Carbohydrate Research, 144 (1985) 163–168
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

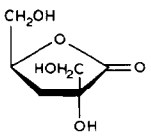
Formation of acid-catalysed dehydration products from α-D-glucoisosaccharinic acid

RAIMO ALÉN
Laboratory of Wood Chemistry, Helsinki University of Technology, SF-02150 Espoo (Finland)
(Received April 16th, 1985; accepted for publication, May 21st, 1985)

The degradation of polysaccharides by alkali with the formation of hydroxy carboxylic acids is important in many technical processes and is responsible for the losses during the processing of wood[1]. One of the main base-catalysed degradation products of cellulose and glucomannans is 3-deoxy-2-*C*-hydroxymethyl-D-pentonic acid (glucoisosaccharinic acid), and the formation of dehydration products from 3-deoxy-2-*C*-hydroxymethyl-D-*erythro*-pentono-1,4-lactone (**1**) is now reported.

Relatively severe acidic conditions were necessary to dehydrate **1** (Table I). Although the rate of disappearance of **1** was dependent on temperature and acid concentration, the more drastic reaction conditions decreased the total yield of products.

Dehydration produced a mixture that, after trimethylsilylation, was resolved by g.l.c. into six main peaks, corresponding to **1** and its diastereomer **2** together with anhydro derivatives (**3–6**) containing a five-membered ring. The number of products can be explained by assuming lactone ring opening in **1** with subsequent inversion of configuration at C-2 (→ **2**) followed by various cyclisation reactions.



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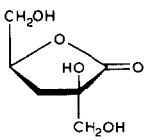

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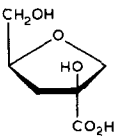

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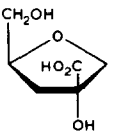

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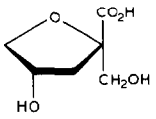

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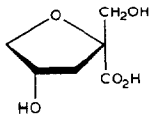

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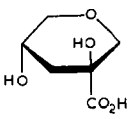

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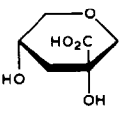

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TABLE I

PRODUCTS OF THE DEHYDRATION OF α-D-GLUCOISOSACCHARINO-1,4-LACTONE (**1**) IN 6.05M SULFURIC ACID[a]

Compound[b]	*Temperature (degrees)*											
	130				*140*				*150*			
	Time (h)											
	1	*2*	*4*	*8*	*1*	*2*	*4*	*8*	*1*	*2*	*4*	*8*
Lactic acid	0.7 (0.9)[c]	0 6 (1.2)	0.4	1.6	0.7 (1.4)	0.9	0.7	1.4	0.7	0.7	1.0	1.1
Levulinic acid	+ (7.1)	+ (21.0)	+	0.3	+ (26.3)	+	+	0.5	0.3	1.6	2.8	6.6
Glycerol	0.8 (1.7)	0.7 (1.6)	0.6	1.0	0.8 (1.5)	0.7	0.7	0.8	0.9	0.8	1.0	0.9
α- (**7**) and β-2′,5-AGISA (**8**)	0.5 (3.6)	0.3 (1.5)	0.4	1.7	0.5 (0.6)	1.0	0.4	1.8	1.3	1.9	2.3	2.3
α-2,5-AGISA (**5**)	1.2 (8.3)	2.5 (7.1)	4.5	9.5	2.4 (6.6)	5.1	9.4	15.5	7.8	12.1	15.6	16.3
β-2,5-AGISA (**6**)	1.5 (4.8)	0.2 (3.4)	0.9	1.4	0.3 (4.1)	1.3	2.2	4.3	2.0	2.8	5.3	7.6
α-2′,4-AGISA (**3**)	2.7 (16.5)	3.3 (16.6)	5.2	14.3	2.3 (10.2)	8.5	7.8	17.2	11.0	16.2	21.7	21.0
β-2′,4-AGISA (**4**)	0 5 (4.8)	0.6 (6.5)	1 1	2.8	0.3 (5.4)	1.5	2.4	4.9	2.5	4.0	6.6	8 5
α-GISL (**1**)	80.6 (25.7)	80.6 (12.1)	73.4	46.9	80.2 (14.3)	64.2	52.9	26.6	52.0	32.3	17.1	5.8
β-GISL (**2**)	3.9 (19.7)	4.5 (19.9)	8.2	12.2	5.4 (19.4)	8.4	15.9	18.5	12.7	16.5	17.7	14.2
Others	7.6 (6.9)	6.7 (9.1)	5.3	8.3	7.1 (10.2)	8.4	7.6	8.5	8.9	11.1	8.9	15.7
Reaction conversion (% of initial **1**)	49.8 (32.7)	51.6 (28.3)	44.2	43.8	43.4 (28.7)	51.1	45.2	39.7	43.2	45.2	42.1	37.6

