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Note

Oxidation of xyloisosaccharinic acid by nitric acid

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The degradation of polysaccharides by alkali with the formation of hydroxy carboxylic acids is important in many technical processes[1]. During kraft pulping of wood, one of the main base-catalysed degradation products of xylan is DL-3-deoxy-2-*C*-hydroxymethyltetronic acid (xyloisosaccharinic acid). In conjunction with our studies of the utilisation of the corresponding DL-3-deoxy-2-*C*-hydroxymethyltetrono-1,4-lactone (**1**), it was of interest to separate and identify by g.l.c.–m.s. the products formed by oxidising one or both of the primary hydroxyl groups of **1** to carboxylic groups; nitric acid was used as the oxidant.

Oxidation produced a mixture that, after trimethylsilylation, was resolved by g.l.c. into ten main peaks (Table I) corresponding to degradation products together with carboxylic acid derivatives (**2**–**6**) containing five carbon atoms.

The most abundant oxidation products, **3** and **2**, were formed by lactonisation of **5** and **4**, respectively; **5** is one of the dicarboxylic acids isolated after treatment

TABLE I

OXIDATION PRODUCTS OF XYLOISOSACCHARINIC ACID BY NITRIC ACID[a]

Product		*Retention time*[b]
Lactic acid	0.6	0.222
Glycolic acid	1.5	0.230
Oxalic acid	6.1	0.266
2-*C*-Carboxy-3-deoxytetrono-1,4-lactone (**2**)	19.1	0.557
Hydroxytartronic acid	4.1	0.585
3-*C*-Carboxy-2-deoxytetrono-1,4-lactone (**3**)	49.9	0.600
C-Hydroxymethyltartronic acid	4.0	0.669
C-(2-Hydroxyethyl)tartronic acid (**4**)	0.5	0.746
3-Deoxy-2-*C*-hydroxymethyltetraric acid (**5**)	4.0	0.756
2-*C*-Carboxy-3-deoxytetraric acid (**6**)	7.2	0.776
Unidentified	3.0	—

[a]Percentage of the total compounds analysed. The total amount of products was ~95 weight % of initial **1**. [b]G.l.c. of Me_3Si derivatives relative to the D-mannono-1,4-lactone derivative.

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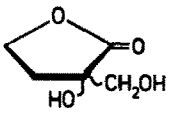
of hydrocellulose with alkali, whereas **4** is formed as the major dicarboxylic acid in oxygen–alkali treatment of xylan[2]. Although, in the case of **4**, the asymmetric centre at C-2 disappeared on oxidation, the g.l.c. peaks for both the lactone derivatives represented, due to various lactonisation possibilities, the pair of enantiomers. In addition to these dibasic acid derivatives (~75% of the total products identified), some fully oxidised derivative, namely, the tribasic acid **6**, was also present.



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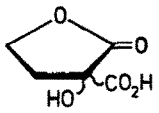

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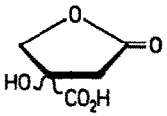

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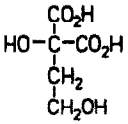

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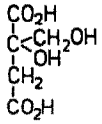

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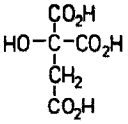

6

Identification of the trimethylsilylated derivatives of **4** and **5** was based on the published mass spectra[2]. The most characteristic ion peaks in these spectra were at *m/z* 422 [$M^+ - CH_2O$] (for the Me_3Si derivative of **5**) and at *m/z* 408 [$M^+ - CO_2$] (for the Me_3Si derivative of **4**) formed by a well-known type of McLafferty rearrangement[3].

In the spectra of the trimethylsilylated lactone derivatives **2** and **3**, the ion peak at *m/z* 247 suggested the cleavage of a methyl group, with the subsequent loss of carbon monoxide, indicative of these structures[4]. A McLafferty-type rearrangement (*m/z* 246 [$M^+ - CO_2$]) was possible only for the former structure. The spectra of the Me_3Si derivative of **3** showed, in addition to an ion peak at *m/z* 173 [$M^+ - CO_2SiMe_3$], a strong ion peak at *m/z* 190 [$M^+ - 100$] probably due to the cleavage of 3-oxo-2-deoxypentono-1,4-lactone.

The presence of **2** and **3** was further confirmed by the opening of their lactone rings with alkali before g.l.c. analysis[5], which resulted in a corresponding increase in the proportions of the acyclic derivatives, **5** and **4**, respectively.

The most prominent ion peaks in the spectrum of the trimethylsilylated derivative of **6** appeared at *m/z* 451 [$M^+ - Me$] and at *m/z* 422 [$M^+ - CO_2$] (a McLafferty-type rearrangement is possible). In this case, a small peak at *m/z* 349 [$M^+ - CO_2SiMe_3$] indicated that fragmentation path *m/z* 466 → 305 [$M^+ - CO_2 - CO_2SiMe_3$] predominated.

