

## Low-molecular Carbohydrates in Algae

### II\*. Synthesis of 1-D-Mannitol Monoacetate and 1,6-D-Mannitol Diacetate

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The isolation of 1-D-mannitol monoacetate from the brown alga *Fucus vesiculosus* was reported in a previous communication\*, and the synthesis of this substance was therefore a matter of some interest. It is known that primary hydroxyl groups are more readily acylated than secondary ones. Thus by benzoylation of mannitol with 2 moles of benzoyl chloride in pyridine, 1,6-mannitol dibenzoate could be obtained in a yield of 80%<sup>1</sup>. Mannitol was consequently acetylated with acetic anhydride (1.5 moles) in pyridine and the reaction products separated on a carbon-Celite column, affording mannitol, monoacetates, diacetates and triacetates in yields of 15, 32, 28 and 16% respectively, calculated on the mannitol. The total recovery, 91%, is exactly the same when calculated on acetic anhydride. As a rather large yield of triacetates was obtained, it is evident that secondary hydroxyl groups have been acetylated to a considerable extent, and it was also evident that the fractions contained different isomerides. Thus the yields of crystalline 1-mannitol monoacetate and 1,6-mannitol diacetate were 26 and 15%, respectively, while only traces of crystalline material could be obtained from the triacetate fraction. The monoacetate was identical with that isolated from *Fucus vesiculosus*.

The method seems to be suitable for the preparation of glycitols, where all primary hydroxyl groups are acetylated. For the preparation of derivatives, in which one of two primary hydroxyl groups is acetylated, however, it is probably restricted to the favourable cases such as mannitol, where these two groups are equivalent.

#### EXPERIMENTAL

Mannitol (12.1 g) was dissolved in boiling pyridine (250 ml) and acetic anhydride (10.2 g, 1.5 moles) freshly distilled over phosphorus pentoxide, was added. The solution was refluxed for 4 hours and then concentrated to a syrup under reduced pressure. The residue was dissolved in water and concentrated again. The last traces of pyridine, which

\* Part I. Preceding paper.

would be harmful to the carbon column, were removed by filtration of an aqueous solution through a column of Amberlite IR 120. The solution was concentrated to 200 ml and put on a column of animal charcoal — Celite, 1 : 1, (35 × 4.5 cm) which was eluted with ethanol (4 000 ml), the concentration of which was increased continuously from 1 to 30 %. The eluate was divided into fractions which were investigated by paper chromatography. Solvent: butanol, ethanol, water, 4 : 1 : 5, reagent: silver nitrate and sodium ethoxide<sup>3</sup>. Appropriate fractions were combined and concentrated.

|                |                             |
|----------------|-----------------------------|
| 400—1 060 ml   | Mannitol 1.8 g              |
| 1 230—1 990 ml | Mannitol monoacetates 4.7 g |
| 2 190—3 500 ml | Mannitol diacetates 4.9 g   |

When the column was eluted with 50 % ethanol (2 000 ml), mannitol triacetates (3.3 g) were obtained.

No separation within the different fractions could be observed either in the carbon column or on the paper chromatogram.

### 1-D-Mannitol monoacetate

The mannitol monoacetate fraction crystallized when concentrated to dryness and by recrystallization from anhydrous ethanol a rather pure substance (4.0 g) m.p. 121—122°, was obtained. Further recrystallizations from the same solvent raised the m.p. to 124—125°, undepressed on admixture with 1-D-mannitol monoacetate from *Fucus vesiculosus*.  $[\alpha]_D^{20} + 5^\circ$  (water, C = 2).

### 1,6-D-Mannitol diacetate

The mannitol diacetate fraction partly crystallized when concentrated to dryness, and by recrystallization from anhydrous ethanol rather pure material (2.6 g) of m.p. 120—122° was obtained. Further recrystallizations raised the m.p. to 125—126°.  $[\alpha]_D^{20} + 3$  (water, C = 2). On periodate oxidation the substance consumed 3.3 moles of periodic acid with formation of 2.2 moles of formic acid. The calculated values are 3 and 2 moles, respectively. No formaldehyde was formed. (Found: C 45.1; H 6.91; Calc. for C<sub>10</sub>H<sub>18</sub>O<sub>8</sub> (266.2): C 45.1; H 6.81.)

### D-Mannitol triacetate

A small quantity of crystalline material (30 mg), melting at 115—121° after several recrystallizations from ethanol, could be obtained from the triacetate fraction. It was not further investigated.

### SUMMARY

1-D-Mannitol monoacetate and 1,6-D-mannitol diacetate have been prepared. The former substance is identical to the mannitol acetate isolated from *Fucus vesiculosus*.

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