[a]Percentage of the total compounds analysed. [b]AGISA, anhydro-D-glucoisosaccharinic acid; GISL, D-glucoisosaccharino-1,4-lactone. [c]The values in parentheses refer to the degradation performed in 11.5M sulfuric acid.

Only small proportions of the derivatives **7** and **8** containing six-membered rings were formed.

The most abundant dehydration products were **3** and **5**; **3** is formed in appreciable amounts during the treatment[2–4] of hexose polysaccharides with alkali. At their maximum concentrations (attained after 4–8 h at 150°), ~50% of the compounds separated comprised anhydroglucoisosaccharinic acids.

The mass spectra of the compounds in g.l.c. peaks 9 and 10 (Fig. 1) were almost identical and corresponded[5,6] to the trimethylsilylated derivatives of **1** and **2**. The most characteristic ion peak of their spectra was at m/z 348 [$M^+ - CH_2O$] formed by a well-known type of McLafferty rearrangement[7].

The mass spectra of the compounds in peaks 5 and 6 were almost identical, as were those of the components in peaks 7 and 8, consistent with the presence of two pairs of diastereomers. The main peaks in these spectra accorded with the data reported[2] for the major diastereomer of 1,4-anhydro-3-deoxypentitol-2-carboxylic acid, which also has a retention time[4] identical with that of peak 7. Furthermore, the relative intensities of the main peaks were nearly identical with those in the spectra of the compounds in peaks 7 and 8.