Interpretations of the mass spectra for other compounds were based on the published data on glycolic acid[4], oxalic acid[6], lactic acid[4], hydroxytartronic acid[7], and *C*-hydroxymethyltartronic acid[8].

EXPERIMENTAL

Oxidation, g.l.c. and g.l.c.–m.s. — DL-3-Deoxy-2-*C*-hydroxymethyltetrono-1,4-lactone (**1**, ~98% pure by g.l.c.) was isolated by vacuum distillation after removal of lignin and cations from the aliphatic acid fraction obtained from a laboratory-scale treatment[9,10] of birch wood with sodium hydroxide.

The calcium salt of **1** [a 10-mg sample of **1** was dissolved in 10 mL of water and neutralised with $Ca(OH)_2$] was oxidised[11] with 0.03 mL of nitric acid (72 weight %) for 24 h at 35°, 24 h at 45°, and then 24 h at 50°. The reaction mixture was diluted with water (10 mL) and, after storage for 12 h, filtered. An internal standard (~6 mg of D-mannono-1,4-lactone) was added to the filtrate which was then concentrated to dryness under reduced pressure at 30–35°, and the residue was trimethylsilylated[5]. In order to eliminate peaks for acid lactones in g.l.c., a portion of the residue was also converted into the corresponding ammonium salts before trimethylsilylation[5].

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.

Mass spectra were recorded with a JEOL JMS-DX303 mass spectrometer coupled with a Hewlett–Packard 5790A gas chromatograph. An SE-54 fused-silica capillary column (25 m × 0.32 mm i.d.; retention times were almost identical to those on an OV-101 column) was used, and the temperature programme was 1 min at 100° and then 15°/min → 230°. Helium was used as the carrier gas (2 mL/min). The following compounds were identified (as their trimethylsilylated derivatives, see Table I).

Glycolic acid: *m/z* 205 (25%), 177 (24), 161 (9), 147 (100), 133 (10), 117 (3), 103 (3), 75 (5), 73 (53), 66 (11).

Oxalic acid: *m/z* 219 (18%), 190 (14), 147 (85), 73 (100), 66 (15).

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

Hydroxytartronic acid (dihydroxymalonic acid): *m/z* 409 (13%), 381 (6), 307 (100), 221 (13), 147 (31), 73 (55).

C-Hydroxymethyltartronic acid: *m/z* 423 (9%), 408 (8), 393 (13), 335 (2), 305 (6), 279 (8), 221 (12), 217 (22), 190 (11), 189 (22), 147 (89), 103 (14), 73 (100).

DL-2-*C*-Carboxy-3-deoxytetrono-1,4-lactone (**2**): *m/z* 275 (18%), 247 (11), 246 (15), 219 (9), 217 (11), 203 (2), 190 (8), 177 (15), 157 (12), 147 (99), 133 (9), 131 (8), 119 (3), 113 (4), 103 (12), 87 (2), 75 (28), 73 (100), 63 (25).

DL-3-*C*-Carboxy-2-deoxytetrono-1,4-lactone (DL-hydroxyparaconic acid; **3**): *m/z* 275 (39%), 247 (11), 233 (7), 231 (14), 217 (5), 203 (5), 190 (41), 185 (11), 173 (62), 157 (9), 147 (100), 133 (14), 131 (11), 129 (10), 113 (8), 103 (4), 87 (11), 75 (75), 73 (94), 63 (21).

C-(2-Hydroxyethyl)tartronic acid (**4**): *m/z* 437 (27%), 408 (18), 379 (24), 335 (29), 320 (4), 305 (87), 246 (14), 221 (10), 190 (14), 177 (6), 147 (76), 133 (9), 115 (31), 103 (100), 73 (69).

DL-3-Deoxy-2-*C*-hydroxymethyltetraric acid (**5**): *m/z* 437 (10%), 422 (18), 349 (14), 337 (11), 335 (32), 319 (16), 305 (16), 303 (6), 291 (13), 273 (10), 259 (5), 245 (14), 231 (5), 221 (11), 217 (34), 147 (63), 133 (16), 115 (8), 103 (21), 73 (100).

2-*C*-Carboxy-3-deoxytetraric acid (**6**): *m/z* 451 (11%), 422 (12), 361 (4), 349 (2), 333 (2), 305 (18), 221 (8), 217 (5), 147 (60), 133 (3), 131 (3), 115 (17), 73 (100).

The molar response factors for the reaction products were calculated[12,13] in relation to that of D-mannono-1,4-lactone. The corresponding values used for glycolic acid, oxalic acid, lactic acid, hydroxytartronic acid, *C*-hydroxymethyltartronic acid, *C*-carboxy-deoxytetrono-1,4-lactone, deoxy-*C*-hydroxymethyltetraric acid, and *C*-carboxy-deoxytetraric acid were 0.42, 0.37, 0.47, 0.75, 0.82, 0.56, 0.89, and 0.84, respectively.

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