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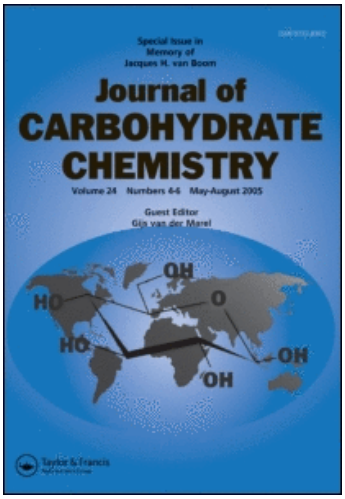


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*COMMUNICATION*

# A PER-O-ISOPROPYLIDENE DERIVATIVE OF (1→4)-β-D-MANNAN

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Isopropylidene acetals of carbohydrates are important as intermediates for the synthesis of other sugar derivatives. The isopropylidenation reaction is generally applied to only low molecular weight carbohydrates. However in 1982, we applied the reaction to a polysaccharide[2] and demonstrated that (1→3)-β-D-glucan was isopropylidenated at the 4- and 6-hydroxyl groups of the D-glucose units. These results suggested that some chemical modification at the unprotected 2-hydroxyl groups might be possible. Consequently, (1→3)-β-D-glucomannan[3,4] was derived from (1→3)-β-D-glucan through inversion of the 2-hydroxyl groups.

We report herein the preparation and structural analysis of per-*O*-isopropylidene derivatives of mannobiose, mannotriose and (1→4)-β-D-mannan.

*Preparation of (1→4)-β-D-mannan, mannobiose and mannotriose.* (1→4)-β-D-Mannan, $[\alpha]_D$ -137° (*c* 1.0, 1M NaOH), was extracted from the seed of Hemp-palm with 10% sodium hydroxide and purified via its copper-complex. 1,4-Linked mannobiose and triose were prepared by acetolysis of the polysaccharide.

*Acetonation of mannobiose and mannotriose.* To a stirred solution of the sample (400 mg) in *N,N*-dimethylformamide (4 mL) were added 2,2-dimethoxypropane (1.2 mL) and *p*-toluenesulfonic



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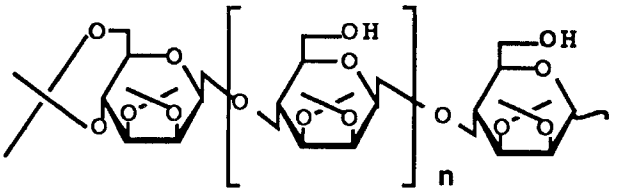

**1** n=0
**2** n=1
**3** n>1

**Fig. 1. Possible structure of isopropylidene derivatives 1, 2 and 3**

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acid (20 mg). The mixture was stirred for 0.5 h at 80 °C (for mannobiose) and for 1.5 h at 80 °C (for mannotriose), cooled, and then treated with Amberlite IRA-410 ($OH^-$) resin to remove the acid. The resin was removed by filtration, and washed with methanol. The combined filtrate and washings were concentrated and the syrupy residue was chromatographed on a column (1.5 cm, diam) of silicic acid (20 g). A 70:1 chloroform-methanol eluate yielded syrupy compound **1**, (130 mg, 26.5%), $[\alpha]_D$ -20.2° (*c* 0.86, $CHCl_3$) from mannobiose and syrupy compound **2**, (320 mg, 60%), $[\alpha]_D$ -2.7° (*c* 0.52, $CHCl_3$) from mannotriose.

Compounds **1** and **2** were acetylated with acetic anhydride and pyridine, and the products subjected to $^1H$ NMR analysis. Spectra were recorded at 270 MHz with a JEOL JNM-GX 270 spectrometer for solutions in $CDCl_3$ with tetramethylsilane as the internal standard. The spectrum of acetylated **1** showed the presence of two acetyl groups (δ 2.0-2.2) and three isopropylidene groups (δ 1.3-1.5). The spectrum of acetylated **2** indicated three acetyl groups and four isopropylidene groups. A sample (5 mg) of each compound **1** and **2** was methylated by the Hakomori procedure.[5] The IR spectra of the methylated products showed no hydroxyl absorption. IR spectra were recorded with a Jasco A-302 Infrared-spectrophotometer.

