

Formation of Acid-Catalysed Dehydration Products from Xyloisosaccharinic Acid

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The anhydroglucoisosaccharinic acids produced from α -D-glucoisosaccharinic acid by acid-catalysed dehydration were separated and identified as TMS derivatives by GLC-MS in a recent study.¹ In the present work, D,L-3-deoxy-2-C-hydroxymethyltetronic acid (xyloisosaccharinic acid) was subjected to a similar dehydration. This acid is one of the main products of base-catalysed degradation of xylan and is formed from hardwood during kraft pulping.²

Dehydration of xyloisosaccharinic acid in aqueous sulfuric acid was carried out under reaction conditions analogous to those previously applied for glucoisosaccharinic acid.¹ In the resulting reaction mixture, carboxylic acid derivatives (1–4) containing five carbon atoms, together with several degradation products, were detected by GLC after trimethylsilylation (Table 1).

The formation of the most abundant reaction product, D,L-2',4-anhydroxyloisosaccharinic acid [(2*S*)- and (2*R*)-1,4-anhydro-2-C-carboxy-3-deoxytetritol] (2) can be explained by the lactone ring opening of 1, followed by intramolecular etherification. In addition to 2, the acid derivatives 3 and 4 (*trans*- and *cis*-4-hydroxy-2-hydroxymethyl-2-butenic acid), present in small proportions, were clearly also formed by elimination of water from this open-chain intermediate. Although relatively severe acidic conditions were necessary for the formation of these products, the more drastic reaction conditions of experiment II compared to I (Table 1) decreased substantially the total yields of the products identified.

In the spectrum of the TMS derivative of the starting material 1, the most characteristic ion peak, formed by a McLafferty-type rearrangement,^{3,4} appeared at *m/e* 246 (M-30). However, this type of rearrangement is not possible for the TMS derivative of 2, and its spectrum therefore showed a prominent M-117 (M-CO₂SiMe₃) ion peak at *m/e* 159. The mass spectra of the TMS derivatives of 3 and 4 were almost identical, showing the fragmentation ion peaks at *m/e* 333 (M-15), *m/e* 318 (M-30), *m/e* 305 (M-15-28), *m/e* 245 (M-103) and *m/e* 231 (M-117). The elution order of these isomers in GLC was not estab-

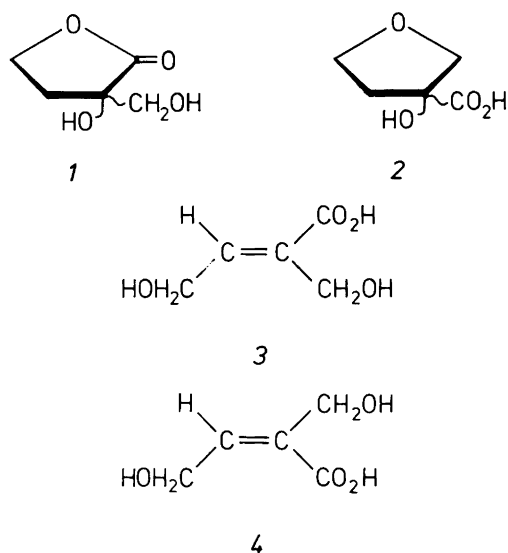


Table 1. Products of the dehydration of xyloisaccharinic acid in 6.05M (I) and 11.5M (II) sulfuric acid at 150°C.^a

Compound	I	II	Retention time ^b
Lactic acid	2.5	1.9	0.211
Glycolic acid	0.2	0.3	0.220
Oxalic acid	0.2	0.3	0.261
2-Hydroxybutanoic acid	1.5	0.8	0.273
Glycerol	0.2	0.2	0.424
Anhydroisaccharinic acid (2)	38.9	30.2	0.464
Xyloisacchararino-1,4-lactone (1)	51.7	57.3	0.506
4-Hydroxy-2-hydroxymethyl-2-butenic acid (3 and 4)	0.2	0.2	0.714 and 0.734 ^c
Others	4.1	8.2	—
Reaction conversion (% of initial 1)	34.3	69.6	

