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Note

Acetonation of laminaratriose and laminaratetraose

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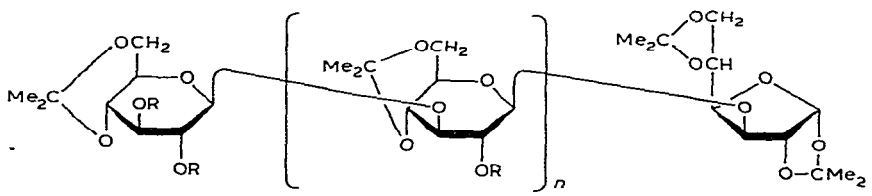
In previous papers[1,2], we reported some interesting isopropylidenated compounds, such as derivatives between two glucose residues, and acyclic dimethyl acetals, which could be obtained from some disaccharides by acetonation with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide or 1,4-dioxane. In continuation of the study, we now describe the result of such acetonation of laminaratriose and laminaratetraose in the former solvent.

Treatment of laminaratriose with an excess of 2,2-dimethoxypropane in dry *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid at 80° gave compound **1** as the major product with small proportions of other products. The n.m.r.



1 R = H, *n* = 1
2 R = Ac, *n* = 1
3 R = H, *n* = 2
4 R = Ac, *n* = 2

spectrum of the acetyl derivative (**2**) of **1** showed the presence of three acetyl and four isopropylidene groups. In addition, a 1,2-*O*-isopropylidene-α-D-glucofuranose residue was verified by a peak at δ 5.75 (d) in the spectrum. The mass spectrum of **2** showed the parent-ion peak at *m*/*z* 775 ($M^+ - CH_3$). Other main peaks were at *m*/*z* 531, 287, and 101, respectively assigned to a tri-*O*-acetyldi-*O*-isopropylideneglucobiose ion, a di-*O*-acetyl-*O*-isopropylideneglucose ion, and a 5,6-*O*-isopropylidene ion.

From these results, **2** was determined to be 3-*O*-(2,2′-di-*O*-acetyl-4,6:4′,6′-di-*O*-isopropylidene-β-laminarabiosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofura-

nose. When 1,4-dioxane was used as the solvent, the reaction did not proceed.

Treatment of laminaratetraose with an excess of 2,2-dimethoxypropane in dry *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid at 80° gave **3** as the major product, with some minor products. The n.m.r. spectrum of the acetyl derivative (**4**) of **3** indicated that **4** contained four acetyl and five isopropylidene groups, one of which was assigned to a 1,2-*O*-isopropylidene group on the α-D-glucofuranose residue. The mass spectrum of **4** showed ion peaks at *m/z* 1019 ($M^+ - CH_3$), 775 (tetra-*O*-acetyltri-*O*-isopropylideneglucotriose ion), 531, 287, and 101. Thus, the structure of **4** was determined to be 1,2:5,6-di-*O*-isopropylidene-3-*O*-(2,2′,2″-tri-*O*-acetyl-4,6:4′,6′:4″,6″-tri-*O*-isopropylidene-β-laminaratriosyl)-α-D-glucofuranose.

EXPERIMENTAL

General. — Evaporations were conducted *in vacuo*. Specific rotations were determined with a Union PM-201 polarimeter. Preparative chromatography was performed on 200-mesh, silica gel (Wako Co.) with the solvent systems specified. *N*,*N*-Dimethylformamide and 1,4-dioxane were distilled before use. N.m.r. spectra were recorded at 90 MHz with a Hitachi R-22 spectrometer for solutions in chloroform-*d*; tetramethylsilane was used as the internal standard, and the sample temperature was 35°. Chemical shifts are given in δ values, and the couplings recorded are first-order spacings. Mass spectra were recorded with a Nippon Denshi JMS-D300 spectrometer operating at 70 eV.

Acetonation of laminaratriose. — To a stirred solution of laminaratriose (300 mg, 0.6 mmol) in *N*,*N*-dimethylformamide (3 mL) were added *p*-toluenesulfonic acid (6 mg) and 2,2-dimethoxypropane (1 mL, 13.5 mol/mol of the sugar). The mixture was stirred for 3 h at 80°, and then treated with Amberlite IRA-410 (OH^-) resin to remove the acid. The resin was filtered off, and washed with methanol. The filtrate and washings were combined, and evaporated, and the syrupy residue was chromatographed in a column (2 cm diam.) of silicic acid (10 g) with chloroform and then chloroform–methanol. A 100:1 chloroform–methanol eluate yielded syrupy **1** (173 mg, 37%).

The syrupy **1** was acetylated with acetic anhydride and pyridine, to give **2**: $[\alpha]_D^{20}$ −39° (*c* 0.66, chloroform); n.m.r.: δ 1.29–1.45 (24 H, 4 Me_2C), 2.00, 2.01, and 2.07 (3 s, 3 AcO), 4.35 (d, $J_{1,2}$ 4 Hz, H-2), 4.5–5.1 (m, 5 H, ring protons), and 5.75 (d, $J_{1,2}$ 4 Hz, H-1); *m/z* 775 ($M^+ - CH_3$), 531 (18), 371 (4), 287 (45), 273 (24), 245 (6), 243 (6), 229 (18), 227 (48), 215 (10), 185 (23), 169 (96), 167 (20), 141 (25), 127 (80), 115 (25), 113 (22), 109 (22), 102 (22), 101 (80), 85 (34), 81 (70), and 43 (100, MeC^+O).

Acetonation of laminaratetraose. — A solution of laminaratetraose (300 mg) in *N*,*N*-dimethylformamide (3 mL) was treated with 2,2-dimethoxypropane (1 mL, 17.5 mol/mol of the sugar) in the presence of *p*-toluenesulfonic acid (6 mg) for 2 h at 80°. The solution was made neutral with Amberlite IR-410 (OH^-) resin, filtered,

and evaporated. The syrupy residue was chromatographed in a column (2 cm diam.) of silicic acid (10 g) with chloroform and then chloroform–methanol. A 100:1 chloroform–methanol eluate yielded a syrup of **3** (144 mg, 31%).

The syrupy **3** was acetylated with acetic anhydride and pyridine, and the acetyl derivative (**4**) was obtained as a syrup; $[\alpha]_D^{20}$ −45° (*c* 1.23, chloroform); n.m.r.: δ 1.03–1.48 (5 Me_2C), 2.00–2.09 (4 AcO), 4.38 (d, $J_{1,2}$ 4 Hz, H-2), 4.5–5.1 (m, 7 H, ring protons), and 5.86 (d, $J_{1,2}$ 4 Hz, H-1); *m/z* 1019 ($M^+ - CH_3$, 0.3), 775 (9), 531 (9), 287 (34), 169 (52), 127 (30), 101 (100), and 43 (92).

REFERENCES

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