The resulting methylated products were hydrolyzed, first with aqueous 90% formic acid (1.5 mL) for 3 h at 100 °C, and then with 0.5M sulfuric acid (2 mL) for 24 h at 100 °C. Each hydrolyzate was neutralized with $BaCO_3$, reduced with $NaBH_4$ (5 mg) and then acetylated with 1:1 pyridine-acetic anhydride (2 mL) for 24 h at room temperature. The partially methylated alditol acetates were analyzed by GLC [Shimadzu Hicap CBP-10 capillary column (25 m × 0.2 mm),

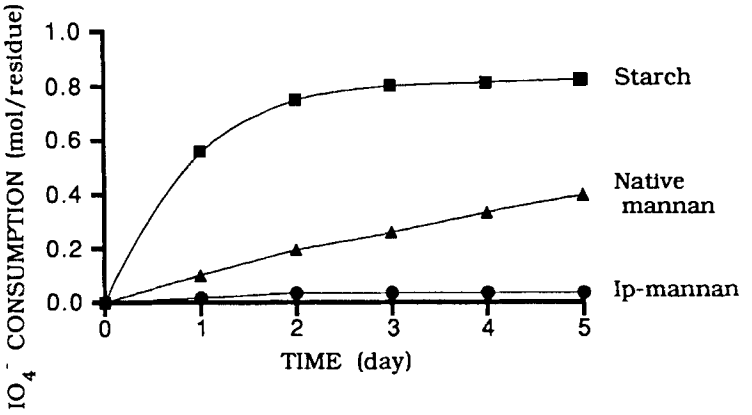


**Fig. 2. Consumption of periodic acid**

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column temperature: 220 °C, carrier gas: $N_2$, 0.5 mL/min] and GC/MS [Shimadzu QP-1000 quadrupole instrument operated in the electron impact mode (70 eV), column temperature: 200-240 °C, 4 °C/min, carrier gas: He, 30 mL/min]. From compound **1**, 1,2,3,4,5-penta-*O*-acetyl-6-*O*-methyl-D-mannitol and 1,2,3,4,5,6-hexa-*O*-acetyl-D-mannitol were detected in a molar ratio of 1:1, calculated from the peak area on the chromatogram. Therefore, the structure of **1** was determined to be 2,3:2',3':4',6'-tri-*O*-isopropylidenemannobiose (see Fig. 1). From compound **2**, 1,2,3,4,5-penta-*O*-acetyl-6-*O*-methyl-D-mannitol and 1,2,3,4,5,6-hexa-*O*-acetyl-D-mannitol were detected in a molar ratio of 2:1. Therefore, the structure of **2** was determined to be 2,3-*O*-isopropylidene-4-*O*-(2',3':2",3":4",6"-tri-*O*-isopropylidenemannobiosyl)-D-mannose (see Fig. 1).

*Acetonation of (1→4)-β-D-mannan.* (1→4)-β-D-Mannan (1 g) was dissolved in dry dimethylsulfoxide (50 mL). To this solution were added 2,2-dimethoxypropane (10 mL) and *p*-toluenesulfonic acid (50 mg). The mixture was stirred for 24 h at 50 °C, diluted with water, the aqueous solution neutralized with aqueous sodium bicarbonate, the solution dialyzed against running water for 4 days and then lyophilized. In order to determine the degree of substitution by isopropylidene groups, aliquots of the isopropylidenated polymer (10 mg) were periodically removed, acetylated and subjected to $^1H$ NMR analysis under the conditions stated above. The progress of the isopropylidenation was repeated five times. The proton ratio between isopropylidene (δ 1.3-1.5) and acetyl (δ 2.0-2.2) groups in the

derivative became approximately constant (2:1). The final product (Ip-mannan, 321.7 mg) had an $[\alpha]_D$ -20.0° (*c* 1.0, dimethyl sulfoxide).

The oxidation of Ip-mannan by sodium periodate was conducted to examine the degree of substitution by isopropylidene groups according to the procedure of Yu and Bishop[6] as described below. A sample (50 mg) of Ip-mannan was oxidized by 0.15M sodium periodate in dimethyl sulfoxide (10 mL) at room temperature in the dark. Aliquots (2 mL) were pipetted at intervals and put into phosphate buffer (20 mL, pH 7.0). After a small amount of potassium iodide was added, the liberated iodine was titrated with 0.1N sodium thiosulfate. Starch and native-mannan as references were oxidized by periodate as shown in Fig. 2, while Ip-mannan was scarcely oxidized. Methylation analysis of Ip-mannan gave predominantly 6-*O*-methyl-D-mannitol. Mannitol and 2,3,6-tri-*O*-methyl-D-mannitol were also obtained. From the results of acetonation of mannobiose and mannotriose, it is reasonable to assume that the most probable structure of Ip-mannan is **3** as shown in Fig. 1, in which the 2- and 3-hydroxyl groups of the internal D-mannose units in the polysaccharide were bridged with one isopropylidene group.

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