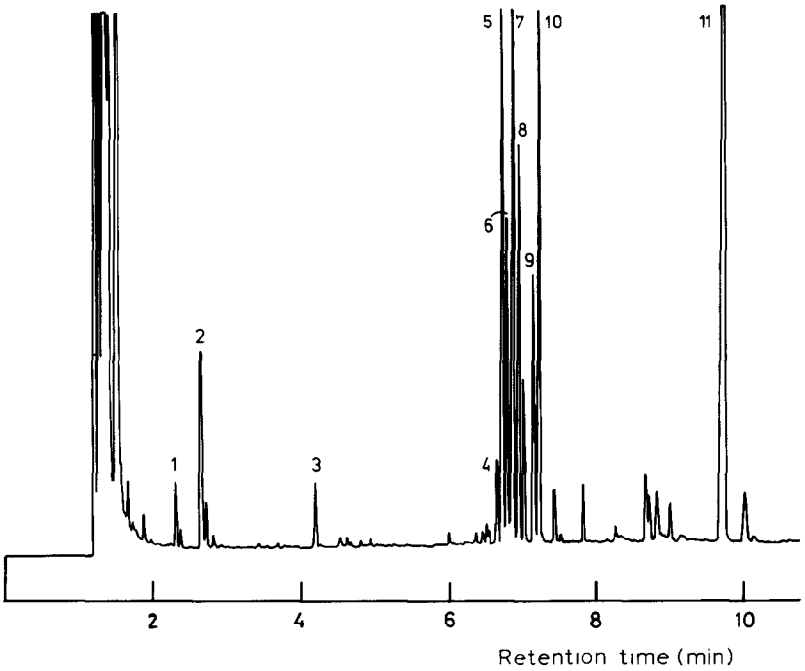

Fig. 1. Gas chromatogram of trimethylsilylated products formed in the dehydration of α-D-glucoisosaccharino-1,4-lactone (**1**). Peaks: 1, lactic acid; 2, levulinic acid; 3, glycerol; 4, α- (**7**) and β-2′,5-anhydro-D-glucoisosaccharinic acid (**8**); 5, α-2,5-anhydro-D-glucoisosaccharinic acid (**5**); 6, β-2,5-anhydro-D-glucoisosaccharinic acid (**6**); 7, α-2′,4-anhydro-D-glucoisosaccharinic acid (**3**); 8, β-2′,4-anhydro-D-glucoisosaccharinic acid (**4**); 9, α-D-glucoisosaccharino-1,4-lactone (**1**); 10, β-D-glucoisosaccharino-1,4-lactone (**2**); and 11, D-mannono-1,4-lactone (internal standard).

Besides the typical fragmentation *m/z* 363 [M^+ – Me], 261 [M^+ – CO_2SiMe_3], and 171 [261 – Me_3SiOH], the spectra derived from the compounds in peaks 5 and 6 showed a significant peak at *m/z* 348 [M^+ – 30] (a McLafferty-type rearrangement is possible) indicative of the trimethylsilylated derivatives of **5** and **6**.

It is clear that the most abundant isomers originated from **1** instead of **2**, so that the compounds in peaks 5–8 are considered to correspond to the trimethylsilylated derivatives of **5, 6, 3,** and **4**, respectively. For these compounds, the diastereomers having the (2*S*,4*S*) configuration were eluted faster than the corresponding (2*R*,4*S*) derivatives.

The spectrum derived from the compounds in the small peak 4 was also similar to those obtained from the trimethylsilylated derivatives of anhydroglucoisosaccharinic acids and is assumed to be due to the pyranoid structure **7** and/or **8**. If two possible stereoisomers were present, they could not be separated by g.l.c.

Interpretation of the mass spectra for other compounds was based on the published data[8–10].

EXPERIMENTAL

Dehydration, g.l.c., and g.l.c.–m.s. — α-D-Glucoisosaccharino-1,4-lactone (**1**, ~10 mg, prepared from lactose[11]) and 6.05M or 11.5M sulfuric acid (2 mL) were heated in Teflon-lined autoclaves (2.5 mL) at various temperatures (attained in <10 min) for various times (see Table I). Each autoclave was cooled, and the contents were diluted with water to 50 mL, neutralised ($BaCO_3$), and filtered. An internal standard (~5 mg of D-mannono-1,4-lactone) was added to each filtrate, which was then passed through a column (100 × 10 mm) of Dowex 50W-X8 (H^+) resin and concentrated to dryness under reduced pressure at 30–35°, and the residue was trimethylsilylated[4].

G.l.c. was performed on a Hewlett–Packard 5880 A instrument equipped with an OV-101 fused-silica capillary column (25 m × 0.32 mm i.d.). The temperature programme was 2 min at 100°, 20°/min → 200°, and 5 min at 200°. The temperature of the injection port and the flame-ionisation detector was 260°. The injection volume was 0.1–0.5 μL and the split ratio was 20:1. The carrier gas was hydrogen at 2 mL/min. A typical chromatogram is shown in Fig. 1. The retention times for the peaks (relative to that of the internal standard) were 0.238, 0.274, 0.431, 0.684, 0.690, 0.696, 0.704, 0.712, 0.735, and 0.741.

