ACTA CHEMICA SCANDINAVICA 5 (1951) 665–668

Action of Strong Acids on Acetylated Glycosides

IX.* Transglycosidation of 6-Glucose β-Maltoside

LENNART ASP and BENGT LINDBERG

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

When starch is hydrolyzed by "malt amylase", the parts of the molecule which contain the 1, 6-linkages are attacked much more slowly than the remainder of the molecule and give rise to the so-called *limit dextrins*, which are polysaccharides containing these 1,6-linkages [1]. The simplest saccharide of this type, *iso*-maltose, has recently been isolated in a crystalline state from amylopectin hydrolysate [2]. A *limit dextrin* with three glucose units has been isolated by Örtenblad and Myrbäck [3], and Myrbäck and Ahlborg [4] have shown that this trisaccharide contains one maltose and one *iso*-maltose bond. There are accordingly two possible structures for this substance, namely 6-glucose α-maltoside and 4-glucose α-*iso*-maltoside, the former of which could conceivably be prepared by a method analogous to the synthesis of *iso*-maltose [5]. In the present paper the synthesis of 6-glucose α-maltoside by such a method is described.

β-6-Glucose β-maltoside hendecaacetate was prepared by the condensation of maltose bromide heptaacetate and β-1,2,3,4-glucose tetraacetate. In order to transform the β-glycosidic linkage into the α-form, the product was treated with titanium tetrachloride in chloroform. In this process the acetoxyl group at carbon atom 1 was simultaneously replaced by chlorine, but by subsequent treatment with mercuric acetate in acetic acid, this substitution was reversed. The β-6-glucose α-maltoside hendecaacetate was obtained as an amorphous powder, the specific rotation of which varied between + 85° and + 97° for different preparations. From the values for the specific rotation of β-6-glucose β-maltoside hendecaacetate (+ 42°), β-gentiobiose octaacetate (— 5°) and β-*iso*-maltose octaacetate (+ 98°), the specific rotation of pure β-6-glucose

* Part VIII, this journal 5 (1951) 340.

α-maltoside hendecaacetate may be estimated to be about + 114°. A similar calculation but based on the specific rotations of β-maltotriose hendecaacetate (+ 86°) [6], β-*iso*-maltose octaacetate and β-maltose octaacetate (+ 63°), gives the value + 111°. The low rotation exhibited by the amorphous β-6-glucose α-maltoside hendecaacetate indicated a low state of purity. The substance was deacetylated and the free trisaccharide obtained as a slightly yellow, amorphous powder which had a specific rotation of + 128°. By paper partition chromatography it was demonstrated that the sample contained not only trisaccharide but also di- and monosaccharides *, but from the intensity of the spots it was evident that the trisaccharide was the chief constituent. The trisaccharide fraction itself almost certainly contained a small amount of unchanged 6-glucose β-maltoside and possibly also altrose derivatives as by-products of the transglycosidation reaction (Compare Part VIII [7]). From analogy with the *iso*-maltose synthesis, however, one may assume that at least 50 % of the amorphous product consists of the desired substance, 6-glucose α-maltoside.

EXPERIMENTAL

β-6-Glucose β-maltoside hendecaacetate

A mixture of β-1,2,3,4-glucose tetraacetate (12 g), freshly prepared silver oxide (11 g), drierite (30 g) and absolute chloroform (60 ml) was shaken mechanically in a brown bottle for one hour. A solution of iodine (225 mg) and amorphous maltose bromide heptaacetate (21 g) in absolute chloroform (60 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 well washed with chloroform. The combined chloroform solutions were washed with a small amount of sodium thiosulfate solution and with water, dried over calcium chloride and concentrated under reduced pressure. The residue was dissolved in boiling ethanol (450 ml) and on cooling almost pure β-6-glucose β-maltoside hendecaacetate (12,8 g), melting at 229—230° **, crystallized out as fine needles. One recrystallization raised the melting point to 233—234°; further recrystallizations did not change this value. The substance showed $[\alpha]_D^{20}$ + 42° (chloroform, $c = 2$).

