

## Low-molecular Carbohydrates in Algae

### III\* Synthesis of 1-D-Mannitol $\beta$ -Glucoside

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The isolation of 1-D-mannitol  $\beta$ -D-glucopyranoside from the brown alga *Fucus vesiculosus* was reported in Part I<sup>1</sup> of this series, and the synthesis of this substance has now been accomplished by conventional methods. 2,3,4,5-Mannitol tetra benzoate was reacted with an equimolecular amount of acetobromoglucose following Reynold's and Evan's modification<sup>2</sup> of the Koenigs-Knorr method. The reaction products were deacylated, and the mannitol monoglucoside isolated by chromatography on a charcoal-Celite column, using the gradient elution techniques. The substance, m.p. 138—139° and  $[\alpha]_D^{20} -20^\circ$  (water,  $c = 2$ ) proved to be identical to that isolated from *Fucus vesiculosus*.

#### EXPERIMENTAL

1.6-Ditrityl-tetrabenzoyl-D-mannitol (10 g) was detritylated by hydrogen bromide in chloroform-acetic acid<sup>3</sup>. The sirup obtained (5.6 g) was not further purified but was dissolved in dry chloroform (14 ml). Freshly prepared silver oxide (3 g) and Drierite (10 g) were added and the mixture was shaken vigorously in a brown bottle for one hour. A solution of iodine (0.5 g) and acetobromoglucose (3.8 g) in dry chloroform (15 ml) was added in ten portions during the next hour and the shaking continued overnight. The mixture was then filtered through a layer of Celite and the filter washed with chloroform. The combined chloroform solutions were washed with a small amount of sodium thiosulphate solution and with water, dried over calcium chloride and concentrated to dryness under reduced pressure. The remaining sirup was dissolved in absolute ethanol, (50 ml) to which sodium (0.2 g) had previously been added, and was kept at 0° overnight. Water (50 ml) was added and ionic material removed by filtration through the Amberlite resins IR 120 and IR 4B. The solution was then concentrated to dryness under reduced pressure. Paper chromatographic investigation of the residue (2.6 g) revealed the presence of mannitol monoglucoside, small amounts of mannitol diglucoside, mannitol and reducing sugars. The residue was dissolved in 1 % ethanol (30 ml) and put on a carbon-Celite column (35 × 4.5 cm). The column was eluted with aqueous ethanol (4 000 ml), the concentration of the ethanol being continuously increased from 1 % to 25 %. The eluate was divided into fractions, which were investigated by means of paper chromatography. Those containing the monoglucoside (between 2 100 and 2 500 ml) were combined and the solvent removed under reduced pressure. The remaining sirup (0.9 g) was dissolved in

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methanol (5 ml) and the solution kept at 0°. The mannitol monoglucoside crystallised slowly, and only after several weeks was the separation complete. Yield 0.7 g (24 %), m.p. 132–134°. One further recrystallization from methanol raised the m.p. to 138–139°, undepressed on admixture with the mannitol monoglucoside from *Fucus vesiculosus*.

#### SUMMARY

1-D-Mannitol  $\beta$ -D-glucopyranoside, identical to the mannitol monoglucoside isolated from *Fucus vesiculosus*, has been synthesized by unambiguous methods.

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