

Separation and Identification of the Silylated Reduction Products from Xyloisosaccharinic Acid (3-Deoxy-2-C-hydroxymethyltetronic Acid) by GLC-MS

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The reduction products from α -D-glucoisosaccharinic acid were separated and identified as TMS derivatives in a recent study.¹ A similar study in which xyloisosaccharinic acid was subjected to reduction is now reported. This acid is one of the major alkaline degradation products of wood xylan and is formed from hardwood during kraft pulping.² The corresponding D,L-3-deoxy-2-C-hydroxymethyltetrono-1,4-lactone (*1*) was isolated in a nearly pure state by distillation and then reduced with sodium borohydride.

Reduction of *1* resulted in a mixture which, after silylation, was resolved into four main peaks by gas chromatography (Table 1). Only small amounts of the corresponding furanoid deoxy-sugar derivatives (*2*) were present in the reduction mixture, which contained mainly the fully reduced derivative, deoxyalditol (*3*). This compound is optically inactive since the asymmetric centre of the racemic starting material at C-2 disappears after reduction.

The mass spectra of peaks A and B are practically identical, showing in addition to the typical frag-

Table 1. Gas chromatographic peaks of the reduction products (TMS derivatives); DC QF-1 (3% 6 m), 60–180 °C, 2.5 °C/min.

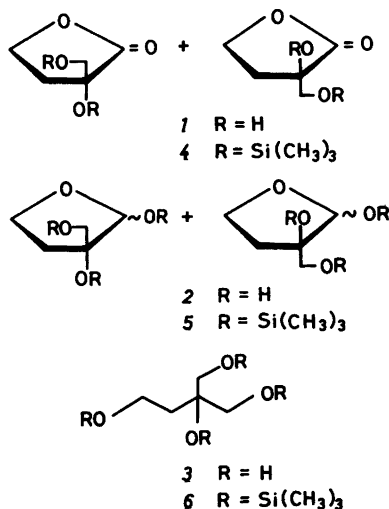
Peak symbol	Total area/%	Relative retention time	Compound
A	7.7	0.70	5
B	6.4	0.74	5
C	85.8	0.83	6
D	0.1	1.00	4

mentation ion peaks $[M-CH_3(15)]$ (m/e 335), $[M-(CH_3)_3SiOH(90)]$ (m/e 260), $[M-(CH_3)_3SiOCH_2(103)]$ (m/e 247) and $[M-15-90]$ (m/e 245), also a prominent $[M-118]$ (m/e 232) ion peak, which has been found to be characteristic for furanoid TMS derivatives.³ Peaks A and B thus represented the two possible pairs of enantiomers for compounds 5. The intense ion peaks at m/e 217, 204 and 191 can also be derived from these structures.

The fragmentation ion peaks $[M-103]$ (m/e 321), $[M-15-90]$ (m/e 319) and $[M-103-90]$ (m/e 231) in the spectrum of C are indicative of the TMS derivative of the corresponding deoxyalditol (*6*). The ion peaks at m/e 307 and 217 suggest further the cleavage of the C₂-C₃ bond and the subsequent loss of trimethylsilanol from this fragment. Peak D corresponds to the TMS derivative of the starting material (*4*), and the most characteristic ion peak $[M-30]$ (m/e 246) in its spectrum is due to a McLafferty-type rearrangement.⁴ The model substances (*4* and *6*) had retention times identical to the last two peaks (C and D).

Experimental. General methods. Gas chromatographic separations and mass spectrometric identifications for trimethylsilylated compounds were performed as described earlier.¹ ¹H NMR spectra were recorded on a Jeol JNM-PMX 60 spectrometer and IR spectra on a Perkin-Elmer 457 spectrometer using KBr pellets. Specific rotations were measured in water at room temperature with a Perkin-Elmer 141 polarimeter.

Materials. D,L-3-Deoxy-2-C-hydroxymethyltetrono-1,4-lactone (*1*) was isolated by vacuum distillation after lignin and cation removal from the acid fraction originating from a laboratory-scale sodium hydroxide cook of birch wood.⁵ A part of it, containing 86% of the racemic 1,4-lactone, crystallized from the distillate and was recrystallized twice from ethyl acetate. This product contained 1.2% impurities, as estimated from the areas of its TMS derivative on the gas chromatogram, m.p. 95.5–96.5 °C, $[\alpha]_D^{22}$ 0 (c 1.0). (Ref. 6, m.p. 95.5–



96.5 °C) IR: 3320, 1745 cm^{-1} . ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOD}$): δ 4.90–4.07 (2 H, m), 3.85 (2 H, s), 2.42 (2 H, t).

The fully trimethylsilylsubstituted lactone (4) was prepared by silylation of 1. MS [m/e (% rel. int.)]: 261 (8), 246 (56), 233 (6), 218 (3), 190 (7), 171 (3), 147 (57), 143 (25), 133 (7), 117 (4), 103 (29), 75 (19), 73 (100).

Reduction of 1 to sugars using sodium borohydride⁷ resulted in a syrup, whose IR spectrum lacked a strong carbonyl band. After silylation the gas chromatographic peaks were: (A and B), 5, MS [m/e (% rel. int.)]: 335 (<1), 260 (<1), 247 (3), 245 (6), 234 (6), 232 (40), 217 (18), 204 (38), 191 (13), 189 (7), 171 (6), 147 (43), 143 (9), 142 (16), 133 (9), 131 (7), 129 (12), 127 (14), 103 (23), 75 (32), 73 (100). (C), 6, see below. (D), 4, see above.

3-Deoxy-2-C-hydroxymethyltetritol (3) was prepared by reducing 1 with sodium borohydride.⁸ The procedure was repeated three times resulting in a syrup that contained 5.5 % impurities. IR: 3380, 1050 cm^{-1} . ^1H NMR (D_2O): δ 4.08 (2 H, t), 3.88 (4 H, s), 2.15 (2 H, t).

The fully trimethylsilylsubstituted deoxyalditol (6) was prepared by silylation of 3. MS [m/e (% rel. int.)]: 321 (29), 319 (1), 307 (<1), 231 (60), 217 (6), 159 (6), 155 (6), 147 (30), 115 (29), 103 (26), 73 (100).

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