Me_3Si derivatives and by ion-exchange chromatography as described previously[11]. The monocarboxylic acid fractions from experiments with **2** were separated into six to eight fractions by preparative anion-exchange chromatography in 0.5M acetic acid. The aldobionic acids were hydrolyzed in 0.05M sulphuric acid at 130° for 3 h, and the products were separated into neutral and acidic fractions.

Identity of the anhydro acids. — The mass spectra of the Me_3Si derivatives of the anhydrohexonic acids I and II (Table I) were almost identical and consistent with those expected for a 3,6-anhydrohexonic acid.

The mass spectrum (AEI Organic MS-20, EI, 70 eV) of 3,6-anhydrohexonic acid I was as follows: *m/e* 466, $M^{+\cdot}$, (0.1% of base peak at *m/e* 73), 451 (2), 376 (0.5), 361 (1), 349 (2), 333 (1.5), 331 (1), 319 (1), 305 (1), 293 (1), 292 (2), 291 (2), 259 (5), 247 (7.8), 231 (1), 220 (7), 217 (10), 205 (2), 204 (2), 169 (2.5), 157 (9), 147 (28), 117 (5.5), 103 (8.5), and 101 (7).

Larger amounts of I were prepared in a separate experiment, and isolated by anion-exchange chromatography in 0.08M sodium acetate and rechromatography in 0.5M acetic acid. Evaporation of a solution of I in 3M hydrochloric acid and trimethylsilylation of the residue yielded a derivative having a mass spectrum compatible with that of a 1,4-lactone of a 3,6-anhydrohexonic acid: *m/e* 289, M−15, (2% of base peak at *m/e* 73), 261 (8), 245 (2), 231 (1.5), 217 (2.5), 215 (1), 199 (2.5), 189 (3), 171 (4), 157 (63), 155 (11), 147 (20), 129 (33), 117 (10), 103 (10), and 101 (13).

The n.m.r. spectrum (^1H, Bruker WH 270) of its sodium salt in D_2O confirmed that I is a 3,6-anhydrohexonic acid: δ 4.36 (1 H, $J_{4,5}$ ~4 Hz, H-4), 4.36 (1 H, $J_{5,6} = J_{5,6'} =$ ~6 Hz, H-5), 4.30 (1 H, $J_{2,3}$ ~5 Hz, H-2), 4.22 (1 H, $J_{3,4}$ ~4 Hz, H-3), 3.94 (1 H, $J_{6,6'}$ ~9 Hz, H-6 or H-6'), and 3.73 (1 H, H-6' or H-6).

The n.m.r. spectrum was interpreted by means of spin-decoupling techniques and by simulation of the spectrum using the given characteristics.

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