^aPercentage of the total compounds analysed. The heating times were 4 h (I) and 1 h (II). ^bGLC of TMS derivatives relative to the D-mannono-1,4-lactone derivative. ^c*cis*- and *trans*-isomers.

lished, although the assumed isomer pair could be readily recognised. The interpretations of the mass spectra of other compounds were based on published data for glycolic acid,⁵ oxalic acid,⁶ lactic acid,⁵ 2-hydroxybutanoic acid⁵ and glycerol.⁷

Experimental

Materials. The compound D,L-3-deoxy-2-C-hydroxymethyltetrono-1,4-lactone (1, ~98% by GLC) was isolated by vacuum distillation after removal of lignin and cations from the aliphatic acid fraction obtained from a laboratory-scale treatment^{3,8} of birch wood with sodium hydroxide.

Dehydration and analytical methods. A 10 mg sample of 1 and 6.05 or 11.5M sulfuric acid (2 ml) were heated in Teflon-lined autoclaves (2.5 ml) at 150°C (attained in <10 min) for 4 h and 1 h, respectively. The autoclaves were cooled and the contents were diluted with water to 50 ml, neutralised (BaCO₃) and filtered. An internal standard (~5 mg of D-mannono-1,4-lac-

tone) was added to the filtrates, which were then passed through a column (100×10 mm) of Dowex 50W-X8 (H⁺) resin and concentrated to dryness under reduced pressure at 30–35°C; the residues were trimethylsilylated.⁹

GLC was performed on a Hewlett-Packard 5880A 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°C, 20°C/min → 200°C, and 5 min at 200°C. The temperature of the injection port and the flame-ionisation detector was 260°C. The injection volume was 1 μl and the split ratio was 20:1. The carrier gas was hydrogen at 2 ml/min.

A Hewlett-Packard 5970A instrument (70 eV) fitted with the same column as above was used for GLC-MS. The temperature programme was 1 min at 50°C, 18°C/min → 275°C, and 35 min at 275°C. The temperature of the injection port was 250°C. The following carboxylic acid derivatives containing five carbon atoms were identified (as their trimethylsilyl derivatives, see Table 1).

D,L-3-Deoxy-2-C-hydroxymethyltetrono-1,4-lactone (D,L-xyloisaccharino-1,4-lactone) (1). MS [*m/e* (rel. int.)]: 261 (11), 246 (57), 233 (12), 218 (4), 190 (8), 171 (4), 147 (57), 143 (26), 133 (8), 117 (4), 103 (30), 75 (20), 73 (100).

(2*S*)- and (2*R*)-1,4-anhydro-2-C-carboxy-3-deoxytetritol [(3*S*)- and (3*R*)-3-hydroxytetrahydrofuran-3-carboxylic acid] (2). MS [*m/e* (rel. int.)]: 261 (4), 233 (13), 190 (9), 171 (8), 159 (66), 147 (92), 143 (6), 133 (8), 129 (8), 103 (11), 75 (15), 73 (100).

cis- and *trans*-4-Hydroxy-2-hydroxymethyl-2-butenic acid (3 and 4). MS [*m/e* (rel. int.)]: 348 (14, M), 333 (3), 318 (5), 305 (3), 245 (26), 231 (22), 147 (57), 133 (14), 129 (45), 117 (40), 103 (36), 89 (7), 75 (18), 73 (100). Because of the low contents of these isomers in the samples, only tentative spectra were obtained.

The molar response factors for the reaction products were calculated^{10,11} in relation to that of D-mannono-1,4-lactone. The corresponding values used for lactic acid, glycolic acid, oxalic acid, 2-hydroxybutanoic acid, glycerol, anhydroxyloisaccharinic acid, xyloisaccharino-1,4-lactone and 4-hydroxy-2-hydroxymethyl-2-butenic acid were 0.47, 0.42, 0.37, 0.53, 0.69, 0.57, 0.62 and 0.78, respectively.

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