A Hewlett–Packard 5992 instrument (70 eV) fitted with an SE-54 fused-silica capillary column (retention times were almost identical to those on the OV-101 column) was used for g.l.c.–m.s. The temperature programme was 1 min at 30°, 15°/min → 255°, and 25 min at 255°. The following compounds were identified (as their trimethylsilylated derivatives) (see Fig. 1).

Lactic acid (peak 1). Mass spectrum: *m/z* 219 (12%), 191 (29), 190 (22), 147 (97), 133 (10), 117 (100), 102 (4), 88 (6), 75 (14), 73 (85), 66 (15).

Levulinic acid (peak 2). Mass spectrum: *m/z* 188 (2%, M^+), 173 (85), 155 (12), 145 (67), 131 (12), 129 (12), 75 (100), 73 (23).

Glycerol (peak 3). Mass spectrum: *m/z* 293 (2%), 218 (42), 205 (80), 147 (100), 133 (26), 129 (12), 117 (43), 103 (30), 73 (88).

α-2′,5-Anhydro- (**7**) and β-2′,5-anhydro-D-glucoisosaccharinic acid (**8**) (peak 4) [(2*S*,4*S*)- and (2*R*,4*S*)-1,5-anhydro-3-deoxypentitol-2-carboxylic acid]. Mass spectrum: *m/z* 363 (5%), 261 (100), 217 (9), 171 (39), 155 (6), 147 (38), 143 (46), 133 (11), 129 (22), 117 (9), 75 (21), 73 (66). Because of the low contents of these compounds in the samples, only tentative spectra were obtained.

α-2,5-Anhydro- (**5**, peak 5) and β-2,5-anhydro-D-glucoisosaccharinic acid (**6**, peak 6) [(2*S*,4*S*)- and (2*R*,4*S*)-2,5-anhydro-3-deoxypentitol-2-carboxylic acid]. Mass spectrum: *m/z* 378 (<1%, M^+), 363 (3), 348 (6), 275 (3), 261 (100), 231 (13), 217 (8), 204 (9), 185 (4), 171 (29), 155 (6), 147 (34), 143 (11), 133 (11), 129 (22), 117 (13), 103 (12), 75 (12), 73 (65).

α-2′,4-Anhydro- (**3**, peak 7) and β-2′,4-anhydro-D-glucoisosaccharinic acid (**4**, peak 8) [(2*S*,4*S*)- and (2*R*,4*S*)-1,4-anhydro-3-deoxypentitol-2-carboxylic acid]. Mass spectrum: *m/z* 378 (<1%, M^+), 363 (5), 261 (32), 217 (10), 204 (6), 185 (16), 171 (44), 155 (24), 147 (47), 143 (7), 133 (12), 129 (27), 117 (11), 103 (8), 75 (14), 73 (100).

α-D-Glucoisosaccharino- (**1**, peak 9) and β-D-glucoisosaccharino-1,4-lactone (**2**, peak 10) [3-deoxy-2-*C*-hydroxymethyl-D-(*erythro* and *threo*)-pentono-1,4-lactone]. Mass spectrum: *m/z* 378 (3%, M^+), 363 (4), 348 (75), 273 (9), 245 (45), 231 (13), 217 (28), 203 (9), 171 (4), 155 (13), 147 (52), 133 (15), 129 (42), 117 (32), 103 (28), 75 (18), 73 (100).

The molar response factors for the reaction products were calculated[12,13] in relation to that of D-mannono-1,4-lactone (peak 11). The corresponding values used for lactic acid, levulinic acid, glycerol, anhydroglucoisosaccharinic acid, and glucoisosaccharino-1,4-lactone were 0.47, 0.39, 0.69, 0.79, and 0.85, respectively.

ACKNOWLEDGMENTS

Financial support from the Ministry of Trade and Industry is gratefully acknowledged. Thanks are also due to Miss A. Siirto for technical assistance, and Mrs. S. Ristlakki (Technical Research Center of Finland) for recording the mass spectra.

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