

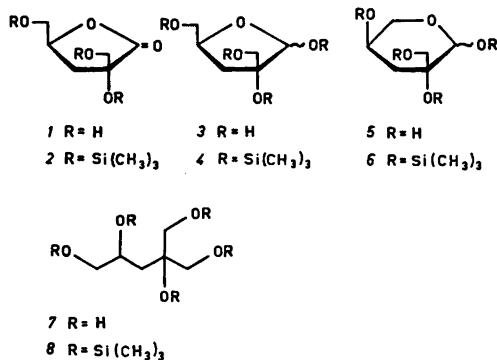
Short Communications

Separation of the Silylated Reduction Products from α -D-Glucoisaccharinic Acid by GLC

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In the cellulose industry enormous quantities of hydroxy acids are formed as waste from wood polysaccharides, especially during kraft pulping.¹ One of the main base-catalyzed degradation products of cellulose and glucomannans is 3-deoxy-2-C-hydroxymethyl-D-pentonic acid (glucoisaccharinic acid). We now have separated and identified the silylated reduction products of the corresponding 3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone (*I*).



Sodium borohydride reduction of *I* resulted in a mixture which after silylation and gas chromatography was resolved into six peaks (Table 1). The compounds identified originated from the furanoid (3) and pyranoid (5) deoxy-sugar derivatives as well as deoxyalditol (7) in the approximate weight proportions 5:1.5:1. Compound 7 can also be prepared from the epimeric *threo*-form² since the asymmetric centre at C-2 disappears after reduction.

The mass spectra of peaks A and C are practically identical, indicating a pair of diastereomers. Besides the typical fragmentation $[M - CH_3(15)]^+ (m/e 437)$, $[M - (CH_3)_3SiOH(90)]^+ (m/e 362)$, $[M - (CH_3)_3SiOCH_2(103)]^+ (m/e 349)$, $[M - 15 - 90]^+ (m/e 347)$, $[M - 118]^+ (m/e 334)$

and $[M - 103 - 90]^+ (m/e 259)$ ion peaks, these spectra show a strong ion peak at $m/e 231$, the formation of which has already been recognized in furanoid TMS derivatives.³ The mass spectra of peaks B and D are also practically identical, and in addition to some of the above-mentioned typical fragmentations, they show significant $m/e 218, 204, 203, 191$ and 116 ion peaks, which are either characteristic for pyranoid TMS derivatives³ or can easily be derived from the expected structure. From the mass spectrum of peak E are observed $[M - 103]^+ (m/e 423)$, $[M - 15 - 90]^+ (m/e 421)$, $[M - 103 - 90]^+ (m/e 333)$ and $[M - 103 - 2 \times 90]^+ (m/e 243)$, all of which are ion peaks indicative of the TMS derivative of the corresponding deoxyalditol (8). The cleavage of the carbon chain and the loss of trimethylsilanol from these fragments yield ion peaks at $m/e 307, 217, 205$ and 129 . In this case close fragmentation analogies have been reported.⁴ Peak F corresponds to the TMS derivative of the starting material (2), and the most characteristic ion peak of its mass spectrum is at $m/e 348$, originating from a McLafferty-type rearrangement.⁵ The last two peaks (E and F) also had identical retention times with the corresponding model substances (8 and 2), and the structures were further supported by other spectral data (¹H NMR, IR).

Experimental. Apparatus. GLC separations were performed after silylation on a Perkin-Elmer 900 instrument equipped with a differential FID and using a stainless steel column (3.175 mm \times 6 m) packed with 3% silicone oil (DC QF-1) on 80–100 mesh Chromosorb W-HMDS. Nitrogen was used as carrier gas (20 ml/min) and the temperature program was 60–180 °C at 2.5 °C/min. The peak areas were measured with a Hewlett-Packard 3380 A electronic integrator. For GLC-MS the compounds were injected into a Perkin-Elmer 270 B instrument (70 eV) fitted with the same column as that used for GLC. The carrier gas was helium. 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.

Trimethylsilylation. For the GLC analysis, the compounds (about 20 mg) were evaporated to dryness and silylated with a ready-made mixture of pyridine, hexamethyldisilazane and trimethylchlorosilane (10:2:1) (1–2 ml).⁶ The solution was warmed to 50–60 °C and allowed

Table 1. Gas chromatographic peaks of the reduction products (TMS derivatives).

Peak symbol	Total area/%	Relative retention time	Compound
A	37.0	0.73	4
B	10.7	0.75	6
C	28.7	0.78	4
D	9.9	0.80	6
E	13.1	0.87	8
F	0.6	1.00	2

to stand at room temperature for 30 min before injection.

Materials. 3-Deoxy-2-*C*-hydroxymethyl-D-erythro-pentono-1,4-lactone (*1*) was prepared from lactose,⁷ m.p. 94–95°C (uncorr.), $[\alpha]_{\text{D}}^{21} + 62.8^\circ$ (c 1.0). (Ref. 7, m.p. 95–96°C, $[\alpha]_{\text{D}}^{25} + 62^\circ$). IR: 3330, 1780 cm⁻¹. ¹H NMR (CDCl₃-CF₃COOD): δ 5.38–4.78 (1 H, m), 4.63 (2 H, d), 4.00 (2 H, s), 2.62–2.30 (2 H, m).

The fully trimethylsilylsubstituted lactone (*2*) was prepared by silylation of *1* as described above, and was gas chromatographically pure MS [*m/e* (% rel. int.)]: 378 (<1, M), 363 (2), 348 (37), 273 (5), 245 (19), 217 (12), 147 (39), 129 (26), 117 (26), 103 (31), 73 (100).

Reduction of *1* to sugars using sodium borohydride² resulted in a colourless syrup, whose IR spectrum lacked a strong carbonyl band at 1780 cm⁻¹. After silylation the mass spectra of the gas chromatographic peaks were: (A & C), *4*, MS [*m/e* (% rel. int.)]: 452 (<1, M), 437 (<1), 362 (<1), 349 (8), 347 (6), 334 (20), 259 (34), 244 (43), 231 (85), 218 (21), 204 (20), 191 (22), 147 (45), 133 (10), 129 (21), 117 (20), 103 (27), 73 (100). (B & D), *6*, MS [*m/e* (% rel. int.)]: 452 (3, M), 362 (1), 349 (5), 347 (4), 334 (13), 218 (91), 204 (21), 203 (14), 191 (44), 163 (18), 147 (46), 129 (12), 117 (10), 116 (13), 73 (100). (E), *8*, see below. (F), *2*, see above. ¹H NMR spectral data for *3* were obtained from the syrup. ¹H NMR (D₂O): δ 5.23 (1 H, s), 5.07–4.73 (1 H, m), 4.12 (2 H, d), 3.87 (2 H, s), 2.38 (2 H, d).

3-Deoxy-2-*C*-hydroxymethyl-D-glycero-pentitol (*7*). *1* was reduced to the alditol using sodium borohydride.⁸ The procedure was repeated three times resulting in a colourless syrup that contained 7.5 % impurities, as estimated from the areas of its TMS derivative on the gas chromatogram. IR: 3380, 1050 cm⁻¹. ¹H NMR (D₂O): δ 4.28–3.87 (1 H, m), 4.07 (4 H, s), 3.57 (2 H, d), 1.82 (2 H, d).

The fully trimethylsilylsubstituted pentitol (*8*) was prepared by silylation of *7* as described above. MS [*m/e* (% rel. int.)]: 423 (<1), 421 (<1), 333 (20), 307 (11), 243 (100), 217 (18), 205 (31), 147 (39), 129 (38), 117 (8), 103 (23), 73 (96).

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