$C_{40}H_{54}O_{27}$ (966.8)	Calc.	C	49.7	H	5.63
	Found	»	49.8	»	5.66

* We are indebted to Fil. lic. Gunnar Neumüller, Biokemiska Institutet, Stockholms Högskola, for carrying out the chromatographic analysis.

** All melting points uncorrected.

β-6-Glucose α-maltoside hendecaacetate

β-6-Glucose β-maltoside hendecaacetate (5 g) was dissolved in absolute chloroform (70 ml) and titanium tetrachloride (6 g) in chloroform (50 ml) was added, whereupon a yellow precipitate was formed. The mixture was refluxed on a glycerol bath, kept at about 70°, for five hours and then after cooling poured into ice water (500 ml). The yellow precipitate dissolved and the almost colourless chloroform layer was separated, washed with ice water (4 × 400 ml), dried over calcium chloride and concentrated under reduced pressure. The residual sirup was dissolved in a solution of mercuric acetate (4 g) in acetic acid (40 ml). After two hours the solution was poured into water (500 ml) and extracted with chloroform (2 × 50 ml). The chloroform solution was washed with sodium hydrogen carbonate solution and water, dried over calcium chloride and concentrated under reduced pressure. The residual sirup was dissolved in boiling ethanol (300 ml) and on cooling unchanged starting material (3.0 g) of m.p. 231—232° precipitated. The mother liquors were concentrated to 5 ml and a further amount of the starting material (0.1 g) was recovered. When the remaining ethanolic solution was poured into water an almost colourless, amorphous powder (1.1 g) precipitated which resisted all attempts to obtain it in a crystalline state. After treatment with acetic anhydride in pyridine, a further amount of rather impure starting material (0.3 g, m.p. 223—224°, $[\alpha]_D^{20}$ + 46°) could be recovered, together with an amorphous powder (0.5 g) which had the specific rotation of + 97°, the chief constituent of which should be β-6-glucose α-maltoside hendecaacetate.

6-Glucose α-maltoside

The amorphous β-6-glucose α-maltoside hendecaacetate described above (1.0 g) was dissolved in absolute methanol (30 ml), the solution chilled to 0° and 0.5 N sodium methylate in methanol (1.5 ml) added. The solution was kept at 0° for 24 hours and was then diluted with water (100 ml). The solution was freed from ionic material by passing through Amberlite resins IR-120 and IR-4B and was then concentrated to a sirup under reduced pressure. The residual water was removed by repeated stirring with absolute ethanol and evaporating to dryness at room temperature in a vacuum desiccator containing calcium chloride. All attempts to crystallize the amorphous product have failed.

Yield 0.45 g. $[\alpha]_D^{20}$ + 128° (water, c = 2).

$C_{18}H_{32}O_{16}$ (504.4)	Calc.	C	42.9	H	6.40
	Found	»	42.0	»	6.45

SUMMARY

A potential *limit dextrin*, 6-glucose α-maltoside, has been prepared by transglycosidation of the corresponding β-glycoside. It could not be obtained in a state of purity.

The authors wish to thank *Statens Naturvetenskapliga Forskningsråd* for financial support.

REFERENCES

1. Myrbäck, K. *Advances in Carbohydrate Chem.* **3** (1948) 251.
2. Montgomery, E. M., Weakley, F. B., and Hilbert, G. E. *J. Am. Chem. Soc.* **71** (1949) 1682.
3. Örtenblad, B., and Myrbäck, K. *Biochem. Z.* **303** (1940) 335.
4. Myrbäck, K., and Ahlborg, K. *Biochem. Z.* **307** (1940) 69.
5. Lindberg, B. *Acta Chem. Scand.* **3** (1949) 1355.
6. Sugihara, J. M., and Wolfrom, M. L. *J. Am. Chem. Soc.* **71** (1949) 3357.
7. Lindberg, B. *Acta Chem. Scand.* **5** (1951) 340.

Received April 16, 1951.